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Preconcentration and determination of heavy metals in water, sediment and biological samples

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Abstract: In this study, a simple, sensitive and accurate column preconcentration method was developed for the determination of Cd, Cu and Pb ions in river water, urine and sediment samples by flame atomic absorption spectrometry. The procedure is based on the retention of the analytes on a mixed cellulose ester membrane (MCEM) column from buffered sample solutions and then their elution from the column with nitric acid. Several parameters, such as pH of the sample solution, volume of the sample and eluent and flow rates of the sample were evaluated. The effects of diverse ions on the preconcentration were also investigated. The recoveries were >95 %. The developed method was applied to the determination of trace metal ions in river water, urine and sediment samples, with satisfactory results. The 3δ detection limits for Cu, Pb and Cd were found to be 2, 3 and 0.2 μg dm^{-3}, respectively. The presented procedure was successfully applied for determination of the copper, lead and cadmium contents in real samples, *i.e.*, river water and biological samples.

Keywords: lead; copper; cadmium; mixed cellulose ester membrane; preconcentration.

INTRODUCTION

Heavy metals are defined as those metals and metalloids generally considered to be of sufficient distribution and abundance to be in some way environmentally or biologically significant as a toxic substance. Heavy metals may originate from various types of sources, such as mining and smelting ferrous ores, the surface finishing industry, energy and fuel production, fertilizer and pesticide industries and applications, metallurgy, the iron and steel industry, electroplating, electrolysis, electro-osmosis, leatherworking, photography, electric appliance manufacture, metal surface treatment, aerospace and atomic energy installation, *etc*. Thus, shortage of metal as a kind of resource is developing and metal also

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create serious environmental pollution, threatening human health and the ecosystem.[1–3]

Cadmium, copper and lead are three elements that are among the most hazardous to human health. Lead pollution in water systems has seriously influenced the quality of life, especially in developing country. Lead is accumulated in tissues and may cause serious health problems for humans and animals. This metal inhibits biosynthesis and affects the kidneys, brain cells and the permeability the liver membrane, thereby reducing some of their functions. It can be accumulated in the body and can promote disturbances such as nausea, vomiting, diarrhea, sweating and, in some cases, convulsions, coma and death.[4,5] Cadmium may cause renal injuries and may interfere with the renal regulation of the calcium and phosphate balance. Cadmium concentrations in urine reflect long term exposure and the quantity of cadmium stored in the body, particularly in the kidney and liver. With commencement of renal damage, excretion of Cd can increase markedly.[6,7]

Copper is an element essential for many biological systems and plays an important role in carbohydrate and lipid metabolism. In general, copper at nearly 40 $\mu g\ dm^{-3}$ is required for normal metabolism of many living organisms; however, in higher levels, it is considered to be toxic and severe oral intoxication will affect mainly the blood and kidneys.[8,9] Whenever toxic heavy metals are exposed to the natural ecosystem, accumulation of metal ions such as lead, cadmium and copper in the human body occurs through either direct intake or the food chain. Therefore, heavy metals should be prevented from reaching the natural environments because of their toxicity.

The determination of trace metals comprises one of the most important targets in analytical chemistry. This interest is also demonstrated in different areas, such as biology and medicine.[10] Various techniques have been applied for the determination of trace heavy metals in aqueous and biological samples. Flame atomic absorption spectrometry (FAAS) has been a very attractive technique for routine metal determinations, owing to its ease of operation, its low acquisition and operating costs compared with inductively coupled plasma optical emission spectrometry (ICP–OES).[11]

Direct instrumental analysis of these samples is difficult because of complex formation and significance of the matrices, which invariably influence normal instrumental analysis. In addition, some metals are present at low concentrations, which are near to or below the limit of detection of the instrument. Moreover, the low level of trace elements in real samples is not compatible with the detection limit of AAS. Preconcentration can solve the above two problems and lead to simplified heavy metal determination. There are many methods of preconcentration, including cloud point extraction,[12–14] coprecipitation,[15–17] cathodic adsorptive stripping voltammetry,[18] ICP–OES,[19,20] microextraction,[21] ion exchange,[22] inductively coupled plasma mass spectrometry,[23] liquid–liquid extraction,[24] electrothermal atomic absorption spectrophotometery[25] and solid phase extraction.[26–28]

Among the various preconcentration methods, solid-phase extraction (SPE) is one of the most effective multi-element preconcentration methods because of its simplicity, rapidity and ability to attain a high concentration factor. In addition SPE provides for the removal of potentially interfering matrices.

