Green reagent for the Determination of Fe, Cd, Cr, Cu and Co in Environmental and Pharmaceutical samples

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ABSTRACT

The author synthesized a Green reagent N, N^1-bis (4-dimethyl amino benzyl) ethylene diamine for the analysis of heavy metals namely Fe, Cd, Cr, Cu and Co by FAAS using Amberlite-XAD-16 in various environmental samples. The results shows good recovery compared with the results obtained with Cytosine. Effects of pH, reagent concentration, flowrate, volume of sample etc were studied.

Keywords: N, N^1-bis (4-dimethyl amino benzyl) ethylene diamine, Amberlite-XAD-16, Cytosine.

1. INTRODUCTION

Solid phase extraction is a versatile preconcentration technique often termed as liquid-solid chromatography and is based on interaction between the solute and fixed active sites on a finely divided solid adsorbent used as the stationary phase. The adsorbent used in this process, has generally a high surface area. Preconcentration methods were employed in order to get required concentrations in terms of sensitivity and selectivity for the analysis of the metal species using Flame Atomic Absorption Spectrometry (FAAS). The literature review shows that several solid phase extractions have been applied for the determination of heavy metals or essential metals in various environmental samples.

Tunceli and Turker[1] explains the speciation of Cr(III) and Cr(VI) in water after preconcentration of its 1,5-diphenylcarbazone complex on Amberlite XAD-16 resin and determination by FAAS. Solid phase extraction of trace metal ions with Amberlite XAD resins prior to atomic absorption spectrometric analysis has been developed by Soylak et al[2]. Multivariate optimization of solvent extraction of Cd(II), Co(II), Cr(VI), Cu(II), Ni(II), Pb(II) and Zn(II) as dibenzyldithiocarbamates and detection by AAS has been developed by Camino et al[3]. Bermejo-Barrera et al[4] described the use of Amberlite XAD-2 loaded with 1-(2-pyridylazo)-2-naphthol as a preconcentration system for river water prior to determination of Cu, Cd and Pb by flame atomic absorption spectroscopy. Manzoori et al[5] made atomic absorption determination of cobalt after preconcentration by 1-(2-pyridylazo)-2-naphthol immobilized on surfactant –coated alumina. Narin et al[6] discussed trace metal ions by AAS in natural

water samples after preconcentration of pyrocatechol violet complexes on an activated carbon column. Soylak[7] reported the separation and enrichment of zinc, copper, iron, cadmium, cobalt and nickel from urine with Amberlite XAD-16 resin. Atomic absorption spectrometric determination of ultra trace amounts of zinc after preconcentration with the ion pair of 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol and ammonium tetraphenylborate on microcrystalline naphthalene or by column method has been developed by Taher[8].

Cesur[9] proposed a solid-phase extraction method for the pre-concentration of manganese, copper, cadmium and lead in water samples prior to their determination by flame atomic absorption spectrometry using phenylpiperazine dithiocarbamate as a reagent. The optimum pre-concentration conditions such as pH, volume of sample solution and the effects of some matrix elements have been investigated. The obtained recovery was nearly 90 to 100 percent, while the enrichment factor was 400 for metal spiked solutions. Maheswari and Subramanian[10] reported a new chelating resin AXAD-16-1,2-diphenylethanolamine, developed by chemically modifying Amberlite XAD-16 with 1,2-diphenylethanolamine to produce an effective metal-chelating functionality for the preconcentration of Mn(II), Ni(II), Cu(II), Zn(II), Cd(II) and Pb(II) and their determination by flame atomic absorption spectrometry. Yamini et al[11] reported a solid phase extraction and flame atomic absorption spectrometric determination of trace amounts of zinc and cobalt ions in water samples. Karatepe et al[12] proposed a sensitive and simple method for the separation/preconcentration of some trace

metal ions as O-O-diethylphosphorodithioic acid ammonium salt (A-DDPT) complexes on a mini chromatographic column filled with chromosorb-105 resin. A simple, fast, and sensitive column solid phase extraction study has been proposed by Tuzen et al[13] for flame atomic absorption spectrometric determination of lead, cadmium, chromium, nickel, copper, and manganese ions on XAD-4 as 1-(2-pyridylazo)2-naphthol (PAN) complexes.

