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Al(III), Cu(II), Co(II), Pb(II), Mn(II), and Fe(III) Determinations in Various Samples by FAAS after Solid Phase Extraction

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Abstract: In this study, a novel method for the preconcentration of Al(III), Cu(II), Co(II), Pb(II), Mn(II), and Fe(III) in the form of their hematoxylin chelates using a column filled with Amberlite XAD-16 resin was proposed. Metal chelates collected on the resin were eluted and their determinations were carried out by flame atomic absorption spectrometry (FAAS). The influences of some analytical parameters including pH, flow rate, sample volume, and the type and concentration of eluent on the preconcentration efficiency were examined. The effects of some interfering ions on the recovery values of analytes were also investigated. While the optimum pH value was 8.5 for Cu(II), Co(II), Mn(II), and Fe(III) ions, it was 6.5 for Al(III) and Pb(II) ions. The appropriate eluent for quantitative elution was 8.0 mL of 1 mol/L nitric acid in acetone. Sample and eluent flow rates were found to be 2.0 mL/min. The maximum sample volume was established by changing it from 50 mL to 2500 mL. The sample volume does not significantly affect recovery within the range of 50-2000 mL of the sample volume for the investigated metal ions. The obtained preconcentration factor was 400. At optimum conditions, the detection limits found as concentration which is threefold of the standard deviation of the blank solution were 0.053 µg/L, 0.080 µg/L, 0.620 µg/L, 1.310 µg/L, 0.330 µg/L and 0.120 µg/L for Al(III), Cu(II), Co(II), Pb(II), Mn(II), and Fe(III) ions, respectively, and the adsorption capacities for these ions were 0.47 ± 0.02 mg/g, 0.81 ± 0.01 mg/g, 0.66 ± 0.01 mg/g, 0.58 ± 0.01 mg/g, 0.91 ± 0.01 mg/g, and 0.73 ± 0.02 mg/g, respectively. By using the certified reference materials, the accuracy of the method was verified. The proposed method was successfully applied to cigarette, hair, and some vegetable species.

Keywords: Metal chelates, hematoxylin, preconcentration, FAAS.

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INTRODUCTION

Heavy metal pollution is a major issue in all around the world. It occurs by means of air, water, soil, and food as a carrier of heavy metals. Particularly, heavy metals can easily enter and accumulate in living organisms through food chain and they have threatened human health. Therefore, the monitoring of the level of trace metals in food and environmental samples is an important task. Some analytical methods such as flame atomic absorption spectrometry (FAAS), electrothermal atomic absorption spectrometry (ETAAS), inductively couple plasma optical emission spectrometry (ICP-OES), and inductively couple plasma mass spectroscopy (ICP-MS) are employed for fast, accurate, and repeatable analysis of heavy metals in various samples [1, 2]. FAAS is widely used due to its good precision, selectivity, low cost, and simplicity. However the direct analysis of heavy metals in complex matrices by FAAS is a challenging matter owing to low concentration of trace metals and matrix effects. Hence, separation/preconcentration techniques such as solid phase extraction (SPE), solvent extraction, ion extraction, cloud point extraction and co-precipitation prior to instrumental measurements are an important requirement in order to achieve accurate and reliable results [3]. Among them, SPE is extensively used due to its simplicity, high preconcentration factor, short extraction time, low consumption of organic solvents, and low cost [4]. Amberlite XAD resins, silica gel, activated carbon, nanomaterials, biological microorganisms, chelating polymers are the most widely employed adsorbents for SPE procedure [5-11].

In particular, Amberlite XAD resins which have satisfied physical properties including porosity, high surface area, and uniform pore size distribution have been widely used as supports for preconcentration of metal chelates. Amberlite XAD-16 is a hydrophobic polyaromatic resin (polystyrene-divinyl benzene copolymer) with a higher surface area (800 m^2/g) and sorption capacity; and has been utilized for separation and preconcentration of many metal ions in different matrices with or without derivatization by various ligands [12].

Hematoxylin is a phenolic chromogenic reagent for the spectrophotometric analysis of some certain metal ions such as Fe(III) and Al(III) [13]. When oxidized, it transforms to haematein which forms strongly colored complexes with some transition metal ions [14]. However, hematoxylin has not yet been used in separation and preconcentration of trace heavy metal ions prior to their determination by FAAS.