Various materials, including amberlite (XAD) resins,[29–32] activated carbon,[32–35] modified silica gel,[36–38] alumina,[39,40] and synthetic zeolites[41] have been widely used for the preconcentration and separation of trace metal ions from various matrices.

The purpose of the present study was to demonstrate the feasibility of using mixed cellulose ester membrane as a solid-phase extractant for the preconcentration of lead, copper and cadmium found at trace level in water and biological samples. In the procedure, the analytes were retained on a short mixed cellulose ester filter column from a buffered sample solution and then eluted from the column with nitric acid. In the development of the procedure, several parameters relevant to the retention and elution of the analytes were examined.

EXPERIMENTAL

Materials

All the reagents used were of analytical reagent grade. Doubly-distilled water (DW) and high purity reagents were used for the preparations of all the standard and sample solutions. Standard stock solutions containing 1000 mg dm^{-3} analyte were prepared from nitrate salts of Cd(II), Cu(II) and Pb(II) in 1 % of HNO_3 in 1-L calibrated flasks (Merck, Darmstadt, Germany, atomic absorption grade). Ammonium chloride buffer solution (0.2 mol dm^{-3}) was prepared by adding an appropriate amount of ammonia to ammonium chloride solution (Merck) to prepare a solution of pH 8. The mixed cellulose ester membrane was purchased from Sartorius, No. 10401706 (USA). A GBC atomic absorption spectrophotometer (AA-932, Dandenong, Victoria, Australia) equipped with a single-element hollow cathode lamp and an 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 Metrohm E-744 model pH meter (Herisau, Switzerland) with a glass electrode was employed for measuring pH values of the aqueous phases. The preconcentration system consisted of cartridge tube with cellulose ester membrane (100 mm height, 25 mm internal diameter) connected to a vacuum system. The instrumental and extraction conditions are listed in Table I.

TABLE I. The instrumental settings for the flame atomic absorption spectrometer

Parameter	Lead	Copper	Cadmium
Wavelength, nm	217	324.8	228.8
Lamp current, mA	5	3	3
Spectral bandwidth, nm	1	0.5	0.5
Air flow rate, dm^3 min^{-1}	8	8	8
Acetylene flow rate, dm^3 min^{-1}	2	1.5	2

Characteristics of the adsorbent material

The microstructure and surface morphology of the adsorbent was characterized by a Phillips PW3710 field emission scanning electron microscope (SEM) at an accelerating voltage of 15.0 kV. The SEM image of the MCEM, showing the highly porous morphology of adsorbent with nanosized pores (200 nm), is presented in Fig. 1.

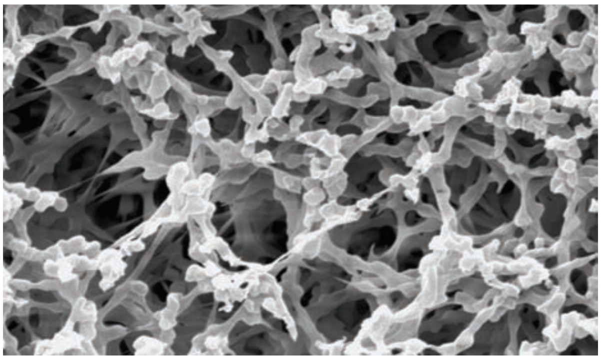

Fig. 1. An SEM image of mixed cellulose ester membrane, 4500×.