A column solid phase extraction method has been developed by Tuzen et al[14] for the determination of copper, iron and zinc ions at trace levels in environmental samples on Amberlite XAD-7 for their flame atomic absorption spectrometry. De Alcantara et al[15] developed a novel analytical method for the determination of Cu, Ni and Pb in aqueous medium by FAAS after pre-concentration on 2-aminothiazole modified silica gel. Duran et al[16] proposed a new method using a column packed with Amberlite XAD-2010 resin as a solid-phase extractant for the multi-element preconcentration of Mn(II), Co(II), Ni(II), Cu(II), Cd(II), and Pb(II) ions based on their complex formation with the sodium diethyldithiocarbamate (Na-DDTC) prior to flame atomic absorption spectrometric (FAAS) determinations. A column solid-phase extraction (SPE) preconcentration method was developed by Liu et al[17], for the determination of Cd, Co, Cu, Ni and Zn ions in natural water samples by flame atomic absorption spectrometry. The procedure is based on the retention of analytes in the form of 2-acetylmercaptophenyldiazoaminoazo benzene (AMPDAA) complexes on a short column of AMPDAA-XAD-4 resin from buffered sample solution and subsequent elution with hydrochloric acid plus sodium chloride. Multiwalled carbon nanotubes (MWNTs) were used as solid phase extractor of Cu(II), Cd(II), Pb(II), Zn(II), Ni(II) and Co(II) ions as ammonium pyrrolidine dithiocarbamate (APDC) chelates, in the study carried out by Tuzen et al[18]. Many authors reported[19-23] solid phase extraction technique for heavy metals.

In the present investigation, the author synthesized a clean and Green reagent N, N[1]-bis (4-dimethyl amino benzyl) ethylene diamine for the analysis of heavy metals namely Fe, Cd, Cr, Cu and Co by FAAS using Amberlite-XAD-16 and the results are compared with the results obtained with Cytosine.

2. Experimental

All Chemicals were analytical grade and procured from Sigma-Aldrich company and double-distilled water was used to prepare all solutions throughout the experiments. A pH meter (Elico, Model LI-129, India) with combined glass electrode was used for pH measurements. A single pan analytical balance (Dhona, Model 100 DS, India) was employed for weighing the samples. A Perkin-Elmer Model Aanalyst100 Flame Atomic Absorption Spectrometer (FAAS) was used to determine metal concentrations using an air-acetylene flame.

2.1. Preparation of the Amberlite XAD-16 column loaded with synthesized reagent

Amberlite XAD-16 was treated with an ethanol–hydrochloric acid–water (2:1:1) solution overnight. Later, the resin was rinsed with double distilled water until supernant water pH became neutral. The packing of the column was done using ethanol as eluent since water makes resin beads float. The resin was saturated by passing 2.5 mL of a 0.01% N, N[l]-bis (4-dimethyl amino benzyl) ethylene diamine solution at a flow rate of 0.5 mL min^{-1}. Later it was washed with water until excess reagent was removed from the resin. All experiments were done in a funnel-tipped glass tube as a column for preconcentration. It was plugged with glass wool and then filled with the XAD-16 to the height of 1.0–1.2 cm. Before sample loading the column was preconditioned by passing a buffer solution.

