The determination of Cu^{2+}, Fe^{3+}, Zn^{2+} and Pb^{2+} in real samples by flame atomic absorption spectrometry after their separation- preconcentration on 2-(2-nitro-phenylazo)-naphthalen-1-ol loaded on activated carbon

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A sensitive and simple method for simultaneous preconcentration of trace heavy metal ions in some cereal and vegetable samples has been reported. The method is based on the adsorption of Cu^{2+}, Fe^{3+}, Zn^{2+} and Pb^{2+} on 2-(2-nitro-phenylazo)-naphthalen-1-ol (NPN) loaded on activated carbon (AC). The adsorbed metals on activated carbon were eluted using 3 ml 4 mol L^{-1} nitric acid. The influences of the analytical parameters including pH, flow rate of sample and eluent, type and concentration of eluent, amount of adsorbent and sample volume were investigated. The effects of matrix ions on the recoveries of analyte ions were also investigated. The recoveries of analytes were generally higher than 95%. The detection limits for Cu^{2+}, Fe^{3+}, Zn^{2+} and Pb^{2+} were 0.17 µg L^{-1}, 0.16 µg L^{-1}, 0.11 µg L^{-1} and 0.12 µg L^{-1} respectively.

Keywords: Solid-phase extraction; FAAS; trace metal enrichment; activated carbon; 2-(2-nitro-phenylazo)-naphthalen-1-ol

1. INTRODUCTION

For designating the level of pollution as the rise in ecological and health problems, required to determination of trace metals in environmental samples [1-3]. These samples have complex matrices therefore direct analysis of these samples is difficult [3-6], and because of low concentration of heavy metals, preconcentration is suggested to solve the above problems.

The advantages of solid phase extraction (SPE) as a preconcentration method are counted as fast, simple and direct application in micro liter volume without any sample loss, higher preconcentration factor, rapid phase separation, time and cost saving [7-10]. The basic principle of SPE is the transfer of analytes from aqueous phase to the active sites of solid phase. A number of supports and chelating ligands have been widely used for the preconcentration and separation of trace metal ions from various matrices [11-19].

Activated carbon (AC) has the ability to absorb both organic and inorganic compounds. Therefore it is widely used for many purposes both in laboratorial and industrial settings. Application of modified AC as supports for SPE has increased enrichment factor for trace metals in different matrices. The separation of metal ions on AC can be improved in presence of chelating agent [8-10].

The purpose of this work is to investigate a preconcentration separation procedure for Cu^{2+}, Fe^{3+}, Zn^{2+} and Pb^{2+} in some cereal and vegetable materials on activated carbon modified with 2-(2-nitro-phenylazo)-naphthalen-1-ol (NPN).

2. EXPERIMENTAL

2.1. Instrumentation

The measurements of metal ions were performed with a Shimadzu 680AA atomic absorption spectrometer equipped with a hollow cathode lamp and a deuterium background corrector, at respective wavelengths using an air-acetylene flame. The instrumental parameters were those recommended by the manufacturer. A Metrohm 691 pH/ion meter with a combined glass–calomel electrode was used for adjustment of test solution pH.

2.2 Reagents

Acids and bases were of the highest purity available from Merck and were used as received. Doubly distilled deionized water was used throughout. The analytical reagent grade nitrate salts of lead, copper, zinc, and iron (Merck, Darmstadt, Germany) were used without any further purification. The pH adjustment was done by the 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] was cleaned in hydrochloric acid for 2 days. Then it was washed with water and dried at 110°C for 1 day.

The 2-(2-nitro-phenylazo)-naphthalen-1-ol (NPN) was prepared according to the literature (Scheme 1) [20].
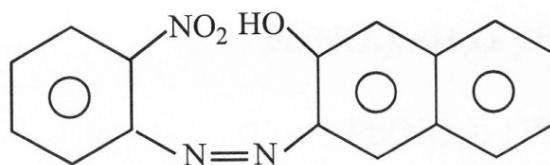
Scheme 1. The structure of chemical reagent.

