PRE-CONCENTRATION AND DETERMINATION OF HEAVY METALS ON MODIFIED ACTIVATED CARBON IN REAL SAMPLES

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ABSTRACT

A sensitive and simple method for the simultaneous pre -concentration of nutritionally important minerals in real samples has been reported. The method is based on the formation of metal complexes by N, N'-diacetyl-4-bromo-2, 6-di (aminomethyl) phenol (DBDP) loaded on activated carbon. The metals content on the complexes are then eluted using 6mL 4M HNO₃, which are detected by AAS at resonance line. In this procedure, minerals such as Ni, Cu, Co, Pb Zn and Cd can be analyzed in one run by caring out the simultaneous separation and quantification of them. At optimum condition the response are linear over concentration range of for 0.03–1.1 $\mu g\ mL^{-1}$ for Ni^{2+} , 0.03–1.0 $\mu g\ mL^{-1}$ for Cu^{2+}, 0.02–1.0 $\mu g\ mL^{-1}$ for Pb^{2+} , 0.02–1.0 $\mu g\ mL^{-1}$ for Co^{2+},0.02–1.1 $\mu g\ mL^{-1}$ Zn^{2+} and 0.05–1.3 $\mu g\ mL^{-1}$ for Cd^{2+}. The detection limits of each element are expressed as the amount of analytes in $\mu g\ mL^{-1}$ giving a signal to noise ratio of 3 are equal to 2.5, 2.4, 1.6, 2.4, 1.9 and 2.1 for Ni^{2+} , Cu^{2+}, Pb^{2+} , Co^{2+},Zn^{2+} and Cd^{2+}. The ability of method for repeatable recovery of trace ion are 99.9, 98.7, 99.2 , 98.7, 98.5and 95.6 with R.S.D of 1.3, 1.4, 1.2, 1.4, 1.7 and 1.4 for Ni^{2+} , Cu^{2+}, Pb^{2+} , Co^{2+},Zn^{2+} and Cd^{2+}. The method has been successfully applied for these metals content evaluation in some real samples including natural water and vegetable.

INTRODUCTION

Nowadays determination of trace metals in environmental samples is essential, because these metals have been used in various industries. Various techniques have been reported for the determination of trace metals in environmental samples. Flame atomic absorption spectrometry (FAAS) has been widely used for the determination of trace metal ions. However, direct determination of metal ions at trace levels by FAAS is limited due to their low concentrations and matrix interferences [1]. In trace analysis, therefore, pre-concentration leads to simplify trace metal determination. Several methods of pre-concentration include solvent extraction [2,3], adsorption [4,5], membrane extraction [6], coprecipitation [7–9], ion-exchange [10,11]. But, solid phase extraction (SPE) is multielement pre-concentration methods because of its simplicity, rapidity and ability to attain a high concentration factor.

Solid phase extraction offers a number of important benefits. It reduces solvent use, solvent exposure, disposal costs and extraction time for sample preparation. Consequently, in recent years SPE has been successfully used for the separation and sensitive determination of metal ions, mainly in water samples.

Among them activated carbon (AC) which is characterized by high adsorption capacity, allowing application under broad pre-concentration conditions due to its ability to adsorb organic compounds and organic metal complexes has widespread application for trace element pre-concentration. Because activated carbon is a type of hydrophobic adsorbent which adsorbs non-polar or little polar substances in aqueous solution, metal ions to be pre-concentrated need to be transformed corresponding metal chelates or precipitate [12-17] or metal hydroxides [18] which could be adsorbed on activated carbon. Metal chelates could provide higher selectivity and high enrichment factors for such a pre-concentration and separation. The mechanism involved in the adsorption of ions as trace compounds by activated carbon is not completely known. The mechanism of sorption is still under investigation and the adsorption of heavy metals on AC could be explained using Langmuir and Freundlich equations. It was assumed that the sorption is quantitative when the chelate contains systems of π-electrons in the molecule and when the centers for binding on carbon and those for the metal ions are spatially separated so that their orbitals do not have a substantial influence [19]. The major advantage of these models is their simplicity; however, the models fail to describe accurately the adsorption equilibrium under varying conditions, such as pH and ionic strength. The adsorption equilibrium studies have revealed that pH is the dominant parameter controlling the adsorption [20]. Therefore, activated carbon (AC) has been used as a collector, permitting the pre-

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concentration and separation of low levels of analytes in several matrices [21-27].

