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Copper, iron, and lead levels in fertilizer and water samples: separation and preconcentration on multiwaled carbon nanotubes

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ABSTRACT

An enrichment-separation method using solid-phase extraction of trace amounts of Fe(III), Cu(II), and Pb(II) as their pyrocatechol violet chelates on multiwaled carbon nanotube column has been established. Analytes were desorbed from the column by using 5 mL of 2.0 M HNO_3. Influences of some analytical parameters like pH and sample volume on the recoveries of the analyte ions were investigated. Effects of matrix ions were also evaluated. The presented procedure was validated by using additional recovery test and analyzing the certified reference materials (SRM 1570a—Trace Elements in Spinach Leaves and TMDA-70 fortified lake water). The application of this method was successfully performed for the determination of copper, iron, and lead levels in various fertilizer samples marketed in Kayseri–Turkey and some water samples.

Keywords: Multiwaled carbon nanotubes; Pyrocatechol violet; Heavy metals; Flame atomic absorption spectrometry; Fertilizer; Solid phase extraction; Preconcentration

1. Introduction

Heavy metals at trace levels are generally a problem in environment [1–4]. They are toxic to men, animals, and plants [5]. The accumulation of heavy metals in environmental samples is an important risk for human life [4–7]. Fertilizers have been one of the pollution resources of heavy metals. One of the sources of toxic and essential trace metals in agricultural soils is natural and mineral fertilizer [8–10]. Due to these important points, the determination of trace metal zcontents of different fertilizers is necessary. These determinations could be performed by the instrumental techniques like atomic absorption spectrometry (AAS), inductively coupled plasma-atomic emission spectrometry, and inductively coupled plasma-mass spectrometry [11–14]. However, lower element levels of analyte elements than detection limits of instruments and interference of the matrix components of analyzed sample [15–18]. To solve these problems, generally preconcentration-separation techniques including membrane filtration, solvent extraction, electroanalytical procedures, and coprecipitation etc. have been used [19–22].

Solid phase extraction procedures for the clean-up and preconcentration of metal ions at trace level in the environmental samples are preferred to other enrichment techniques because of its simplicity [23–26]. Various new materials as solid-phase extractor that have high surface area and high adsorption capacities

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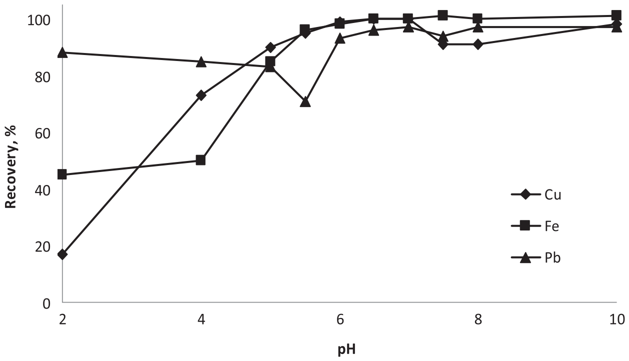

Fig. 1. Effect of pH on the recoveries of analytes on multiwaled carbon nanotubes ($N = 3$, eluent: 2.0 mol L^{-1} HNO_3).

have been used for the solid-phase extraction studies [27–30]. Nanomaterials including carbon nanotubes have been also used for this purpose [31–35].

Pyrocatechol violet is one of the chelating agents for metal ions; it has been used on the spectrophotometric determination and preconcentration of various metal ions in environmental samples [36–38]. The formation of pyrocatechol violet metal complexes is at ML_n (M: metal, L: pyrocatechol violet) [37–39].

In the present study, the optimal conditions for the adsorption of Fe(III), Cu(II), and Pb(II) as their pyrocatechol violet chelates on multiwaled carbon nanotube have been investigated. In the determination of analyte levels, flame atomic absorption spectrometer technique was used.