General procedure

A cartridge tube (100 mm length and 38 mm i.d) with mixed cellulose ester membrane (0.83 mm thickness and 36 mm i.d) was used as a preconcentration column. An aliquot of the sample solution (25 mL) containing 10–100, 12–350 and 0.8–35 μg dm^{-3} of Cu, Pb and Cd, respectively, were passed through the column at a flow rate of 1.0 ml min^{-1}. Then, the metals retained on the column were completely dissolved in 2 mL of HNO_3 (1.5 mol dm^{-3}). The concentration of metals in the final solution was determined by FAAS. A blank solution was also run under the same analytical conditions without the addition of Cu, Pb and Cd. A fresh cartridge tube with mixed cellulose ester membrane was used for each experimental run.

RESULTS AND DISCUSSION

Nowadays, membrane filtration is one of the important enrichment techniques for trace heavy metal ions. In membrane filtration, the collection of traces metal ions is performed very quickly by filtration under suction with the aid of a vacuum aspirator.[42,43] Initial experiments showed that MCEM has a tendency to retain lead, copper and cadmium. Hence, a column containing MCEM adsorbent was chosen for the preconcentration of lead, copper and cadmium and their subsequent determination by flame atomic absorption spectrometry. In order to obtain the best performance for the flow system, the effects of various chemicals and instrumental variables on the preconcentration and determination of the metal ions were studied and optimized using the one-at-a-time optimization method. Therefore, the various analytical parameters, such as pH, sample volume, amount of sorbent, flow rate and the matrix effect were investigated and optimized.

Effect of the pH

The pH value of a sample solution is one of the most important variables controlling the adsorption of the metal ions on the column. Therefore in order to determine the optimum pH, the effect of pH in the range 4–9 on the retention by the column was investigated. The effect of pH on the retention of Cu, Pb and Cd on the MCEM column is shown in Fig. 2, from which it can be seen that a pH value of 8 found to be the optimum for the quantitative extraction of the metal ions and the metals recovery was about 99 %. Therefore, pH 8.0 was selected for the all subsequent experiments.

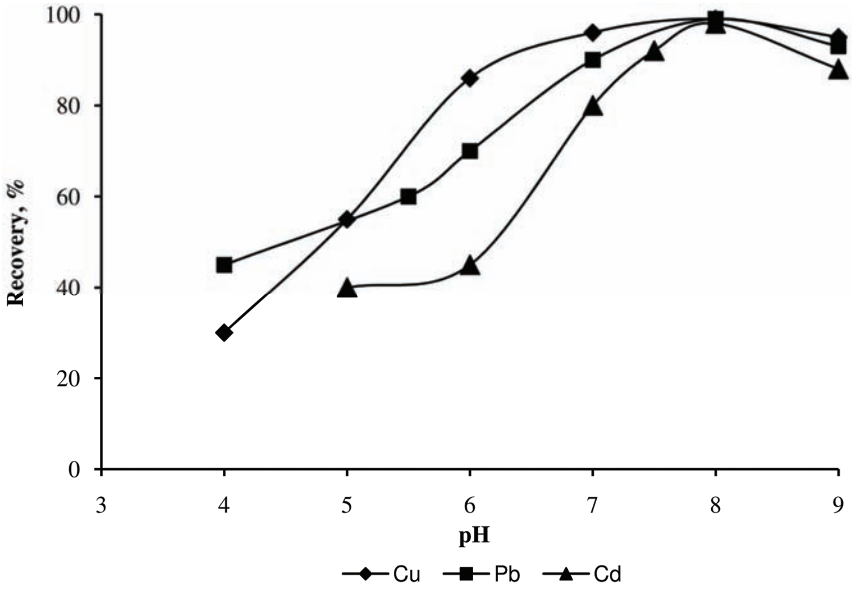

Fig. 2. Effect of pH on retention of metal ions by MCEM column. Conditions: copper, lead and cadmium concentration: 25 μg dm^{-3}; sample volume: 50 mL; flow rate: 1 mL min^{-1}.

Sample flow rate

The sample flow rate through the column is a very important parameter, since this is one of the steps that control the analysis time.[44] The influence of the sample flow rate on the preconcentration efficiency was tested at flow rates of 5.0–60 mL min^{-1}. A flow rate in the range of 5.0–10 mL min^{-1} had no significant effect on the recoveries of the investigated elements. In addition, it was found that analytical signal decreased slightly on increasing the sample flow rate to above 10 mL min^{-1} because of incomplete retention of the metal ions on the column. Therefore, a sample flow rate of 10 mL min^{-1} was selected for further studies (Fig. 3).