The purpose of this work is to pre-concentration and separate of Ni^{2+}, Cu^{2+}, Pb^{2+}, Co^{2+}, Zn^{2+} and Cd^{2+} on activated carbon(AC) modified with N,N'-diacetyl-4-bromo-2,6-di(aminomethyl) phenol (DBDP) . The influences of the some analytical parameters including pH and sample volume on the quantitative recoveries of the analytes were investigated.

EXPERIMENTAL SECTION

Reagents

All reagents and solvents were standard analytical grade and used without further purification. Doubly distilled deionized water was used throughout. The pH adjustment was done by addition of dilute nitric acid or sodium hydroxide to phosphate solution for preparing the desired pH buffer solution. Activated carbon (AC) (gas chromatographic grade, 40–60 mesh from Merck), were soaked in hydrochloric acid for 2 d, it was then washed with water and dried at 110 °C for 1 d. The ligand N, N'-diacetyl-4-bromo-2, 6-di (aminomethyl) phenol (DBDP) was synthesized according to literature [28].

Apparatus

A Metrohm 691 pH /Ion meter with a combined glass and calomel electrode has been used for measurement and adjustment of test solutions pH. The evaluation of ions content were carried out on a Shimadzu 680 A atomic absorption spectrometer with a hallow cathode lamp and a deuterium background corrector, at respective resonance line using an air – acetylene flame.

Procedure

Preparation of DBDP impregnated activated carbon
Activated carbon powder (Merck) was treated with 20% HCl, washed with de-ionized water and oven-dried at110 °C. Ligand loaded activated carbon was prepared by dissolving a weighed amount of DBDP in water to the required amount of activated carbon. After 24 h, the solutions were filtered through the filter paper and activated carbons were washed with distilled water until the filter out was no longer alkaline. Finally, the mixtures were dried at 110 °C overnight. The solid phase columns were initially preconditioned with solution with desired pH. For the final optimum experiments the solid phase was prepared as follow: 25 mg DBDP per 600 mg of AC.

Extraction procedure
The pH of model solutions containing 0.05 μg mL^{-1} of ions metal was adjusted to the desired pH value by adding Nitric acid and NaOH solution. Before each operational cycle the solid phase was preconditioned with the buffer solution. The samples were passed through the column of modified activated carbon with the aid of a suction pump at a flow rate 4 mL min^{-1}, to affect the deposition of analyte.

Desorption procedure
The adsorbed ions were desorbed by adding 6 mL of 4.0 M nitric acid at column for 10 min and then were passed through the column with a flow rate of 2.0 mL min^{-1}. The analyte ions in the eluent were determined by flame atomic absorption spectrometer.

Pretreatment of real samples
Vegetables. All vegetable samples were purchased from Gachsaran Iran. Afterwards, they were taken in small mesh. A 40 g vegetable sample was heated in silica crucible for 3 h on a hot plate and the charred material was transferred to furnace for overnight heating at 650 °C. The residue was cooled, treated with 10.0 mL concentrated nitric acid and 3 mL 30% H_2O_2 again kept in furnace for 2 h at the same temperature so that no organic compound traces are left. The final residue was treated with 3 mL concentrated hydrochloric acid and 2-4 mL 70% perchloric acid and evaporated to fumes, so that all the metals change to respective ions. The solid residue was dissolved in water, filtered and by keeping the pH at 8.0 made up to 250 mL by addition of Nitric acid and NaOH solution. The dissolved solution was suitably diluted and metals concentration was determined after suitable pre-concentration using AAS.

River water samples. River water samples were collected from Rivers Iran(jamsher in Gachsaran). Before the analysis, the samples were filtered through a cellulose membrane filter (Millipore) of pore size 0.45 mm. The organic content of the water samples were oxidized in the presence of 1% H_2O_2 and addition of concentrated nitric acid. The water samples were filtered through a filter paper. After acidification to 1% with concentrated nitric acid, they were stored in polyethylene bottles for determination of Heavy metals keeping the pH at 8.0 made up to 250 mL by addition of Nitric acid and NaOH solution [29].

RESULT AND DISCUSSION

Due to the existence of a donating nitrogen atom as well as -O (OH) group and NH group in DBDP, it was expected that loading of DBDP to OA Increase both the stability and selectivity of its complex toward ions.