3. RESULTS AND DISCUSSION
3.1. Effect of pH on adsorption of metal ions

The influence of pH on the adsorption of heavy metal ions on Amberlite XAD-16 functionalized N, N[1]-bis (4-dimethyl amino benzyl) ethylene diamine was studied by taking 20 μg of each individual metal ion solution in the pH range from 2.0 to 9.0. The data corresponding to each element is shown in Table 5.1 and graphically presented in Figure 5.1. The recoveries were higher at a pH value of 6.0 for all selected metals i.e. Fe, Cd, Cr, Cu and Co. Hence a pH of 6.0 was chosen for the simultaneous determination of metal ions in water samples.
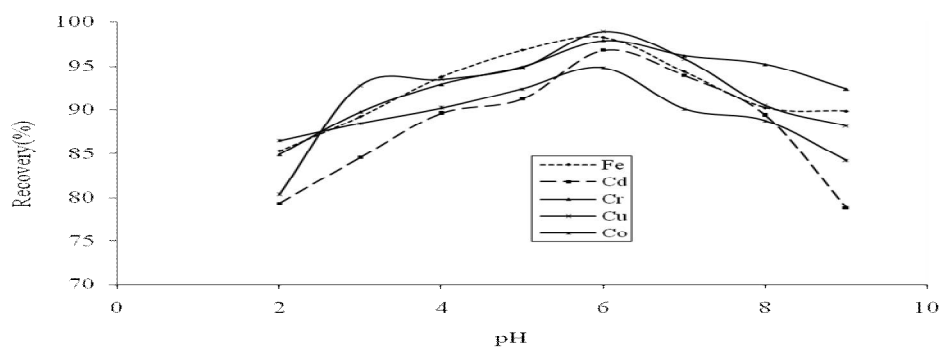
Figure.1. Effect of pH

3.2. Effect of sample volume

Studies were performed with sample solutions of large volume to explore the possibility of enriching low concentrations of metal ions. For this purpose 25, 50, 75, 100, 150 and 200 mL of sample solutions containing 5 mg of Fe, Cd, Cr, Cu and Co were passed through the micro-column at 2.0 mL min^{-1} flow rate. The recovery values were quantitative (>95%) at 100 mL of sample volume. In this experiment, 100 mL of sample solution was adopted for the preconcentration of analytes from the water samples.

3.3. Effect of flow rate of sample solution

The flow rate of the sample solution affects the adsorption of metal ions on the chelating resin. Therefore, the effect of the flow rate of sample solution was examined in the flow rate range of 0.5-5.0 mL min^{-1}. It was found that the retention of the metal ions were quantitative upto 2.0 mL min^{-1} flow rate. The data corresponding to each element is presented in Figure 2. The recoveries of the analytes decrease slightly when the flow rate is over 2.0 mL min^{-1}. Thus, a flow rate of 2.0 mL min^{-1} is employed as an optimum flow rate.
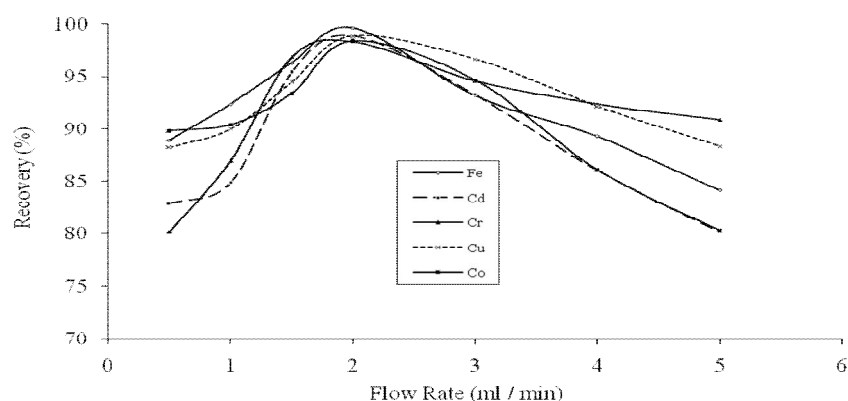

Figure.2. Effect of flow rate of sample solution on retention of metal ions on XAD-16- chelating resin

3.4. Effect of eluent concentration and volume

To obtain quantitative recovery, the effect of eluent concentration and volume was investigated. For this reason various concentrations of HNO$_3$ in acetone were studied for the elution of retained metal ions from the micro column at a flow rate of 2.0 mL min^{-1}. As can be seen, 2.5 mol L^{-1} HNO$_3$ in acetone was sufficient for the elution of metal ions. The effect of eluent volume on the recovery of metal ions was also studied by keeping the HNO$_3$ in acetone concentration of

2.5 mol L^{-1}, it was found that 10 mL of 2.5 mol L^{-1} HNO$_3$ in acetone is sufficient for quantitative recoveries (>95%) of metal ions.