In this study, a new preconcentration method has been proposed for FAAS determination of Al(III), Cu(II), Co(II), Pb(II), Mn(II), and Fe(III) on Amberlite XAD-16 as hematoxylin chelates. The effects of some analytical parameters including pH, flow rate, sample volume, and the type and concentration of eluent on the preconcentration efficiency were examined. The optimized method was applied for the determination of target metal ions in various real samples including potato, tomato, hair and cigarette.

MATERIALS and METHODS

Instruments

A Perkin Elmer Analyst 700 FAAS instrument (Waltham, MA, USA) was used for the determination of Al(III), Cu(II), Co(II), Pb(II), Mn(II), and Fe(III). The analytes were determined under the optimized measurement conditions presented in Table 1. For pH measurements, a Metrohm 780 pH meter (Herisau, Switzerland) was used. Ultrapure water was obtained using a Milli-Q Water Purification System (Millipore, Bedford, MA, USA).

Table 1. Measurement parameters for determination of the analyte ions by FAAS.

Metal ion	Wavelength (nm)	Slit width (nm)	Lamp current (mA)	Air flow rate (L/min)	Acetylene flow rate (L/min)	Burner height (cm)	Acetylene flow pressure (kg/cm^2)
Al(III)	309.2	0.5	2.0	8.0	2.0	3.25	0.4
Cu(II)	324.8	0.5	2.0	10.0	2.0	10.5	0.3
Mn(II)	279.5	1.0	10.0	10.0	2.0	10.5	0.3
Pb(II)	217.0	0.7	12.5	10.0	2.0	10.5	0.3
Fe(III)	248.3	0.7	11.0	10.0	2.0	10.5	0.3
Co(II)	240.7	0.8	6.0	10.0	2.0	10.5	0.3

Reagents and Solutions

In this study, all chemicals were of analytical reagent grade and used without further purification. Ultra pure water was employed for all dilutions. The metallic standard solutions used for calibration were prepared by diluting a stock solution of 1000 mg/L of the given metal salt purchased by Sigma–Aldrich (Milwaukee, USA). The proposed preconcentration procedure was not applied to standard calibration solutions. Working standard solutions were prepared by suitable dilution of the stock solutions. Amberlite XAD-16 (non-ionic divinyl polystyrene; specific area 800 m^2/g and bead size; 20-60 mesh) was procured from Sigma–Aldrich (Milwaukee, USA).

A hematoxylin solution (6.0 x 10^{-3} mol/L, Sigma–Aldrich, USA) was prepared daily by dissolving the requisite amounts of hematoxylin in water/ethanol (1/1, v/v).

Certified reference materials (NIES CRM No.13 Human Hair, Virginia Tobaco Leaves (CTA-VTL-2), and NIST SRM 1515 Apple Leaves) were used in order to check the accuracy of the method.

In order to adjust pH, HCl/KCl buffer solution were prepared by mixing of appropriate volume of 0.1 mol/L hydrochloric acid and potassium chloride solutions for pH between 2.0-3.0. CH_3COO^-/CH_3COOH buffer solution were prepared by mixing appropriate volumes of 0.1 mol/L acetic acid and 0.1 mol/L sodium acetate solutions for pH between 4.0-7.0. NH_4^+/NH_3 buffer solution was prepared by mixing of appropriate amounts of 0.1 mol/L ammonia and 0.1 mol/L ammonium chloride solution for pH between 8.0-10.0.

Preparation of the Column

0.6 g of Amberlite XAD-16 was loaded after washing with methanol, 1 mol/L HNO_3 solution and water, respectively, into a 10 mm x 200 mm glass column with a glass frit resin support. The resin bed was approximately 1.5 cm. The column was preconditioned by the blank solution prior to each use. After the elution, the resin in the column was washed with a 10-15 mL of the elution solution and of water in a subsequent manner.

General Preconcentration Procedure

The proposed method was tested with model standard solutions containing analyte ions (8 µg Al(III), 10 µg Cu(II), 30 µg Co(II), 40 µg Pb(II), 25 µg Mn(II), and 10 µg of Fe(III)) before application. 10.0 mL of buffer solution (to give the desired pH between 2.0-10.0) and 1.2 mL of 6.0×10^{-3} mol/L hematoxylin solution were added to 50-60 mL of solution. 0.6 g Amberlite XAD-16 column was preconditioned with the relevant buffer solution. Metal-hematoxylin solution was passed through the Amberlite XAD-16 column at a flow rate of 1.0-10.0 mL/min. After passing of this solution, the column was washed twice with 10.0 mL of water. The metal chelates adsorbed on the column were eluted with 8.0 mL of 1.0 mol/L HNO_3 in acetone. The eluted solution was evaporated to near dryness and then diluted to 5.0 mL with 0.01 mol/L HNO_3. The eluent was analyzed by FAAS for the determination of metal concentration.