2. Experimental

2.1. Instruments

The metal content was determined using Perkin-Elmer Model 3110, flame atomic absorption spectrometer (Norwalk, CT, USA) The operating parameters for AAS determinations were set as recommended by the manufacturer. The excitations were done using air/acetylene flame.

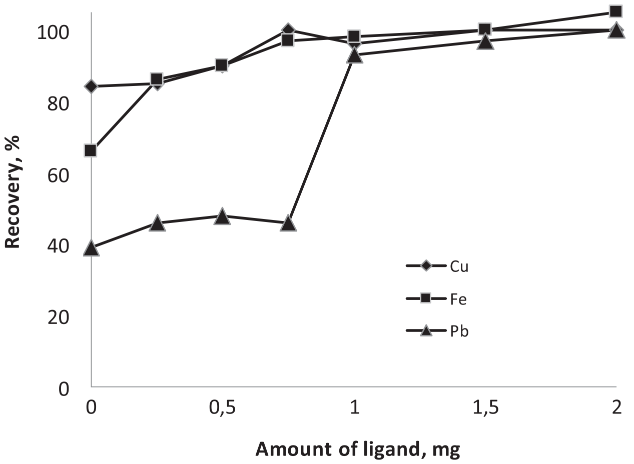

Fig. 2. Effect of amount of pyrocatechol violet on the recoveries of analytes on multiwaled carbon nanotubes ($N = 3$, pH = 6.0).

A pH meter, Nel pH-900 Model glass electrode was used for measuring the pH values in the analyte solutions. The water used in all the experiments was purified in a Human model RO 180 water purification system (HUMAN Corp. Seoul, Korea). Its conductivity was 1 μS cm^{-1}.

2.2. Reagents and solutions

High purity reagents from Merck, Darmstadt were used. 1,000 mg L^{-1} analyte were prepared from their nitrate salts in 1% of HNO_3. Dilute standard solutions and model solutions were prepared daily from the stock standard solutions. Multiwaled carbon nanotubes were purchased from Aldrich, Milwaukee, WI, USA. 0.1% (m/V). 0.1% (m/V) solution of pyrocatechol violet

Table 1
Effects of some eluents on the recovery of analyte ions ($N = 3$)

Eluent			Recovery (%)		
Type	Concentration (mol L^{-1})	Volume (mL)	Fe	Cu	Pb
HCl in acetone	1	10	100 ± 1	97 ± 1	78 ± 1
HCl in acetone	2	10	101 ± 2	98 ± 1	86 ± 1
HNO_3 in acetone	1	10	100 ± 1	100 ± 2	93 ± 1
HNO_3 in acetone	2	10	99 ± 1	98 ± 1	97 ± 1
HCl	1	10	97 ± 2	101 ± 2	69 ± 3
HCl	2	10	98 ± 2	103 ± 3	73 ± 1
HNO_3	1	10	97 ± 3	100 ± 1	94 ± 1
HNO_3	2	10	99 ± 1	100 ± 1	98 ± 1
HNO_3	2	5	99 ± 1	99 ± 1	97 ± 2

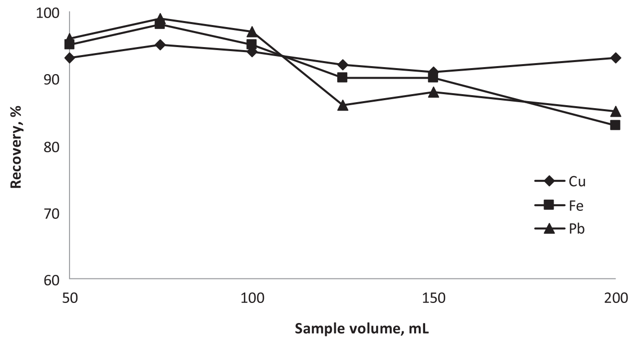

Fig. 3. Effect of sample volume on the recoveries of analytes ($N = 3$, pH = 6.0).

(Sigma Chem. Co. St. Louis) was prepared by dissolving in water. The buffer solutions given in Literature [40] were used in the present preconcentration work.