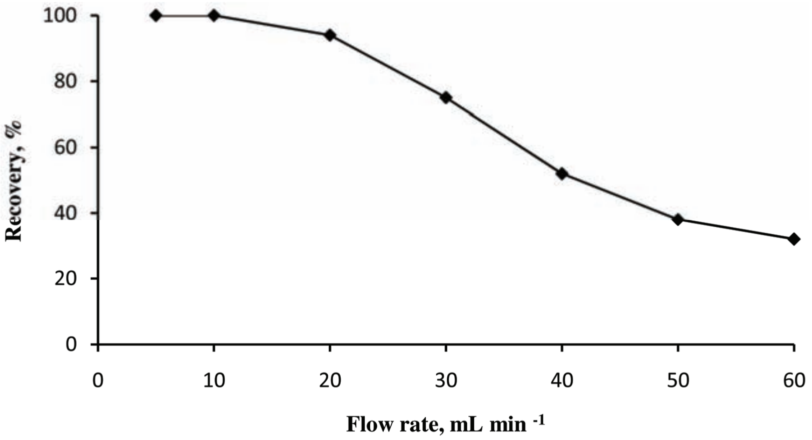

Fig. 3. Influence of flow rate on retention of metal ions by MCEM column. Conditions: copper, lead and cadmium concentration: 25 µg dm^{-3}; sample volume: 50 mL; pH 8.

Influence of sample volume

In order to explore the possibility of enriching low concentrations of the analytes from large sample volume, the effect of the volume of the sample solution on the metal sorption was studied by passing 25–400 mL volumes through the column. In this work, the amounts of analyte added were constant. The results are shown in Fig. 4. The adsorption of the metal ions by MCEM was not affected by the sample volume below 200 mL. Above this volume, the percent sorption of the analytes decreased. In the present study, sample solution volume of 200 mL of was adopted for the preconcentration of the investigated ions from synthetic water samples; the adsorbed metals can be eluted with 2 mL of HNO_3 and an enrichment factor of 100 was thus achieved by this technique (Fig. 4).

Effect of eluent volume

The effect of eluent volume on the desorption of the analytes was studied by keeping the eluent concentration constant at 0.1 mol dm^{-3} and varying it volumes from 0.5 to 3.0 mL. The experimental results indicated that with 2.0 mL HNO_3, quantitative recoveries (>98 %) for the target analytes could be obtained. Therefore, 2.0 mL of eluent was selected for the subsequent experiments.

Adsorption capacity

In order to successfully represent the dynamic adsorptive behavior, it is important to have a satisfactory description of the equation state between the two phases composing the adsorption system. Several isotherm models are available. In this study, the Langmuir adsorption isotherm was employed. The Langmuir model assumes uniform energies of adsorption onto the surface and no transmigration of the adsorbate in the plane of the surface. The Langmuir Equation may be written as:

$$\frac{c_{\mathrm{e}}}{q_{\mathrm{e}}}=\frac{1}{bQ_{\max}}+\frac{c_{\mathrm{e}}}{Q_{\max}} \tag{1}$$

where c_e is the equilibrium concentration (mg dm^{-3}), q_e is the amount adsorbed at surface equilibrium (mg g^{-1}) and Q_{max} and b are Langmuir constants related to the adsorption capacity and the energy of adsorption, respectively. It is clear from Table II and Fig. 5 that the Langmuir model provided a good fit throughout the concentration range. The applicability of the isotherm models and the high values of the correlation coefficients (R^2 = 0.978, 0989 and 0.998, respectively) for Cu, Pb and Cd, suggest favorable and monolayer adsorption. The values of Q_{max} as determined from the Langmuir plots are 24, 17 and 16 mg g^{-1} for Cu, Pb and Cd, respectively. According to the results, the maximum capacity of the adsorbent under column conditions, due to the shorter contact time, is slightly lower than under batch conditions, which is apparently quite expected. The values of the constants of the Langmuir isotherm model are given in Table II.