Sampling

Hair samples were collected from male subjects who especially work in battery production and soldering in Kocaeli, Turkey. The hair samples (approximately 2 mm) were cut with sterilized stainless steel scissors from the nape of the scalp. All hair samples were sealed in plastic bags prior to analysis. Samples collected were weighed about 1.0 g.

In spring and summer of 2015, the vegetables including potato and tomato were collected from production sites in Adapazarı, Turkey. The vegetables were washed with distilled water, air-dried for 72 h, crushed, passed through a 2 mm mesh sieve and stored at ambient temperature until analysis.

The test samples for cigarettes are brands of commonly smoked in Istanbul. These samples were purchased in packet with seals from a retailer at local market in Bahçelievler, Turkey. The samples were stored in a cool and dry place before analysis.

Digestion Procedures

Hair samples were treated with a 10.0-mL mixture of HNO_3 and $HClO_4$ (6:1, v/v) and consequently heated at 200 ^{o}C until obtaining a clear solution. It was diluted to 25 mL with 0.01 mol/L HNO_3.

For digestion of the vegetables, from each dried sample, 1.0 g ground fine particles were added to a flask containing concentrated HNO_3 (5.0 mL) and concentrated HCl (15.0 mL; *aqua regia*). The flask was covered with a watch glass and then was allowed to stand for at least 16 h. Afterwards, the mixture was heated gradually and boiled under reflux for 2 h. After cooling and rinsing with 20 mL of ultra pure water, the rinse water was recovered in the digestion flask. After filtration, filtrates were used to make a volume of up to 100 mL using 0.01 mol/L

HNO_3. The samples were refrigerated in acid-washed polyethylene bottles at 4 °C before final analysis of metal ions.

For cigarettes, sample mineralization with a mixture of HNO_3 and H_2O_2 included the following stages:

a) 0.5 g from the sample dried to a constant weight were initially placed in borosilicate test tubes. Then the Teflon collector for removal of the discharged gases was fixed. 6.0 mL HNO_3 (65%) were added to each test tube through the openings of the collector, and the heating block was heated to 40 °C for 30 min. Consequently, the temperature was increased to 100 °C. The temperature was kept constant until the abatement of the reaction.

b) 1.0 mL H_2O_2 (30%) was added through the collector openings dropwise after cooling, then the thermos block was heated again to 15 °C for 30 min. In case of need, H_2O_2 addition was continued till the solution was clear enough. Consequently, the solution was quantitatively placed in a measuring flask, which was filled with 0.01 mol/L HNO_3 to the 25 mL. Blank digestions were also performed in the same way.

RESULTS and DISCUSSION

Influences of pH

The pH study was performed to find its effect on the degree of metal sorption using the column process and the pH effect was evaluated in the pH range 2.0-10.0 by using different buffer solutions. The effect of pH on the recovery of target metal ions is shown in Figure 1. The optimum pH value is 8.5 for Cu(II), Co(II), Mn(II), and Fe(III), and 6.5 for Al(III), and Pb(II).

The studies were also carried out at the same pH range without hematoxylin. The recoveries of related metal ions were below 20%. It can be concluded that hematoxylin as a chelating reagent increases the efficiency for preconcentration on Amberlite XAD-16 resin column.