Certified reference materials such as SRM 1570a—Trace Elements in Spinach Leaves and TMDA-70 fortified lake water were used from the National Institute of Standard Technology (NIST, Gaithersburg, MD, USA) and from National Water Research Institute, Environment Canada (Burlington, ON, Canada), respectively, to check the accuracy of the proposed method.

2.3. Preconcentration procedure

Two hundred milligrams of multiwaled carbon nanotube was loaded into a 10 mm × 150 mm glass column with a glass frit resin support after washing with 2 mol L^{-1} HNO_3 and water successively. Before each use, 2 mol L^{-1} HNO_3 solution and water were passed through the column in order to clean it [41,42]. Then, the multiwaled carbon nanotube column was conditioned to the desired pH values with buffer solutions prior to loading sample solution.

Forty milliliter of working solutions containing 10–40 μg of each analytes were adjusted to the desired pH. Then pyrocatechol violet was added to form the metal chelates. After 10 min, the solution was loaded to the column and the flow was by gravity. After passage of the solution was over, the column was washed with desired buffer solution. The metals were recovered with the aid of 5 mL of 2 mol $L^{-1}HNO_3$. The analyte concentrations in the final solution were determined by flame atomic absorption spectrometer.

2.4. Applications

In order to digest the samples, an open digestion vessel was used. One gram of SRM 1570A Spinach Leaves certified reference material and/or 1.0 g of herbal tea were digested with 15 mL concentrated HNO_3 at 100–150˚C. The mixture was then evaporated almost to dryness and mixed with 15 mL concentrated HNO_3 and 5 mL of H_2O_2, then again evaporated to near dryness. After evaporation, 20 mL of water was added and the sample was mixed. The resulting mixture was filtered through a 589/3 blue ribbon filter paper (B125 mm, Schleicher & Schuell, Dassel, Germany). The filtrate was diluted to 25 mL with water and the procedure is described in Section 2.3 was then applied. The analytes in final solution were determined by FAAS.

This method was applied to TMDA-70 fortified lake water. From 25 mL of TMDA-70 fortified water certified reference material was taken in a beaker. The

Table 2
Effects of some concomitants on the recoveries of analytes ($N = 3$)

Concomitants	Concentration (mg L^{-1})	Added as	Recovery (%)		
			Fe	Cu	Pb
Na^+	20,000	NaCl	101 ± 1	100 ± 1	101 ± 1
CO_3^{2-}	300	Na_2CO_3	100 ± 1	95 ± 1	98 ± 2
Cl^-	35,000	NaCl	101 ± 1	100 ± 1	101 ± 1
SO_4^{2-}	500	Na_2SO_4	101 ± 1	94 ± 2	99 ± 1
$PO4_4^{3-}$	1,000	$Na_3PO_4.12H_2O$	100 ± 1	99 ± 1	102 ± 2
Pb^{2+}	20	$Pb(NO_3)_2$	96 ± 1	100 ± 1	–
Cu^{2+}	15	$Cu(NO_3)_2.3H_2O$	94 ± 1	–	98 ± 1
Fe^{3+}	20	$FeCl_3$	–	100 ± 1	97 ± 1
Mn^{2+}	50	$Mn(NO_3)_2.4H_2O$	98 ± 2	95 ± 1	95 ± 1
Zn^{2+}	10	$Zn(NO_3)_2.6H_2O$	97 ± 2	96 ± 2	96 ± 1
Cd^{2+}	20	$Cd(NO_3)_2.4H_2O$	95 ± 1	100 ± 1	98 ± 1
Ni^{2+}	20	$Ni(NO_3)_2.6H_2O$	98 ± 2	95 ± 2	99 ± 1
Co^{2+}	25	$Co(NO_3)_2.6H_2O$	94 ± 2	94 ± 2	96 ± 1