2.3. Preparation of NPN-coated activated carbon

A Pyrex glass column containing 0.6 g of activated carbon in water suspension was 10 cm long and 1cm in internal diameter. The bed height in the column was approximately 1 cm. The AC (600mg) was impregnated with NPN solution through the column packed with AC at a flow rate of 0.2 mLmin^{-1}. The filtrate was collected and analyzed for un-adsorbed NPN with the UV–vis spectrophotometer at maximum wavelength. The column was then washed twice with 5mLwater and the filtrates were analyzed for ligand that was released. The optimum amount of NPN on the AC column was 10 mg.

2.4. Preconcentration procedure

The pH of the solution was adjusted to 3.5 with buffer and passed through the NPN-loaded AC column at a flow rate of 3 mLmin^{-1} with the aid of a suction pump. The analyte was then eluted with 3 mL of 4.0 molL^{-1} HNO$_3$. The metal ions content of the eluent was measured by FAAS.

2.5. Pretreatment of real samples

Accurately weighted amounts of dried and crushing vegetables, cereals in small mesh were heated in silica crucible for 3 h on a hot plate and the charred material was transferred to furnace for overnight heating at 650 $^\circ$C. The residue was cooled, gain kept in furnace for 2 h at the same temperature, to decompose organic matter completely. 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 3.5 made up to 250 mL by addition of diluted HNO_3 solution [21].

3. RESULTS AND DISCUSSION

In preliminary experiments, it was observed that the preconcentration of the metals with the untreated AC is not suitable for Co, Ni, Cu and Pb. Therefore, NPN-AC seems to be a better sorbent in simultaneous sorption of the studied elements. Due to the existence of a donating atoms as well as N and O (OH and NO_2) group in NPN was expected to increase both the stability and selectivity of its complex toward ions.

3.1. Effect of the amount of activated carbon

In the adsorption step, an appropriate amount of activated carbon should be used in order to obtain quantitative retention of metals. On the other hand, an excess amount of the sorbent also prevents the quantitative elution of the retained metals by a small volume of eluent. The influences of the amounts of activated carbon filled to the column were also investigated. The results are given in Figure 1. The recoveries of analytes were increased with increasing amounts of AC and reach to quantitative value of 0.6 g of activated carbon.
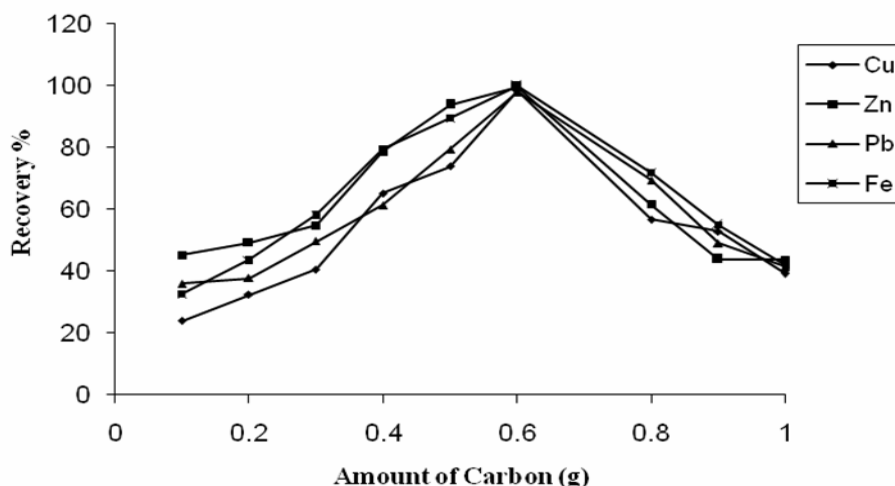
Fig. 1. Effect of amount of activated carbon on recovery of metal ions (N = 3).