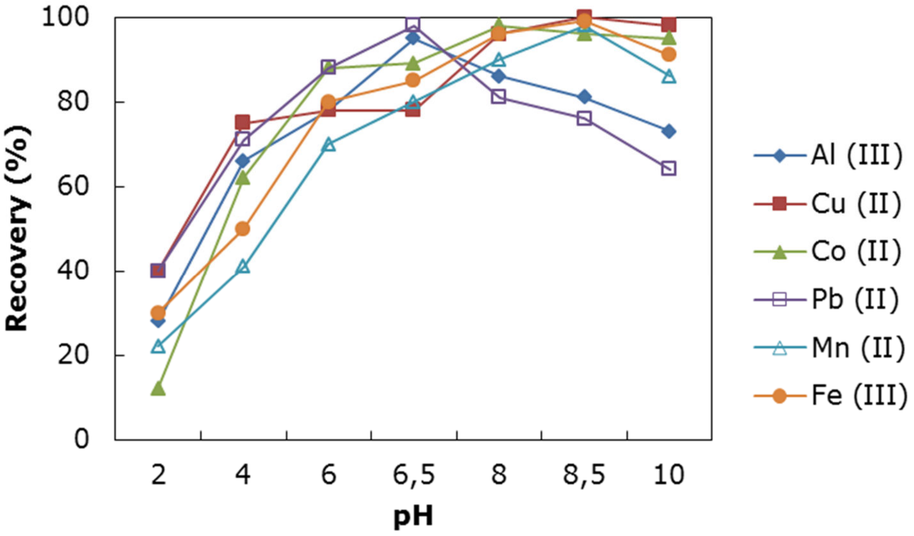

Figure 1. Effect of pH on recovery of investigated metal ions.

Effect of Amounts of Hematoxylin

The effect of the amount of hematoxylin on the quantitative recoveries of the metal ions studied was also investigated. 0.2-1.6 mL portion of a 6.0 x 10^{-3} mol/L hematoxylin solution was added to a model solution containing 5-20 µg of each analyte ion. The amounts of analyte ions adsorbed on Amberlite XAD-16 resin were determined by the proposed method. Over 1.0 mL of 6.0 x 10^{-3} mol/L hematoxylin solution, Al(III), Cu(II), Co(II), Pb(II), Mn(II), and Fe(III) were quantitatively adsorbed. Hence all further studies were performed by using 1.2 mL of 6.0 x 10^{-3} mol/L hematoxylin.

Effect of the Type of Elution Solution

The effect of the various eluents on the recoveries of Al(III), Cu(II), Co(II), Pb(II), Mn(II), and Fe(III) ions from the Amberlite XAD-16 resin column was examined by using 8.0 mL of each eluent solution. This volume was determined according to previous studies in the literature and from our experiences. Recoveries obtained with all eluent solutions for each analyte ion are given in Table 2. According to these results, 8.0 mL of 1.0 mol/L HNO_3 in acetone was used as an eluent for further applications.

Table 2. Effect of the eluent type on recoveries (N=3).

Eluent type	**Recovery (%)**					
	Al(III)	**Cu(II)**	**Co(II)**	**Pb(II)**	**Mn(II)**	**Fe(III)**
Acetone	71 ± 1	96 ± 2	85 ± 2	24 ± 2	100 ± 3	66 ± 2
0.5 mol/L HNO_3	81 ± 1	86 ± 2	90 ± 1	87 ± 3	88 ± 2	76 ± 2
1.0 mol/L HNO_3	95 ± 2	92 ± 1	89 ± 2	99 ± 2	90 ± 3	88 ± 3
0.5 mol/L HCl	46 ± 3	89 ± 2	71 ± 3	86 ± 1	78 ± 1	84 ± 2
1.0 mol/L HCl	61 ± 1	92 ± 3	83 ± 1	92 ± 3	85 ± 1	88 ± 1
1.0 mol/L HNO_3 in acetone	95 ± 3	99 ± 2	96 ± 2	98 ± 1	100 ± 1	96 ± 1

Effect of Flow Rate and Sample Volume

The effect of flow rate on the sorption was investigated by varying the flow rate from 1.0 to 10.0 mL/min at optimum conditions. It was observed that the best results were reached at 2.0 mL/min for retention and elution steps.

In order to investigate the possibility of enriching low concentration of the analyte ions from large sample volumes, the effects of the sample solution volume on the recoveries of the metal ions were also tested in the range of 50-2500 mL. The results are given in Fig. 2. According to these results, the recoveries of analyte ions were not affected until 2000 mL. Above 2000 mL, the recoveries of the target ions decrease probably owing to the excess analytes loaded over the the column capacity with increasing sample volume. In the light of this result found, preconcentration factor was calculated to be 400 for the analyte ions when the final volume was 5.0 mL.