Table 3
Addition-recovery test to natural water samples as an application of presented solid phase extraction method (Sample volume: 100 mL, $N = 5$)

Analyte	Added (μg L^{-1})	Tap water		Spring water		River water	
		Found (μg L^{-1})	Recovery (%)	Found (μg L^{-1})	Recovery (%)	Found (μg L^{-1})	Recovery (%)
Fe	0	17 ± 3	–	31 ± 1	–	35 ± 7	–
	100	112 ± 14	95 ± 1	128 ± 22	97 ± 2	131 ± 8	96 ± 2
	200	213 ± 05	98 ± 2	223 ± 8	96 ± 2	225 ± 11	95 ± 2
	400	415 ± 07	98 ± 1	427 ± 9	97 ± 1	422 ± 8	96 ± 2
	600	604 ± 06	97 ± 2	625 ± 4	99 ± 1	618 ± 7	97 ± 1
Cu	0	BDL	–	BDL	–	BDL	–
	100	97 ± 2	97 ± 2	95 ± 3	95 ± 2	97 ± 6	97 ± 1
	200	196 ± 3	98 ± 1	198 ± 2	99 ± 1	210 ± 11	101 ± 2
	400	392 ± 7	98 ± 1	402 ± 2	100 ± 1	401 ± 1	100 ± 1
	600	600 ± 1	100 ± 1	572 ± 5	95 ± 2	607 ± 6	101 ± 1
Pb	0	BDL	–	BDL	–	BDL	–
	100	94 ± 5	94 ± 1	97 ± 3	97 ± 1	96 ± 2	97 ± 3
	200	196 ± 2	97 ± 1	201 ± 1	100 ± 1	196 ± 4	98 ± 1
	400	384 ± 3	95 ± 1	387 ± 3	97 ± 1	393 ± 5	98 ± 1
	600	57.2 ± 2	95 ± 1	582 ± 3	97 ± 2	564 ± 6	94 ± 1

Note: BDL: Below the detection limit, mean ± standard deviation.

pH of the samples was adjusted to six with buffer solution. Then the procedure is described in Section 2.3 which was then applied.

One gram of fertilizer sample was digested with 10 mL of distilled at 100°C. The resulting mixture was then filtered through a 589/3 blue ribbon filter paper (B125 mm, Schleicher & Schuell, Dassel, Germany). The filtrate was diluted to 25 mL with water and the procedure is described in Section 2.3 which was then applied. Fe, Cu, and Pb in final solution were determined by FAAS.

3. Results and discussion

3.1. Effect of pH on sorption

In the solid-phase extraction studies for metal ions at trace levels for preconcentration and separation and complex formation between metal and ligand, pH of solution is an affective factor [41–45]. The influences of the pH of the working solutions that contain analytes were investigated at the pH range of 2.0–10.0 keeping other parameters constant. The results were given in Fig. 1. The recovery values of analyte ions were quantitative (>95%) at the pH range of 6.0–7.0. The pH 6.0 is selected for further works. This pH value is agree with the literature works about the solid-phase extraction works for metal ions by using pyrocatechol violet as chelating agent [36,38]. The pH 6.0 was adjusted by using dihydrogen phosphate/disodium hydrogen phosphate buffer solution.

3.2. Influences of concentration of pyrocatechol violet

Different concentration of pyrocatechol violet (0.1%, w/v), ranged 0.0–2.0 mg were studied to find the optimum concentration of pyrocatechol violet. The results are given in Fig. 2. It was found out that, the recovery value without pyrocatechol violet was not quantitative (<95%). However, the recoveries of analytes were quantitative for all the analytes in the range of 1.0–2.0 mg when the metals were previously complexed with the ligand. It was established that the optimum quantity of pyrocatechol violet was 1.5 mg and therefore preconcentration studies were carried out using that mass of the ligand.