3.2. Effect of pH

In the solid phase extraction studies, pH of the working solution is main factor for the quantitative adsorption of analytes on solid phase. In order to optimize the sorption conditions for the retention of the ions on modified AC, the effects of pH was investigated in the pH range of 2–8 by using column packed with 0.6 g modified AC. Figure 2 shows that the optimal pH value was in 3.5. Considering these results, the pH 3.5 has been recommended for subsequent experiments.

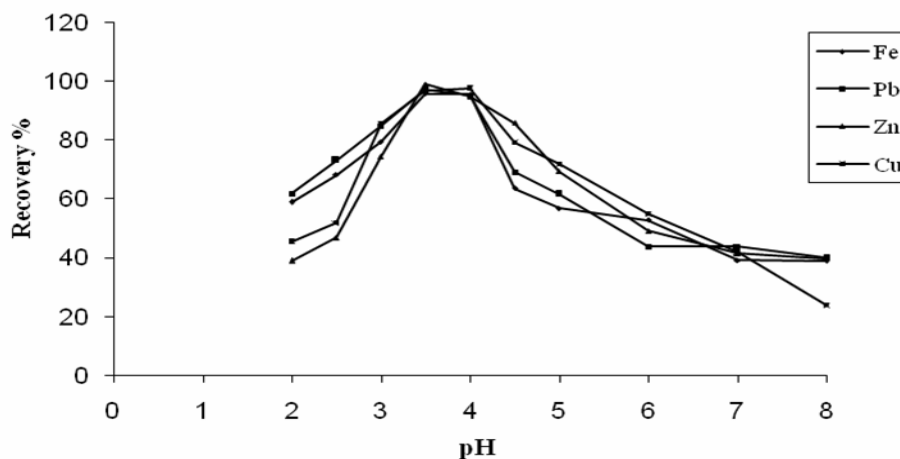**Fig. 2.** Effect of pH on recovery of metal ions (N = 3).

3.3. Effect of the NPN amounts

The effects of the ligand amount on the retention of the analyte ions on NPN-AC were also examined. The results are depicted in Figure 3. The recoveries of analytes were quantitative, till the addition of 10 mg ligand. After that, the recovery values decreased, probably due to the formation of charged complex which could not been completely retained on solid phase.
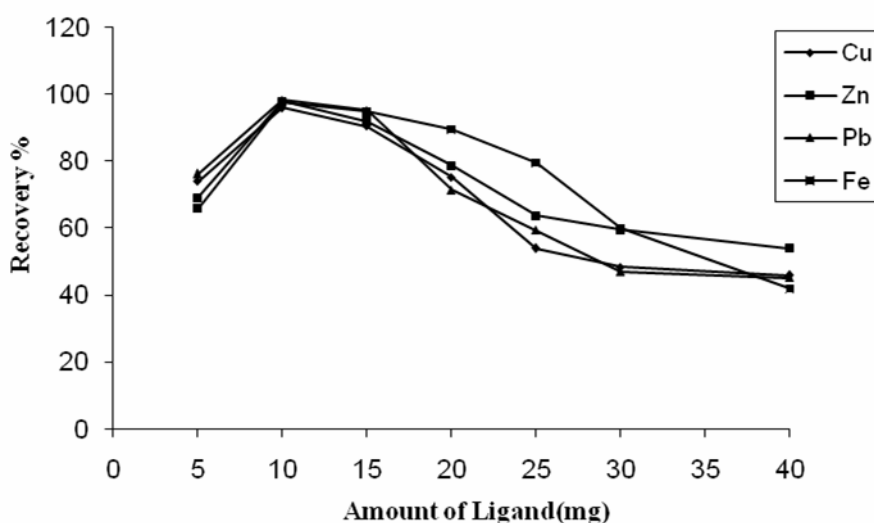
Fig.3. Effect of amount of ligand loaded on recovery of metal ions (N = 3).