Effect of Activated Carbon

The DBDP -AC can retain all of the mention metal ions while the untreated activated carbon cannot

quantitatively retain Cu, Ni, Co, Pb, Zn and Cd. Evidently; the pre-concentration of the metals with the untreated activated carbon is not suitable for Cu, Ni, Co, Pb Zn and Cd. Therefore, DBDP-AC seems to be a better sorbent in simultaneous sorption of Cu, Ni, Co, Pb, Zn and Cd. The effects of the amount of activated carbon at fix value of DBDP on the sorption of metal ions at pH 8 were examined in the range of 200-1000 mg. The results are given in Fig 1. Quantitative recoveries (> 95%) of the working elements were observed in the range of 600 mg of activated carbon. Above 600 mg, the recoveries were below 95% with 6 mL of the eluent. In the proposed procedure, 600 mg of activated carbon is recommended.

Effect of pH on recovery

In the solid phase extraction studies for heavy metal ions based on chelation, the influence of pH of the aqueous solution one of the main factor for quantitative recoveries of the analytes. Due to this important point, the influences of pH were investigated at the pH ranges 2–10 for both sorbents with model solutions, keeping the other parameters constant. Analyte deposition depended on the sample pH, and as shown in Fig. 2, high deposition efficiency was achieved at a pH of 8.0. The progressive decrease in the retention of analytes at a
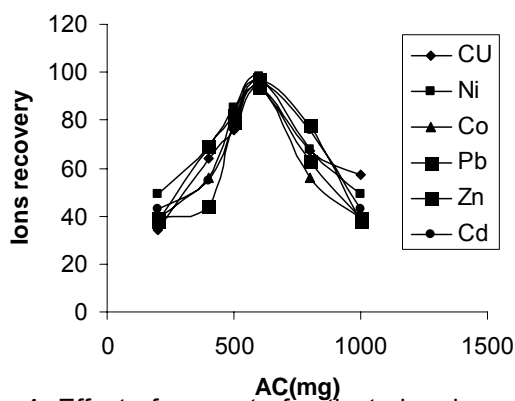

Fig 1. Effect of amount of activated carbon on recovery of metal ions (N=3), pH=8.0, Eluent: 6 mL 4.0 M HNO_3
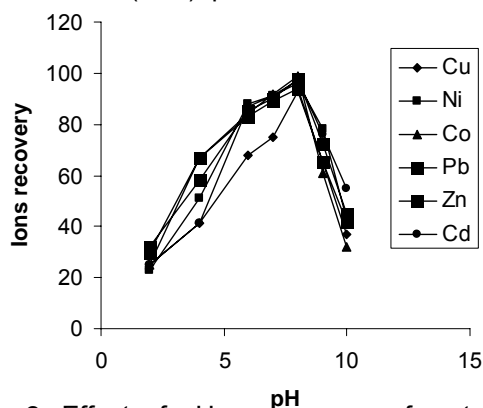

Fig 2. Effect of pH on recovery of metal ions (N=3), eluent: 6 mL 4.0 M HNO_3.

low pH is due to the competition of the hydrogen ion with the analytes for reaction with DBDP. To achieve high efficiency and good selectivity, a pH of 8.0 was selected for subsequent work.

Effect of ligand amount on recovery

The effects of the ligand amount on the retention of the analyte ions on DBDP were also examined and are depicted in Fig. 3. The recoveries of analytes were quantitative up by the addition of 25 mg ligand. After that, the recovery values decreased, probably due to the formation of charged complex which could not be completely retained on solid phase.

Sample flow rate

Two important factors for the quantitative recoveries and desorption of metal chelates on the solid-phase extraction studies are flow rates of the sample and eluent solutions. The influences of the flow rates of the sample and eluent solution for the recoveries of analytes were investigated in the flow rate ranges of 2-1 0 mL/min. The recovery values for analyte ions were quantitative in all the working range of sample flow rates. The quantitative recovery values for eluent solution were obtained at the flow rate range of 2-4 mL/min. All further studies were performed at the sample and eluent flow rates of 4.0 mL/min.