3.5. Effect of amount of XAD-16- chelating resin on preconcentration of metal ions

The amount of Amberlite XAD-16 functionalized N, N^1-bis (4-dimethyl amino benzyl) ethylene diamine chelating resin required for effective preconcentration of metals was studied in the range of 0.3 to 3.0 g. The results indicate that 1.0 g of XAD-16- N, N^1-bis (4-dimethyl amino benzyl) ethylene diamine chelating resin is

suitable for quantitative recovery (>98%) of all five metal ions. So, 1.0 g of XAD-16-chelating resin is recommended for further studies.

3.6. Efficiency of sorption of metal ions

The efficiency of sorption was expressed as the concentration of the analyte retained on the sorbent during preconcentration. The quantitative sorption of Fe, Cd, Cr, Cu and Co from aqueous solution was studied by taking 30 μg of each element in 100 mL, and passed through the column containing 1.0 g of XAD-16-

N, N^1-bis (4-dimethyl amino benzyl) ethylene diamine chelating resin. The elements adsorbed on XAD-16- N, N^1-bis (4-dimethyl amino benzyl) ethylene diamine chelating resin was eluted with 10 mL of 2.0 mol l^{-1} HNO_3 in acetone, and determined by FAAS. The data corresponding to each element are presented in Table 1. The results show that sorption efficiency of metal ions was quantitative (>96%) on XAD-16- N, N^l-bis (4-dimethyl amino benzyl) ethylene diamine chelating resin.

Table 1: Recovery of metal ions from aqueous solution after preconcentration

Metal	Metal added to 100 mL, (μg mL^{-1})	Metal absorbed (μg)	Recovery[a], (%)
Fe	30	29.32	97.72
Cd	30	28.86	96.20
Cr	30	28.34	94.46
Cu	30	29.16	97.20
Co	30	28.92	96.42

a- Recovery for four determinations

3.7. Recoveries of heavy metals from spiked water samples

The efficiency of procedure was examined by determining the concentration of metal ions in spiked water samples. Deionized double distilled water was spiked with known amounts of metal standards (10 to 50 μg L^{-1}) and the percent recoveries of each element are determined and given in Table 2. The percentage recoveries for

different metal ions are 98.98 for Fe, 98.46 for Cd, 98.38 for Cr, 99.48 for Cu and 98.72 for Co with a percent of Relative Standard Deviation (RSD) from 2.38 to 3.52. These results show that the XAD-16- N, N^1-bis (4-dimethyl amino benzyl) ethylene diamine chelating resin is very useful for the preconcentration of Fe, Cd, Cr, Cu and Co from natural water samples.

Table 2: Recovery of trace metal ions from spiked water samples after preconcentration

Concentration of each metal spiked, (μg L^{-1})	Metal	Found, (μg L^{-1})	Recovery[a], (%)	RSD[a], (%)
10	Fe	9.886	98.86	2.38
	Cd	9.836	98.36	3.48
	Cr	9.836	98.36	3.40
	Cu	9.940	99.40	2.88
	Co	9.870	98.70	3.20
20	Fe	19.784	98.92	3.32
	Cd	19.656	98.28	2.98
	Cr	19.676	98.38	3.42
	Cu	19.884	99.42	3.22
	Co	19.936	98.68	2.86
30	Fe	29.682	98.94	3.52
	Cd	29.538	98.46	3.32
	Cr	29.514	98.38	3.48
	Cu	29.832	99.44	2.78
	Co	29.610	98.70	2.96
40	Fe	39.592	98.98	3.46
	Cd	39.376	98.44	3.26
	Cr	39.328	98.32	3.50
	Cu	39.792	99.48	2.92
	Co	39.872	98.68	3.22
50	Fe	49.490	98.98	3.42
	Cd	49.210	98.42	3.22
	Cr	49.170	98.34	3.24
	Cu	49.720	99.44	2.84
	Co	49.860	99.72	3.36

[a] Recovery and RSD for five determinations

3.8. Effect of coexisting ions

The effects of common coexisting ions on the adsorption of the studied metal ions on XAD-16-N, N¹-bis (4-dimethyl amino benzyl) ethylene diamine chelating resin were investigated. In these experiments, 100 mL solution of 5 mg mL^{-1} Fe, Cd, Cr, Cu, and Co containing the added interfering ions was treated according to the general procedure. The results are presented in Table 3. The tolerance limits of the coexisting ions, defined as the largest amount making the recovery of the studied elements less than 90%, were found to be 10000 μg mL^{-1} for Na$^+$, K$^+$; 5000 μg mL^{-1} for Ca^{2+}; 4000 μg mL^{-1} for Mg^{2+};