3.4. Type and volume of the eluent

The nature and concentration of eluting agents were found to have a significant effect on the elution process of the retained ions from the solid phase. As could be seen from Fig. 2, the uptake of these metal ions was negligible at pH <3; therefore, the acidic eluents are the best solution for extraction of adsorbed ions. Different eluting solutions given in Table 1 were used for elution of ions, which retained on NPN-AC. The effect of eluent volumes and concentrations on the recoveries of the analytes were also investigated. Quantitative recoveries of Cu^{2+}, Fe^{3+}, Zn^{2+} and Pb^{2+} ions were obtained with 3 mL of 4 mol L^{-1} HNO_3 as compared to other eluents. Therefore, 3 mL of 4 mol L^{-1} HNO_3 was used in the subsequent Experiments.

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

Acid	Recovery %			
	Cu	Zn	Pb	Fe
4 mol L^{-1} Hcl	95.6	87.2	79.3	93.9
4 mol L^{-1} H$_3$PO$_4$	76.4	72.3	69.4	78.1
4 mol L^{-1} H$_2$SO$_4$	78.2	75.4	72.0	87.1
4 mol L^{-1} HOAC	76.3	63.7	56.1	54.9
1 mol L^{-1} HNO$_3$	71.4	65.8	69.3	78.4
2 mol L^{-1} HNO$_3$	97.3	96.0	96.9	97.1
3 mol L^{-1} HNO$_3$	98.6	96.9	98.6	97.4
4 mol L^{-1} HNO$_3$	97.5	101.3	99.7	98.9

3.5. Flow rates

The effects of the sample and eluent flow rates on the retentions and recoveries of analyte ions on the adsorbent were also examined in the flow rate range of 1–12mLmin^{-1} under optimal conditions with model solutions containing analyte elements. All the analyte ions were quantitatively retained and recovered in the sample and eluent flow range of 1–3 mLmin^{-1}. After 3 mL min^{-1}, the recoveries were not quantitative due to insufficient contact between analytes and adsorbent. In the all-further works, 3 mL min^{-1} was selected as sample and eluent flow rate.

3.6. Sample volume

The effect of the sample solution volume on the metal sorption was studied by passing 100–2000mL volumes through the column at a 3 mLmin^{-1} flow rate. The adsorption of the metal ions was not affected by sample volume below 1500 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 1500 mL. In the present study 1650mL of sample solution was adopted for the preconcentration of the investigated ions, the adsorbed metals can be eluted with 3 mL of 4 molL^{-1} HNO$_3$ and a preconcentration factor of 550 is achieved.

3.7. Interferences

In order to assess the possible analytical applications of the preconcentration procedure presented, the effect of some foreign ions which interfere with the determination of trace of these ions or/and often accompany analyte ions in various real environmental samples was examined with the optimized conditions. The results are summarized in Table 2. The tolerance limit is defined as the ion concentration causing a relative error smaller than ±5% related to the preconcentration and determination of analytes. The tolerable levels of the some heavy metal ions are suitable for the separation and preconcentration of ions in the real samples examined present study, because the levels of transition metals in these samples are lower than their interferic level. It can be seen that the major matrix ions in the real samples show no obvious interference with the preconcentration of the mentioned ions.

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

Ion	Tolerance limit ion (mg L^{-1})
Na^+, K^+, Li^+, Ca^{2+}, Mg^{2+}	1000
I^-, Br^-	900
Cr^{3+}, Cd^{2+}, SO_4^{2-}	700
HCO_3^-, CO_3^{2-}	600
Ni^{2+}, Co^{2+}, Mn^{2+}	550
SCN^-	400
Ag^+	150