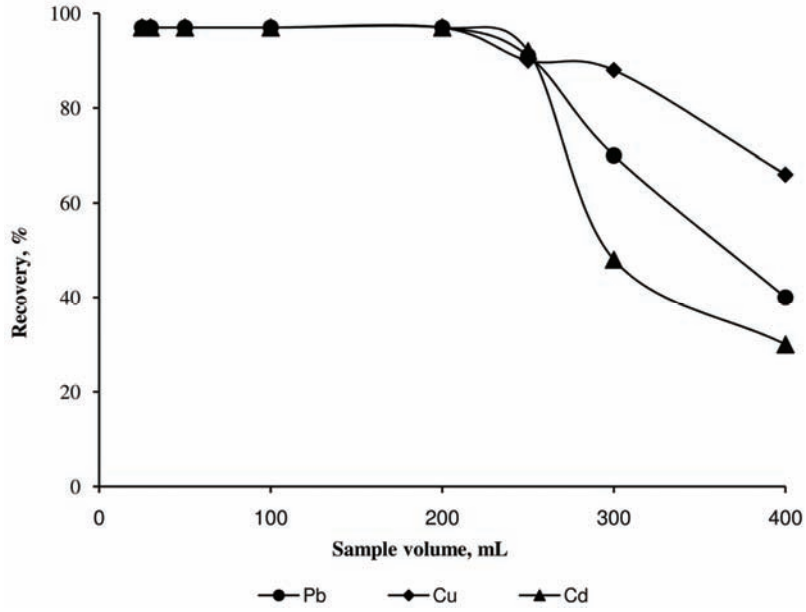

Fig. 4. Influence of sample volumes on the recovery of metal ions. Conditions: copper, lead and cadmium concentration: 25 µg dm^{-3}; flow rate: 1 mL min^{-1}; pH 8.

Interference studies

In order to assess the effects of commonly co-existing ions, which could interfere with the determination of Cu, Cd and Pb, several analytes were tested at the concentration levels at which they may occur in the sample concerned. The results are given in Table III. The tolerance limit is defined as the ion concentration causing a relative error smaller than ±4 % related to the preconcentration and determination of the analyte ions. The ions normally present in water did not interfere under the employed experimental conditions. In addition, some of the transition metals at mg dm^{-3} levels did not interfere with the recoveries of the analyte ions. These results show that the proposed preconcentration/determination method could be applied to highly saline samples and the samples that contain some of the transition metals given in Table III at mg dm^{-3} levels.

TABLE II. The Langmuir isotherm model constants

Langmuir parameter	Cu	Pb	Cd
$Q_{\max}$ / mg g^{-1}	24	17	16
b / mg^{-1} L^{-2}	0.178	0.053	0.062
R^2	0.997	0.989	0.998

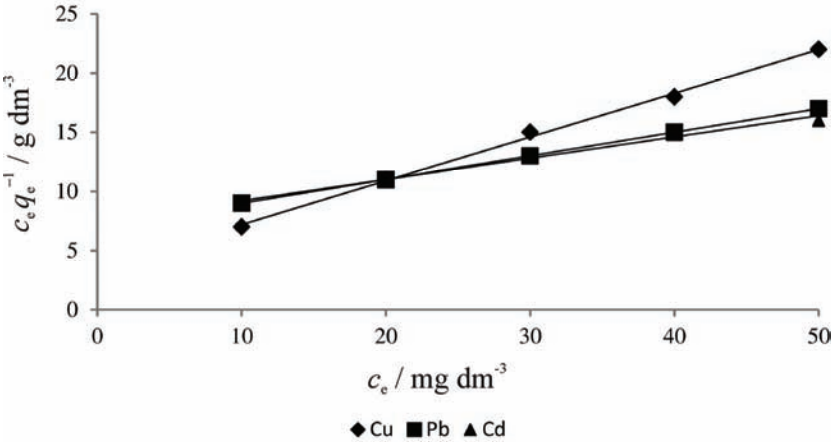

Fig. 5. Langmuir plots for adsorption of metal ions on MCEM.