1500 μg mL^{-1} for Al^{3+}, Zn^{2+}; 200 μg mL^{-1} for Pb^{2+}. The tolerance limits for anions were found to be 4500 for Cl$^-$, SO_4^{2-}; 4000 for CH$_3$COO$^-$, NO_3^-; 2000 for PO_4^{3-} and 50 for $Cr_2O_7^{2-}$. These are the concentration limits in μg mL^{-1} that caused less than two percent error on recovery of studied metal ions. The results in Table 5.8 indicate that various cations and anions present in water samples do not interfere in the analysis of Fe, Cd, Cr, Cu and Co under reported conditions.

Table 3: Effect of coexisting ions on the determination of trace metals in water samples

S.No.	Coexisting ion	Tolerance limit[a], (μg mL^{-1})
1.	Na$^+$, K$^+$	10000
2.	Ca^{2+}	5000
3.	Mg^{2+}	4000
4.	Al^{3+}	1500
5.	Pb^{2+}	200
6.	Zn^{2+}	100
7.	Cl$^-$, SO$_4^{2-}$	4500
8.	CH$_3$COO$^-$, NO$_3^-$	4000
9.	PO$_4^{3-}$	2000
10.	Cr$_2$O$_7^{2-}$	50

[a] Tolerance limit, which is caused upto $\pm$2% error in % recovery.

4. APPLICATIONS

4.1. Application of method to natural water samples

The proposed procedure was applied for the preconcentration and determination of trace metal ions in natural water samples. The natural water samples were collected in and around Tirupati, India. Pretreatment of natural water samples were carried out according to the procedure described in experimental section. Analysis of Fe, Cd, Cr, Cu and Co in natural

water samples was carried out and the results are presented in Table 4,5.

Critical study of the results revealed that the preconcentration of metals by solid-phase column extraction is more effective and sensitive. The solid-phase column extraction is more convenient for the combination with FAAS. It allows preconcentration from a larger sample volume, establishing higher preconcentration factor, simple storage and transportation of pre-treated samples.

Table 4: Determination of Fe, Cd, Cr, Cu and Co in water samples

S.No.	Origin of Sample	Metal ion found[a], (μg L^{-1})				
		Fe	Cd	Cr	Cu	Co
1.	Tap water	14.46	3.78	0.32	9.82	BDL
2.	Kalyani Dam Reservoir	12.84	9.92	2.32	12.26	0.34
3.	Swarnamukhi River	16.78	10.82	7.28	14.22	1.80

BDL – below detection limit.
[a] average of four determinations

Table 5: Comparision of Fe, Cd, Cr, Cu and Co in various water samples

S.No	Metal	Water Samples	Standard Method[f]	Present Method	C.V.
1	Fe	SAMPLE-I[b]	1.0	0.98±0.02	2.04
		SAMPLE-II[c]	0.95	0.92±0.04	4.34
		SAMPLE-III[d]	0.90	0.88±0.02	2.28
		SAMPLE-IV[e]	0.90	0.90±0.06	6.66
2	Cd	SAMPLE-I	0.90	0.88±0.04	4.54
		SAMPLE-II	0.75	0.72±0.02	2.78
		SAMPLE-III	0.80	0.76±0.01	1.32
		SAMPLE-IV	0.75	0.68±0.02	2.24
3	Cr	SAMPLE-I	0.98	0.95±0.04	4.20
		SAMPLE-II	0.92	0.90±0.02	2.22
		SAMPLE-III	0.90	0.86±0.06	6.98
		SAMPLE-IV	0.90	0.89±0.02	2.24
4	Cu	SAMPLE-I	0.95	0.94±0.04	4.26
		SAMPLE-II	1.0	0.98±0.04	4.08
		SAMPLE-III	1.2	1.0±0.02	2.00
		SAMPLE-IV	0.98	0.98±0.02	2.04
5	Co	SAMPLE-I	0.88	0.86±0.02	2.32
		SAMPLE-II	0.75	0.74±0.02	2.70
		SAMPLE-III	0.66	0.62±0.02	3.22
		SAMPLE-IV	0.70	0.68±0.02	2.94

a- average of five determinations,
b- collected near dairy industry, Chandragiri, Andhra Pradesh, India.
c- collected near Sugar Industry, Gajulamandyam, Andhra Pradesh, India.
d- collected near Lanco cement Industry, Srikalahasti, Andhra Pradesh, India.
e- collected near industrial area, Renigunta, Andhra Pradesh, India.
f- using cytosine procured from local market as standard reagent.