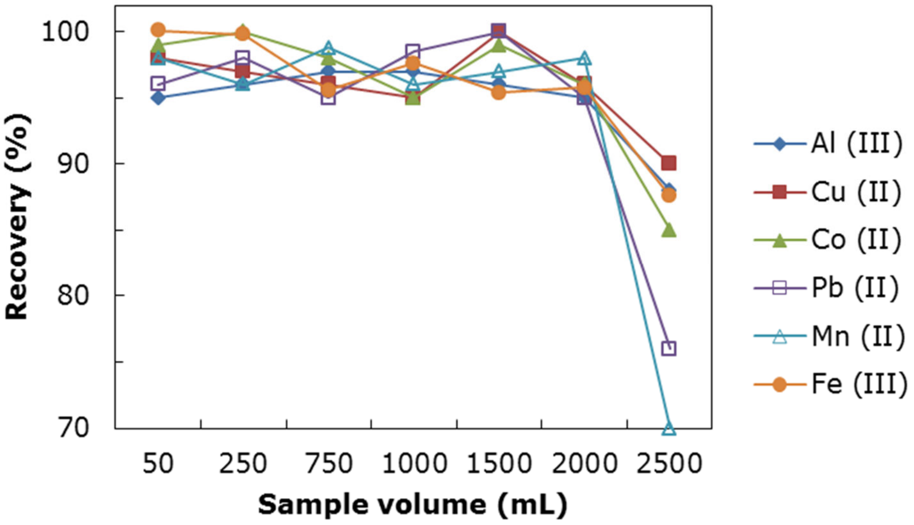

Figure 2. The effect of sample volume on the recoveries of metal ions.

Effect of Coexisting Ions

The influences of possible matrix ions on the recoveries of analytes were also examined by a generic procedure. The obtained experimental results are showed in Table 3. The tolerance limit is defined as the ion concentration inducing a relative error smaller than ± 3% related to the preconcentration and determination of the analyte ions. The results given in Table 2 showed that the existence of high concentrations of some cations and anions has no obvious influence on the metal ions adsorption at optimum conditions.

Total Sorption Capacity

The sorption capacity of the resin is described as the amount of metal adsorbed by 1.0 g of resin. A suitable aliquot of metal ion chelate at appropriate pH value was loaded onto the column filled with 1.0 g of resin. The eluate was determined by FAAS as described in the general procedure until the resin was saturated. This procedure was repeated for each analyte ions. The sorption capacity for each analyte ion on the sorbent was calculated from the difference between the metal ion concentration before and after desorption. The obtained results are presented in Table 4.

Resin Reusability Study

In order to determine the potential reusability of the resin, the resin was subjected to several adsorption-elution cycles at optimum conditions. Ten runs were performed on the same day and the next ten runs were made the following day. According to the obtained results, a small decrease in the recoveries occured after 50 cycles. The resin could be utilized up to 70 runs in succession without any appreciable loss in the sorption efficiency.

Detection Limits

The detection limits based on the concentration corresponding to three times the standard deviation of blank signal were found to be 0.053 µg/mL for Al(III), 0.08 µg/mL for Cu(II), 0.62 µg/mL for Co(II), 1.31 µg/mL for Pb(II), 0.33 µg/mL for Mn(II) and 0.12 µg/mL for Fe(III) using a synthetic sample volume as blank.

Accuracy of the Results

The accuracy of the proposed method was checked by determination of the metal ions in the certified reference materials, NIES CRM No.13 Human Hair, Virginia Tobaco Leaves (CTA-VTL-2), and NIST SRM 1515 Apple Leaves. The results in Table 5 show that developed method was in a good agreement with the certified values and is free from interferences of the various constituents.

Application to Real Samples

The presented method was applied to the determination of Al(III), Cu(II), Co(II), Pb(II), Mn(II), and Fe(III) ions in potato, tomato, hair, and cigarette. The results are summarized in Table 6. Accordingly, relative standard deviations (RSDs) of the method were lower than 8%, showing that the developed method has good precision for the analysis of trace metal ions studied from different samples.

Table 3. Influences of some foreign ions on the recoveries of metal ions (N=3).