3.3. Effect of eluent type

Due to the importance of eluent type on the quantitative recoveries of the analytes from adsorbents [46–52], the influences of various eluting agents and their volume on the desorption of adsorbed pyrocatechol violet analyte chelates from the multiwaled carbon nanotube column were also investigated keeping other

Table 4
Addition-recovery test for fertilizers and chamomile tea ($N = 5$)

Analyte	Added ($\mu g\,g^{-1}$)	Ammonium nitrate fertilizer		Monopotassium phosphate fertilizer		Chamomile Tea	
		Found ($\mu g\,g^{-1}$)	Recovery (%)	Found ($\mu g\,g^{-1}$)	Recovery (%)	Found ($\mu g\,g^{-1}$)	Recovery (%)
Fe	0	33.6 ± 1.2	–	5.6 ± 0.4	–	107 ± 5	–
	10	43.5 ± 0.8	99 ± 2	15.3 ± 0.6	97 ± 2	117 ± 2	100 ± 1
	20	52.6 ± 1.0	95 ± 3	25.5 ± 1.3	99 ± 1	128 ± 2	103 ± 2
	40	73.3 ± 1.3	100 ± 2	44.5 ± 1.0	97 ± 2	147 ± 4	100 ± 1
	60	96.2 ± 1.1	103 ± 2	64.2 ± 1.2	98 ± 2	170 ± 2	105 ± 4
Cu	0	1.3 ± 0.1	–	BDL	–	7.4 ± 0.5	–
	10	11.1 ± 0.2	98 ± 1	9.8 ± 0.1	98 ± 2	16.8 ± 1.2	94 ± 2
	20	21.0 ± 0.0	99 ± 2	19.1 ± 0.3	96 ± 2	26.6 ± 0.8	97 ± 2
	40	39.1 ± 0.0	96 ± 1	38.2 ± 0.2	95 ± 3	46.5 ± 0.6	98 ± 1
	60	60.7 ± 0.1	101 ± 2	57.9 ± 0.5	97 ± 3	64.9 ± 1.3	96 ± 1
Pb	0	BDL	–	BDL	–	BDL	–
	10	9.5 ± 0.4	95 ± 3	9.8 ± 0.1	98 ± 1	9.6 ± 0.2	96 ± 2
	20	19.8 ± 0.6	99 ± 1	19.3 ± 0.8	97 ± 2	19.1 ± 0.6	96 ± 1
	40	39.5 ± 0.3	98 ± 2	38.6 ± 1.2	97 ± 1	40.3 ± 0.5	101 ± 2
	60	57.0 ± 2.3	95 ± 2	56.2 ± 0.7	94 ± 3	58.7 ± 1.2	97 ± 2

Note: BDL: Below the detection limit, mean ± standard deviation.

parameters constant. The results are summarized in Table 1. The study found out that 5 mL solution of 2 mol L^{-1} HNO_3 was sufficient to recover the quantitative values >95% for the analyte ions studied, and thus desorption of metals in this work were performed by using 5 mL of 2 mol L^{-1} HNO_3. 2 mol L^{-1} HNO_3 in acetone was not preferred as an eluent due to the difficulties of working with solutions containing acetone by flame AAS [53]. All further works were performed by using 5 mL of 2 mol L^{-1} HNO_3.

3.4. Flow rates

The influence of sorption and desorption of the sample on eluent flow rates was investigated. The sample and eluent flow rates had no significant influence on the recoveries and retentions of the analytes at the range of 1.0–2.0 and 1.0–1.5 mL min^{-1}, respectively. In all other works, 2.0 mL min^{-1} for sample flow rate and 1.5 mL min^{-1} for eluent flow rate were selected.

3.5. Sample volume

The influences of volume of sample solution on the recoveries of Cu(II), Fe(III), and Pb(II) on multiwaled carbon nanotube column were also examined. The results are depicted in Fig. 3. The recovery values for all the studied analyte ions were quantitative upto 100 mL of sample volume. It was found out that beyond 100 mL of sample solution, the recovery values decreased with increasing sample volume. The preconcentration factor was found to be 20 upon comparing by sample volume for each analytes (100 mL) and the eluent volume (5 mL).