3.8. Analytical performance

By passing 100 mL solution of 0.5-10 μgL^{-1} of all ions understudy, the calibration curves, repeatability and reproducibility were obtained. The effluent was sent to AAS for evaluating ions content. The sensitivity of developed method was reproduced by detecting the limit of detection (LOD), defined as the lowest concentration of metal ions below which quantitative sorption of the metal ion is not perceptibly seen. The limits of detection (LOD) of the present work were calculated under optimal experimental conditions after application of the preconcentration procedure to blank solutions (without samples or standards). The limits of detections based on three times the standard deviations of the blank (N= 6, LOD= Xb+3s, where LOD is the limits of detection and Xb is the blank value) for Cu^{2+}, Fe^{3+}, Zn^{2+} and Pb^{2+} were found to be 0.18, 0.16, 0.11 and 0.12 μgL^{-1}, respectively [22]. The characteristic performances of the method which presented in Table 3 show good linear range, low detection limits, high reproducibility and low relative standard deviation for all elements.

Table 3. Specification of presented method at optimum conditions for each element (N=6).

Parameters	Cu	Pb	Zn	Fe
Linear range ($\mu g\ L^{-1}$)	0.37-300	0.26-300	0.23-300	0.35-300
Detection limit (ng ml^{-1})	0.17	0.12	0.11	0.16
R.S.D. %	1.9	1.9	1.4	1.7
Recovery %	98.7	97.1	98.4	98.9

3.9. Applications to real samples

In order to assess the applicability of the method to real samples, with different matrices containing varying amounts of a variety of diverse ions, it was applied to the separation and recovery of ions from different matrices such as vegetables and cereals. Spiking experiments using standard addition method checked reliabilities. The percentage of recoveries and relative standard deviation for each element in spiked vegetable and water samples are given in Tables 4-5. As seen, the results of three analyses of each sample show that, in all cases, the ions recoveries are almost quantitative with a low R.S.D.

Table 4. Recovery of trace elements from spiked cereal samples that irrigated with tap water and waste water after application of presented procedure. (N=3)

Ion	irrigated with tap water				irrigated with waste water				
	Added*	Found*	RSD%	Rec.%	Added*	Found*	RSD%	Rec.%	
Cu	0.000	0.106	1.9	-	0.000	0.427	1.8	-	
	0.050	0.158	2.4	104.0	0.050	0.480	1.4	105.0	
	0.500	0.606	1.9	100.1	0.500	0.926	1.8	99.9	
Zn	0.000	0.067	1.9	-	0.000	0.224	2.0	-	
	0.050	0.117	1.8	99.0	0.050	0.276	1.5	103.0	
	0.500	0.565	2.1	99.6	0.500	0.723	1.9	99.8	Lentil
Fe	0.000	0.919	2.0	-	0.000	1.410	1.8	-	
	0.050	0.971	1.7	104.0	0.050	1.463	1.8	105.0	
	0.500	1.420	1.8	100.2	0.500	1.908	2.1	99.6	
Pb	0.000	0.065	1.7	-	0.000	0.394	1.8	-	
	0.050	0.108	1.9	103.0	0.050	0.442	2.0	96.0	
	0.500	0.558	2.1	100.4	0.500	0.896	1.8	100.2	
Cu	0.000	0.134	1.8	-	0.000	1.424	2.0	-	
	0.050	0.182	1.5	96.0	0.050	1.476	1.8	104.0	
	0.500	0.633	1.7	99.7	0.500	1.923	1.5	99.8	
Zn	0.000	0.235	2.1	-	0.000	1.525	1.6	-	
	0.050	0.283	2.0	96.0	0.050	1.577	1.3	103.0	
	0.500	0.736	2.1	100.2	0.500	2.027	1.8	100.4	Wheat
Fe	0.000	1.715	1.3	-	0.000	4.574	1.6	-	
	0.050	1.766	1.5	102.0	0.050	4.623	1.8	98.0	
	0.500	2.215	1.7	99.9	0.500	5.074	2.1	100.1	
Pb	0.000	0.213	2.1	-	0.000	1.010	1.4	-	
	0.050	0.265	2.0	104.0	0.050	1.061	1.7	102.0	
	0.500	0.713	1.7	99.9	0.500	1.512	2.1	100.4	