TABLE III. Tolerance limits of interfering ions in the determination of 50 µg dm^{-3} of Cu, Pb and Cd

Ion	Metal to interferent ratio (w/w)		
	Cu	Pb	Cd
Na^+	1/5000	1/5000	1/5000
K^+	1/10000	1/10000	1/10000
Mg^{2+}	1/2000	1/2000	1/2000
Cl^-	1/2000	1/2000	1/2000
CO_3^{2-}	1/3000	1/3000	1/3000
Ni^{2+}	1/1000	1/1000	1/1000
V^{3+}	1/1000	1/1000	1/1000
Pb^{2+}	1/2000	–	1/2000

TABLE III. Continued

Ion	Metal to interferent ratio (w/w)		
	Cu	Pb	Cd
Mn^{2+}	1/1000	1/1000	1/1000
Cr^{3+}	1/1000	1/1000	1/1000
Ca^{2+}	1/2000	1/2000	1/2000
Al^{3+}	1/2000	1/2000	1/2000
Cd^{2+}	1/2000	1/2000	–
Zn^{2+}	1/2000	1/2000	1/2000
Fe^{3+}	1/2000	1/2000	1/2000
Cu^{2+}	–	1/2000	1/2000
Ba^{2+}	1/1000	1/1000	1/1000
Ag^{+}	1/1000	1/1000	1/1000

Statistical evaluation of the method

The limits of detection (*LOD*) of the proposed method for the determination of the investigated elements were studied under optimal experimental conditions by applying the procedure for blank solutions. The detection limits of the investigated elements based on three times the standard deviations of the blank ($k = 3$, $N = 10$) were 2 μg dm^{-3} for Cu(II), 3 μg dm^{-3} for Pb(II) and 0.2 μg dm^{-3} for Cd(II). The values of the limit of quantification (*LOQ*) were obtained as 7, 8 and 0.6 μg dm^{-3} for Cu, Pb and Cd, respectively ($S/N = 10$). The reproducibility of the presented procedure was evaluated by a model solution containing heavy metal ions ($N = 6$). The relative standard deviations (*RSD*) of these determinations were below 4.7 %.

The calibration curves for analyte ions were drawn after setting various parameters of FAAS, including wavelength, slit width, lamp current, at the optimum level. The optimum concentration ranges and regression equations for analytes are given in Table IV. The statistical calculations are based on the average of triplicate readings for a standard solution of the analyte ions.

TABLE IV. Analytical characteristics of the calibration curves of the analytes

Analyte	Correlation coefficient	Linear range, μg dm^{-3}	*RSD* / %
Cu	0.9995	10.0–100	3.2
Pb	0.9997	12.0–350	4.3
Cd	0.9998	0.8–35	1.8

Addition/recovery tests

Tests of addition/recovery in the experiments for analyte ions were performed for river water samples. The results are given in Table V. Good agreement was obtained between the added and measured analyte amounts. The recovery values for copper, cadmium and lead were in the range of 92–105 %. These values are quantitative and show that the presented method can be applied for the separation–preconcentration of analyte ions in real samples and the results indicate the applicability of the developed procedure for the determination of cadmium, copper and lead free of interference.

TABLE V. Application of the presented procedure to the analysis of a river water sample from Tehran City, Iran

Analyte	Concentration, μg dm^{-3}		Recovery, %
	Added	Found[a]	
Cu	–	40.0±0.5	–
	30	68.2±0.2	94
	40	81.0±0.6	102
	50	88.0±0.8	96
Pb		125±1.0	
	100	227±2.0	102
	150	273±1.5	99
	200	331±2.1	103
Cd		12.0±0.3	
	10	21.2±0.6	92
	15	26.5±0.5	97
	20	33.0±0.9	105

[a] Average of three determinations ± *SD*

Accuracy of the method

In order to evaluate the accuracy of the proposed preconcentration method, the analytes were determined in certified standard reference material (RM 8704 Buffalo River sediment). The sediment sample was dissolved and the column preconcentration procedure was applied to the sediment solution. The results obtained from the analysis of the certified reference material are depicted in Table VI, from which it can be seen that the achieved relative error values (%) were lower than 5%, meaning that the described method has good accuracy. The results obtained from the proposed method were in a good agreement with the certified values for Pb, Cd and Cu. In addition, the accuracy of the proposed procedure was also checked by analysis of urine samples by electrothermal atomic absorption spectrometry (ET–AAS). There was no significant difference at the 95 % confidence limit between the results obtained by proposed method and ET–AAS (see Table VII).