Type and volume eluent

The nature and concentration of eluent were found to have a significant effect on the desorption process of lead from the column. Different eluents, such as HCl, HNO_3, H_3PO_4 and H_2SO_4 at various concentrations, were examined and the results are shown in Table 1 and Fig.4. From Table 1 and Fig.4, it is obvious that concentration of 4.0 M of nitric acid with volume 6 mL were sufficient for quantitative recovery of absorbed lead.
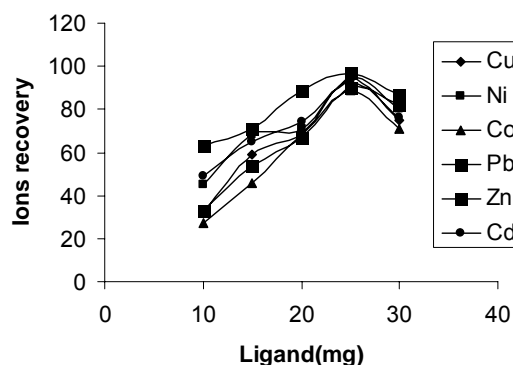

Fig 3. Effect of amount of ligand loaded on recovery of metal ions (N=3), pH=8.0, eluent: 6 mL 4.0 M HNO_3 .

Table 1. Effect of eluent condition on ion recoveries efficiency(N=3).

Type and concentration of the eluent	Ions recovery					
	Cu	Ni	Co	Pb	Zn	Cd
HNO_3 2M	78	82	75	69	73	69
HNO_3 4M	94	93	98	98	94	96
HCl 2M	35	46	39	49	35	51
HCl 4M	76	67	72	69	78	69
H_3PO_4 2M	25	30	31	29	26	37
H_3PO_4 4M	57	62	59	67	69	57
H_2SO_4 2M	41	35	38	33	39	42
H_2SO_4 4M	65	71	62	76	74	73
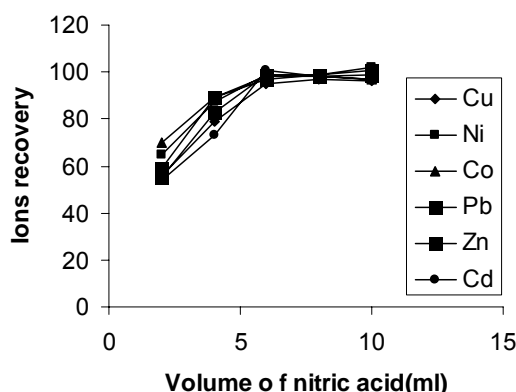
Figure 4. Effect of volume of nitric acid on recovery of metal ions (N=3), pH=8.0, eluent: 6 mL 4.0 M HNO_3.

Table 2. Effects of the matrix ions on the recoveries of the examined metal ions(N=3).

Ion	Added As	Tolerance Limit Ion, mg L-1
Na^+	NaCl	1500
K^+	KCl	1200
Li^+	LiCl	900
Mg^{2+}	$MgCl_2$	700
HCO_3^-	$NaHCO_3$	425
PO_4^{3-}	Na_3PO_4	400
Ba^{2+}, Ca^{2+}	*Nitrate salt*	500
Ag^+, Al^{3+}, Cr^{3+}, Hg^{2+}	*Nitrate salt*	250

Sample volume

The effect of the sample solution volume on Cu, Ni, Pb Zn, Cd and Co sorption was studied by passing100-1200 mL volumes through the column at a 4 mL min^{-1} flow rate. The adsorption of the metal ions was not affected by sample volume below 800 mL. Above this volume of sample solution, the percent sorption

decreased for the analytes. The recoveries of analytes decrease probably due to the excess analytes loaded over the column capacity with increasing sample volume above 800 mL. In the present study 800 mL of sample solution was adopted for the pre-concentration of the investigated ions, the adsorbed metals can be eluted with 6 mL 4 mol L^{-1} HNO_3 and a pre-concentration factor of 290 is achieved.

Interferences

In order to examine the effect of the various tested metal ions in the optimum conditions, extraction of these metal ions in the presence of some selected metal ions have been carried out which prompted us to perform an intensive selectivity study to evaluate the possible interference of some metal ions in the process of selective solid phase extraction of Cu, Ni, Pb Zn, Cd and Co.

Interferences that may be concomitant with this ion were investigated. The interference effect of calcium, magnesium and other alkali and alkaline earth ions presented in Table 2 display that these ions up to 1000 fold are negligible and this high selectivity enables the method for accurate and precise determination of Cu, Ni, Pb Zn, Cd and Co content in real samples.