			Recovery (%)					
Cations/ Anions	**Added as**	**C (mg/L)**	**Al(III)**	**Cu(II)**	**Co(II)**	**Pb(II)**	**Mn(II)**	**Fe(III)**
Na^+	NaCl	500	95 ± 1[a]	96 ± 1	97 ± 3	97 ± 2	96 ± 1	95 ± 2
K^+	KCl	500	97 ± 2	95 ± 1	95 ± 2	98 ± 3	98 ± 2	96 ± 1
Ca^{2+}	$CaCl_2$	400	96 ± 2	98 ± 3	96 ± 2	97 ± 1	100 ± 1	97 ± 2
Mg^{2+}	$MgCl_2$	200	95 ± 1	95 ± 1	97 ± 1	95 ± 2	95 ± 2	96 ± 3
Ni^{2+}	$Ni(NO_3)_2$	100	96 ± 3	96 ± 2	95 ± 3	96 ± 3	97 ± 3	98 ± 1
Cd^{2+}	$Cd(NO_3)_2$	100	95 ± 2	98 ± 2	97 ± 2	97 ± 2	98 ± 2	95 ± 2
Sn^{2+}	$SnCl_2$	300	96 ± 2	96 ± 3	97 ± 3	95 ± 1	99 ± 1	98 ± 1
Cr^{3+}	$Cr(NO_3)_3$	600	99 ± 1	98 ± 2	96 ± 2	97 ± 2	100 ± 1	96 ± 1
Ag^+	$AgNO_3$	150	98 ± 1	96 ± 1	97 ± 1	96 ± 3	95 ± 3	97 ± 1
V^{5+}	V_2O_5	50	96 ± 3	95 ± 2	96 ± 2	98 ± 2	97 ± 3	97 ± 3
Bi^{3+}	$Bi(NO_3)_3$	50	96 ± 1	96 ± 3	95 ± 1	95 ± 3	96 ± 1	95 ± 2
PO_4^{3-}	Na_3PO_4	5000	96 ± 2	96 ± 2	99 ± 2	99 ± 2	96 ± 2	96 ± 3
Cl^-	NaCl	4000	97 ± 2	97 ± 1	98 ± 1	95 ± 3	98 ± 1	97 ± 2
SO_4^{2-}	Na_2SO_4	3000	97 ± 3	95 ± 2	96 ± 3	97 ± 3	99 ± 2	96 ± 1

[a] Mean ± standard deviation.

Table 4. Total sorption capacity of the metal ions on Amberlite XAD-16 (Experimental conditions: Amberlite XAD-16: 1.0 g; Al(III): 50-800 µg, pH 6.5; Cu(II): 50-1400 µg, pH 8.5; Co(II): 60-1100 µg, pH 8.5; Pb(II): 70-1000 µg, pH 6.5; Mn(II):50-600 µg, pH 8.5; Fe(III): 80-900 µg, pH 8.5; flow rate: 2.0 mL/min for each element).

Metal ion	**Capacity (mg/g)**
Al(III)	4.7 ± 0.2
Cu(II)	8.1 ± 0.1
Co(II)	6.6 ± 0.1
Pb(II)	5.8 ± 0.1
Mn(II)	9.1 ± 0.1
Fe(III)	7.3 ± 0.2

Table 5. The results for reference standard materials (N=5).

	SRM 515 Apple Leaves (μg/g)		**CRM 13 Human Hair (μg/g)**		**CTA-VTL-2 Virginia Tobacco Leaves (μg/g)**	
Metal ion	**Certified value**	**Found value**	**Certified value**	**Found value**	**Certified value**	**Found value**
Al(III)	289 ± 9	284 ± 4	120[a]	118 ± 2	1682[a]	1679 ± 18
Cu(II)	5.64 ± 0.24	5.61 ± 0.10	15.3 ± 1.3	14.9 ± 0.7	18.2 ± 0.9	17.9 ± 0.7
Co(II)	0.09[a]	0.08 ± 0.01	0.07[a]	0.06 ± 0.01	0.429 ± 0.026	0.424 ± 0.03
Pb(II)	0.470 ± 0.024	0.468 ± 0.08	4.6 ± 0.4	4.5 ± 0.3	22.1 ± 1.2	20.8 ± 1.1
Mn(II)	54 ± 3	53.42 ± 0.7	3.9[a]	3.8 ± 0.3	79.7 ± 2.6	77.6 ± 1.3
Fe(III)	83 ± 5	81 ± 0.9	140[a]	138 ± 3	1083 ± 33	1080 ± 24

[a]:informative value.

Except for Pb, there is no information about maximum Al, Cu, Co, Mn, and Fe levels in foodstuff in the Turkish Food Codex (TFC, regulation no 2011/28157) [15]. When the results of samples in terms of Pb contents are examined, it is seen that Pb levels in potato and tomato samples are higher than their maximum permissible limit (0.10 mg/kg) of the TFC.