Comparison with other preconcentration studies

A comparison of the presented procedure with other preconcentration systems for the determination of cadmium, copper and lead can be seen in Table VIII. Analytical features, such as enrichment factor and detection limits, of the proposed method are comparable to those of other methods described in the literature.

TABLE VI. The levels of analyte ions in the reference material (*N* = 6)

Element	Content, mg kg^{-1}		*RSD* / %	Relative error, %
	Certified value	Observed value[a]		
Cu	98.6	97.2±1.40	2.1	–1.4
Pb	161	154±2.20	1.9	–4.3
Cd	3.5	3.38±0.09	0.5	–3.4

[a] Mean of six determinations at the 95 % confidence limit

TABLE VII. Determination of Cu, Pb and Cd in a urine samples

Element	Concentration, μg dm^{-3}		Relative error, %
	Present method[a]	ET–AAS method	
Cu	58.4±0.75	61.3±0.25	–4.7
Pb	81.4±0.57	85.3±0.51	–4.5
Cd	1.20±0.21	1.22±0.15	–1.6

[a] Mean of six determinations at the 95 % confidence limit

TABLE VIII. Comparison of the proposed method with previously reported methods

Elements	Enrichment factor	*LOD* / μg dm^{-3}	Reference
Cu, Pb	20, 20	1.1, 6.1	45
Cu, Cd	35, 38	1.8, 1.6	46
Cu, Pb	100, 100	0.54, 4.5	27
Pb, Cd	19.6, 15.1	4.6, 0.74	6
Pb, Cu, Cd	60, 60, 60	0.02, 3.1, 0.9	42
Pb, Cu, Cd	20, 20, 20	22.5, 1.0, 1.1	47
Pb, Cu, Cd	100, 100, 100	2.0, 3.0, 0.2	Present work

CONCLUSIONS

The developed procedure is very simple, sensitive and shows high tolerance to interference ions. Due to its good analytical characteristics, such as detection limit, enrichment factor and precision, the method is suitable for trace element analysis. In addition, no modification or functionalization of the employed adsorbent is required. The recoveries of the studied analytes were nearly quantitative. The accuracy of the results was verified by analyzing a certified reference material and spiked water samples. The recoveries for these elements were very satisfactory, which evidence for the reliability of the proposed method in the analysis of real samples.

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ИЗВОД

ПРЕДКОНЦЕНТРИСАЊЕ И ОДРЕЂИВАЊЕ ТЕШКИХ МЕТАЛА У ВОДИ, СЕДИМЕНТУ И БИОЛОШКИМ УЗОРЦИМА

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У овом раду развијена је осетљива и прецизна метода за колонску предконцентрацију при одређивању јона Cd, Cu и Pb у узорцима речне воде, урина и седимента пламеном атомском апсорпционом спектрометријом. Овај поступак је заснован на ретенцији аналита на колони од мембране естра мешане целулозе (MCEM) из пуферованог раствора узорка и њиховог елуирања из колоне азотном киселином. Проучен је утицај неколико параметара, као што су pH раствора узорка, запремине узорка и елуента и брзине протока узорка. Испитани су и утицаји разних јона на преконцентрацију. Принос аналитичког поступка је увек био >95 %. Овај метод је примењен на одређивање трагова металних јона у узорцима речне воде, урина и седимента, са задовољавајућим резултатима. Границе детекције 3δ за Cu, Pb и Cd су биле 2, 3, односно 0,2 μg dm^{-3}. Изложени поступак је успешно примењен за одређивање бакра, олова и кадмијума у стварним узорцима као што су речна вода и биолошки узорци.

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