Calibration graphs and precisions

The calibration curve were obtained using 250 mL 0.05-2.0 µg mL^{-1} ions solutions at pH=8.0 in the optimum condition. The eluting solution was sent to AAS for evaluating ion content and results are shown in Table 3. The results indicate that calibration curve was 0.02–1.0 µg mL^{-1} for Pb^{2+}, 0.02–1.0 µg mL^{-1} for Co^{2+}, 0.02–1.1 µg mL^{-1} for Zn^{2+} and 0.05–1.3 µg mL^{-1} for Cd^{2+} using DBDP . Relative standard deviation of measurement was found for copper, nickel, cobalt, lead, zinc and Cadmium, i.e. 1.3, 1.4, 1.2, 1.4, 1.7 and 1.4 respectively. Detection limits for this ion is 2.5, 2.4, 1.6, 2.4, 1.9 and 2.1 for Ni^{2+} , Cu^{2+}, Pb^{2+} , Co^{2+},Zn^{2+} and Cd^{2+} respectively.

In order to investigate reproducibility of the method at optimum condition six experiments for separation-pre-concentration of these ions on modified activated carbon are conducted and the results of recovery are 99.9, 98.7, 99.2 , 98.7, 98.5and 95.6 for Ni^{2+}, Cu^{2+}, Pb^{2+}, Co^{2+}, Zn^{2+} and Cd^{2+} indicating the high repeatable results.

Table 3. Specification of presented method at optimum conditions for each element(N=3)

Parameters	Ions					
	Cu	Ni	Co	Pb	Zn	Cd
Linear Range (µg mL^{-1})	0.03–1.0	0.03–1.1	0.05–1.1	0.02–1.0	0.02–1.1	0.05–1.3
Detection Limit(µg mL^{-1})	2.4	2.5	2.4	1.6	1. 9	2. 1
RSD %	1.4	1.3	1.4	1.2	1.7	1.4
Recovery %	98.7	9 9.9	98.7	99.2	98. 5	95. 6

Table 4. Recovery of trace elements from Vegetable sample after pre-concentration on Activated carbon modified with DBDP (N=3)

Ion[a]	Vegetable			
	Added	Founded	*RSD %*	Recovery %
Cu	0	56.3	2.2	---
	75	132.3	0.9	101.3
Ni	0	80.6	1.4	---
	75	154.6	0.8	98.7
Co	0	70.6	1.6	---
	75	147.1	0.9	102
Pb	0	45.6	1.8	---
	75	121.9	1.0	101.7
Zn	0	67.6	1.4	---
	75	144.2	1.0	102.1
Cd	0	51.3	1.6	---
	75	124.3	0.9	97.3

a) All values are µg L^{-1}

Table 5. Recovery of trace elements from water sample after pre-concentration on Activated carbon modified with DBDP (N=3)

Ion[a]	Water			
	Added	Founded	RSD %	Recovery %
Cu	0	63.4	1.4	---
	100	164.7	0.9	101.3
Ni	0	51.4	1.5	---
	100	149.2	1.0	97.8
Co	0	68.5	1.3	---
	100	167.2	0.9	98.7
Pb	0	72.3	1.5	---
	100	175.2	0.9	102.9
Zn	0	65.3	1.7	---
	100	168.0	0.9	102.7
Cd	0	34.3	1.3	---
	100	135.9	0.9	101.6

a) all values are µg L^{-1}

Applications

To evaluate the applicability of the pre-concentration and solid phase extraction of metal ions, it was applied to the determination of Ni^{2+}, Cu^{2+}, Pb^{2+}, Co^{2+}, Zn^{2+} and Cd^{2+} in vegetable and water samples. The results were summarized in Tables 4 and 5. Satisfactory recoveries were obtained for spiked analyte ions. The recoveries were higher than 95%, thus confirming the accuracy of the presented procedure.

CONCLUSION

A simultaneous pre-concentration of Cu, Ni, Pb Zn, Cd and Co from aqueous solution on an activated carbon impregnated with DBDP column was successfully developed. The conditions for pre-concentration of metal ions were selected using model solutions. The accuracy and precision of the proposed SPE method was reported in term of recovery (%) ranging from 95 to 104%, and R.S.D. (%) ranging from 0.9 to 1.8%. The proposed method can be applicable for the determination of trace metal ions in a variety of real samples with low detection limit, high accuracy and high precision.

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