Additionally, Pb average concentration in the hair samples was found to be 6.43 ± 0.6 mg/kg and a similar observation (8.67 ± 13.83 mg/kg) were also reported by Li *et al.* in case of lead content for the scalp hair of residents living in the mining areas in China [16]. Moreover this value is higher than Pb levels of another study (≤ 4.60 ± 0.57 mg/kg) based on ETAAS in literature [17]. Consequently, these results obtained for lead determination show that people in the battery and soldering work areas are more susceptible to lead pollution and thus, it should be paid more attention to the monitoring of their lead levels.

Cigarette samples presented the highest Al, Cu, Mn, and Fe values according to other samples, while they gave the lowest Pb value. These results are almost comparable with some studies done in literature [18-20].

Table 6. The results of Al(III), Cu(II), Co(II), Pb(II), Mn(II), and Fe(III) ions in potato, tomato, hair, and cigarette samples by the proposed method.

Metal ion	Potato (mg/kg)	Tomato (mg/kg)	Hair (mg/kg)	Cigarette (mg/kg)
Al(III)	9.42 ±0.3	1.31 ±0.2	85 ± 3.4	835 ± 8
Cu(II)	3.67 ±0.1	2.48 ± 0.4	21 ± 2.7	41 ± 2
Co(II)	0.098 ± 0.01	0.85 ± 0.1	0.85 ± 0.3	0.75 ± 0.09
Pb(II)	2.14 ± 0.2	1.21 ± 0.2	6.43 ± 0.6	0.641 ± 0.2
Mn(II)	11.45 ± 0.3	96 ± 2.1	31.4 ± 0.9	109 ± 3
Fe(III)	82.5 ± 2.0	2.17 ± 0.3	140 ± 4.4	540 ± 6

Comparison with the other SPE methods

The new method was compared with other SPE methods based on Amberlite XAD resins in terms of preconcentration factor, limit of detection, sorption capacity, and relative standard deviation (Table 7). The preconcentration factor of the analyte ions is superior to those of SPE methods described in Table 7. The obtained results related to sorption capacity, LOD and RSD are also comparable to those of other preconcentration studies in Table 7.

Table 7. Comparison of the developed method with the other some SPE methods.

Chelating agent	Studied metal ions	PF	LOD (µg/L)	Sorption capacity (mg/g)	RSD (%)	Reference
Amberlite XAD-4/SAB	Cu, Ni, Co, Fe	240	0.40-0.90	8.14-11.13	< 5	5
Amberlite XAD-4/PAN	Cd, Co, Ni, Mn, Zn, Pb, Cu	160-400	0.09-1.30	0.030-0.050*	< 5	21
Amberlite XAD-7/MDTC	Pb, Cu, Co, Fe, Ni, Cd, Zn	-	2.10-4.19	9.14-10.43	< 5	22
Amberlite XAD-1180/PV	Fe, Pb	100	0.37, 0.20	-	< 10	23
Amberlite XAD-16/PAN	Ni, Cd, Co, Cu, Pb, Cr	200	0.056-0.268	4.7-5.0	< 8	24
Amberlite XAD-1180/ EBBR	Cu	60	1.3	0.90	3.3	25
Amberlite XAD-7/PAR	Co	200	0.1	-	13	26
Amberlite XAD-4/DPKT	Co, Ni, Fe, Cu	200-300	30-50	2.0	< 2	27
Amberlite XAD-2010/Na-DDTC	Mn, Co, Ni, Cu, Cd, Pb	100	0.08–0.26	5.7-6.3	< 5.1	28
Amberlite XAD-1180/TAN	Cu, Ni, Pb, Cd Mn	50-200	0.03-1.19	0.30-0.77	< 5.1	29
Amberlite XAD-4/DDTP	Cd, Pb	6-13	0.02-2.0	-	< 13	30
Amberlite XAD-8/AMOTACTA	Cu	200	0.20	2.37	< 4.1	31
Amberlite XAD-7/PAR	Cu, Ni, Zn	200-400	0.013-0.027	-	< 3.2	32
Amberlite XAD-16/ 8-hydroxyquinoline	Cu, Zn	80, 147	0.16, 0.2		1.2, 2.2	33
Amberlite XAD-16/Hematoxylin	Al, Cu, Co, Pb, Mn, Fe	400	0.053-1.310	0.47-0.91	< 5	Present study

PF: Preconcentration factor, LOD: Limit of detection, RSD: Relative standard deviation, PAN: 1-(2-pyridylazo)-2-naphtol, MDTC: Morpholine dithiocarbamate, Na-DDTC: Sodium diethyldithiocarbamate, PV: Pyrocatechol violet, EBBR: Eriochrome blue black R, PAR: 4-(2-pyridylazo) resorcinol, SAB: Salicylaldehyde benzoylhydrazone, DPKT: Di-2-pyridylketone thiosemicarbazone, TAN: 1-(2-thiazolylazo)-2-naphthol, DDTP: O,O-diethyldithiophosphate, and AMOTACTA: Carbothioamide derivative. *mmol/g.