3.6. Effect of concomitant ions

Matrix effects are one of the main problems in the spectrometric determinations of metal ions in the saline samples [54–65]. The effects of concomitant ions of the preconcentration of the metal ions on multiwaled carbon nanotubes were examined under the optimized working conditions. The limit of tolerance for analytes is defined as the ion concentration causing a relative error smaller than ±5% related to the enrichment, separation, and determination of iron, copper, and lead. The results are summarized in Table 2. These levels show that the procedure can be applied to real samples that contain these matrix components.

3.7. Analytical figures

The limit of detection (LOD) of Cu(II), Fe(III), and Pb(II) were estimated as follows: $LOD = 3 \times s/m$, where s is the standard deviation of ten measurements of the blank and m is the slope of the calibration graph. The detection limits for Cu(II), Fe(III), and Pb(II) with a preconcentration factor 20 were 6.0, 5.9, and 2.8 $\mu g\,L^{-1}$, respectively.

Table 5
Applications of presented method to certificated reference materials ($N = 3$)

Analyte	TMDA-70 fortified lake water		SRM 1570a-Trace Elements in spinach leaves	
	Concentration ($\mu g\,L^{-1}$)		Concentration ($\mu g\,g^{-1}$)	
	Certificated value	Found value	Certificated value	Found value
Fe	918	872 ± 45	–	121 ± 10
Cu	995	964 ± 30	12.2	11.9 ± 0.2
Pb	1,108	1,048 ± 58	–	BDL

Note: Mean ± standard deviation.

Table 6
Application of presented work to some fertilizer and herbal tea sample ($N = 3$)

Sample	Concentration ($\mu g\,g^{-1}$)		
	Fe	Cu	Pb
Ammonium nitrate fertilizer 1	2.1 ± 0.4	BDL	BDL
Ammonium nitrate fertilizer 2	21.0 ± 1.0	BDL	BDL
Ammonium nitrate fertilizer 3	25.7 ± 1.0	3.3 ± 0.3	BDL
Ammonium nitrate fertilizer 4	16.5 ± 1.2	BDL	BDL
Monopotassium phosphate fertilizer 1	7.4 ± 0.7	BDL	BDL
Monopotassium phosphate fertilizer 2	2.8 ± 0.6	BDL	BDL
Rosehip tea	132 ± 4	1.7 ± 0.7	BDL

Note: BDL: Below the detection limit, mean ± standard deviation.

The addition-recovery test were performed for the various natural water samples given in Table 3 and two fertilizer samples and a herbal tea sample in Table 4 in order to get the analytical performance of the presented solid-phase extraction procedure. As it can be shown in Tables 3 and 4, added analyte ions could be generally quantitatively recovered from the real samples. This show that method could be applied to natural water, fertilizer, and herbal tea samples.

3.8. Applications to real samples

The method was applied for preconcentration and eventual determination of the various analytes of trace elements in SRM 1570, spinach leaves and TMDA-70 fortified lake water. Certificated reference materials were used to establish the validity of the procedure as shown by the results that are presented in Table 5. The presented procedure was applied to separation, preconcentration, and determination of iron, copper, and lead contents on some fertilizer samples produced and retailed in Turkey as well as a herbal tea sample which qualified the presented method. The results are given in Tables 5 and 6 and are in good agreement with reference values.

4. Conclusion

The pyrocatechol violet—enhanced sorption of the test analyte chelates on multiwaled carbon nanotubes. The analyte ions were quantitatively recovered from carbon nanotubes column under optimized conditions. The influences of matrix ions had no significant effect on either sorption or desorption of the targeted analytes. The desorption of the attached metal complexes was easily done by stripping with a dilute solution of nitric acid, thus regeneration the packing material. The presented preconcentration method was reliable as it achieved a preconcentration factor of 20, had high recovery values and was not significantly affected by matrix.

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