*µg g^{-1} of sample

Table 5. Recovery of trace elements from spiked vegetable samples that irrigated with tap water and waste water after application of presented procedure. (N=3)

Ion	irrigated with tap water				irrigated with waste water				
	Added*	Found*	RSD%	Rec.%	Added*	Found*	RSD%	Rec.%	
Cu	0.000	0.141	1.6	-	0.000	0.595	2.1	-	
	0.050	0.192	1.8	103.0	0.050	0.647	2.0	104.0	
	0.500	0.642	1.5	100.2	0.500	1.093	1.9	99.6	
Zn	0.000	0.035	1.5	-	0.000	0.122	1.7	-	
	0.050	0.086	1.4	102.0	0.050	0.174	1.5	105.0	
	0.500	0.537	2.1	100.3	0.500	0.622	1.8	100.1	Gardencress
Fe	0.000	1.429	1.7	-	0.000	2.192	2.0	-	
	0.050	1.477	1.7	96.0	0.050	2.242	1.7	100.0	
	0.500	1.928	1.9	99.9	0.500	2.694	2.1	100.3	
Pb	0.000	0.043	1.6	-	0.000	0.347	1.9	-	
	0.050	0.094	2.1	102.0	0.050	0.399	1.6	104.0	
	0.500	0.542	1.9	99.8	0.500	0.846	1.7	99.9	

Cu	0.000	0.171	1.6	-	0.000	0.797	2.2	-	
	0.050	0.224	1.8	105.0	0.050	0.845	1.8	95.0	
	0.500	0.672	2.1	100.2	0.500	1.299	2.0	100.3	
Zn	0.000	0.061	1.5	-	0.000	0.169	1.5	-	
	0.050	0.113	1.7	104.0	0.050	0.220	1.9	102.0	
	0.500	0.563	2.0	100.3	0.500	0.672	1.6	100.5	Radish
Fe	0.000	0.580	1.9	-	0.000	0.961	1.6	-	
	0.050	0.629	2.1	97.0	0.050	1.013	2.1	103.0	
	0.500	1.081	1.6	100.2	0.500	1.464	2.0	100.5	
Pb	0.000	0.114	1.7	-	0.000	0.428	1.8	-	
	0.050	0.162	2.1	97.0	0.050	0.477	1.9	97.0	
	0.500	0.612	1.6	99.7	0.500	0.929	1.9	100.2	
Cu	0.000	0.165	1.7	-	0.000	0.784	1.9	-	
	0.050	0.208	1.2	104.0	0.050	0.835	1.9	102.0	
	0.500	0.655	2.1	99.8	0.500	1.283	1.6	99.8	
Zn	0.000	0.041	1.9	-	0.000	0.165	1.5	-	
	0.050	0.091	1.4	99.0	0.050	0.214	1.8	97.0	
	0.500	0.542	1.8	100.2	0.500	0.664	2.1	99.8	Spinach
Fe	0.000	0.178	1.9	-	0.000	0.991	1.3	-	
	0.050	0.229	2.0	103.0	0.050	1.041	1.9	101.0	
	0.500	0.676	1.4	99.6	0.500	1.489	2.0	99.7	
Pb	0.000	0.040	1.7	-	0.000	0.214	1.6	-	
	0.050	0.089	1.8	98.0	0.050	0.263	1.5	99.8	
	0.500	0.539	1.6	99.7	0.500	0.714	2.0	99.9	

$*\mu g\ g^{-1}$ of sample

4. CONCLUSION

A new method was developed for the determination of trace metals. The procedure offers a useful multi-element preconcentration technique in various samples including vegetable and cereal samples with acceptable accuracy and precision. The other main advantages of the method include simplicity, time saving, no requirements of sophisticated instruments, and cost effectiveness. Modified activated carbon on the column could be used all through the studies without any lost of its adsorption properties. The possibilities of using the extraction system in modified AC for the preconcentration and separation of the metallic cations in solutions with relatively high contents of salts are extended.

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