CONCLUSION

In the present study, a new method for solid phase extraction of trace metals, Al(III), Cu(II), Co(II), Pb(II), Mn(II), and Fe(III) prior to their determinations by FAAS was developed. The conditions of preconcentration and elution were investigated and optimized. At optimum conditions, the method has high preconcentration factor, and low RSD and LOD values. In addition, the proposed method is not influenced by many foreign ions present together with analyte ions. Certified reference materials were also used for method validation and the results showed that the developed method was in good agreement with certified values and it is suitable for the analysis of metal ions studied in real samples. This method based on the sorption of hematoxylin-metal chelates on Amberlite XAD-16 provides simple, fast, and low-cost preconcentration procedure for accurate and precise quantification of target analyte ions in some vegetable, human hair and cigarette samples.

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Türkçe Öz ve Anahtar Kelimeler

Katı Faz Ekstraksiyonu Sonrası FAAS ile Çeşitli Örneklerde Al(III), Cu(II), Co(II), Pb(II), Mn(II) ve Fe(III) Tayini

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Öz: Bu çalışmada, Amberlite XAD-16 reçinesi ile doldurulmuş bir kolon kullanarak hematoksilin kelatları şeklinde Al(III), Cu(II), Co(II), Pb(II), Mn(II) ve Fe(III) iyonlarının ön derişiklendirilmesi için yeni bir yöntem önerilmiştir. Reçinede toplanan metal kelatları elüe edilmiş ve tayinleri alev atomik absorpsiyon spektrometrisi (FAAS) ile yapılmıştır. Ön derişiklendirme etkinliğine pH, akış hızı, örnek hacmi ve elüentin konsantrasyonu gibi bazı analitik parametrelerin etkisi incelenmiştir. Analitlerin geri kazanım değerlerine girişim yapan bazı iyonların etkisi de incelenmiştir. Cu(II), Co(II), Mn(II) ve Fe(III) iyonları için en uygun pH değeri 8,5 iken Al(III) ve Pb(II) iyonları için en uygun değer 6,5 olarak tespit edilmiştir. Kantitatif elüsyon için en uygun elüentin, aseton içindeki 8,0 mL 1 mol/L nitrik asidin çözeltisi olduğu belirlenmiştir. Örnek ve elüent akış hızları 2,0 mL/dak olduğu bulunmuştur. En yüksek örnek hacmi, bu değerin 50 mL'den 2500 mL'ye değiştirilmesi ile bulunmuştur. Örnek hacmi, geri kazanıma 50-2000 mL örnek hacmi aralığında çalışılan metal iyonları için belirgin şekilde etki etmemektedir. Elde edilen ön derişiklendirme faktörü 400'dür. En uygun koşullarda, kör çözeltinin standart sapmasının üç katı olarak bulunan ve konsantrasyon cinsinden tayin sınırları Al(III), Cu(II), Co(II), Pb(II), Mn(II) ve Fe(III) iyonları için sırasıyla 0,053 µg/L, 0,080 µg/L, 0,620 µg/L, 1,310 µg/L, 0,330 µg/L and 0.120 µg/L olarak bulunmuştur. Söz konusu iyonlar için adsorpsiyon kapasiteleri de 0,47 ± 0,02 mg/g, 0,81 ± 0,01 mg/g, 0,66 ± 0,01 mg/g, 0,58 ± 0,01 mg/g, 0,91 ± 0,01 mg/g, and 0,73 ± 0,02 mg/g olarak bulunmuştur. Onaylı referans malzemeleri kullanarak yöntemin kesinliği doğrulandı. Önerilen yöntem sigara, saç ve bazı sebze türlerine başarıyla uygulanmıştır.

Keywords: Metal kelatları, hematoksilin, ön derişiklendirme, FAAS.