4.2. Procedure for the determination of Co in pharmaceutical samples

Different pharmaceutical tablets containing vitamin B_{12} were milled and homogenized thoroughly. The sample decomposition was carried out on a hot plate using concentrated nitric acid and hydrogen peroxide. After decomposition, the samples were filtered through a quantitative paper filter and diluted to 50 mL with 0.5 mol L^{-1} NaOH in order to reduce the acidity as well as to facilitate pH adjustment. The samples were subjected to the solid phase extraction as already described, by using the optimized experimental conditions. Cobalt was determined by FAAS. To check the accuracy of the results obtained by this method and to evaluate the applicability of the procedure proposed, the results were compared with standard reagent.

Table 6: Determination of cobalt in pharmaceutical samples

Sample	Synthesized reagent ($\mu g\ g^{-1}$)	Standard reagent($\mu g\ g^{-1}$)[c]
Forten	83.16±3.52[a]	85.74±8.02[a]
Cobaglobal	183.08±9.76[b]	198.60±11.39[b]

a- no difference at 95% probability level by t-Test,
b- no difference at 95% probability level by t-Test,
c- cytosine procured from local market.

REFERENCES

1. Tunceli A and Turker AR. Speciation of Cr(III) and Cr(VI) in water after preconcentration of its 1,5-dipheylcarbazone complex on amberlite XAD-16 resin and determination by FAAS. Talanta. 2002;57(6):1199-1204.
2. Soylak M, Elci L and Dogan M. solid phase extraction of trace metal ions with Amberlite XAD resins prior to AAS analysis. Journal of Trace and Microprobe Techniques. 2001;19(3):329-344.
3. Camino M, Bagur MG, Sanchez-Vinas M, Gazquez D and Romero R. Multivariate optimization of solvent extraction of Cd(II), Co(II), Cr(VI), Cu(II), Ni(II), Pb(II) and Zn(II) as dibenzyldithiocarbamates and detection by AAS. Journal of Analytical Atomic Spectrometry. 2001;16(6):638-642.
4. Bermejo-Barrera P, Martinez Alfonso N, Daz Lopez C and Bermejo Barrera. A. Use of Amberlite XAD-2 loaded with 1-(2-Pyridylazo)-2-naphthol as a preconcentration system for river water prior to determination of Cu^{2+}, Cd^{2+} and Pb^{2+} by FAAS. Mikrochimica Acta. 2003; 142(1-2):101-108.
5. Manzoori JL, Sorouradin MH and Shabani AMH. Atomic absorption determination of cobalt after

preconcentration by 1-(2_pyridylazo)-2-naphthol immobilized on surfactant-coated alumina. Microchemical Journal. 1999;63(2):295-301.

6. Narin I, Soylak M, Elci L and Dogan M. Determination of trace metal ions by AAS in natural water samples after preconcentration of pyrocatechol violet complexes on an activated carbon column. Talanta. 2000;52(6):1041-1046.

7. Soylak M and Dogan M. Separation and enrichment of zinc, iron, copper, cadmium, cobalt and nickel from urine with Amberlite XAD-16 resin. Trace Elements and Electrolytes. 1996; 13(3):130-132.

8. Taher MA. Atomic absorption spectrometric determination of ultra trace amounts of zinc after preconcentration with the ion pair of 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol and ammonium tetraphenylborate on microcrystalline naphthalene or by column method. Talanta. 2000;52(2):181-8.

9. Cesur H. Determination of Mn(II), Cu(II), Cd(II) and Pb(II) by FAAS after solid phase extraction of their Phenylpiperizine dithiocarbamate complexes onto activated carbon. Turk J Chem. 2003;27:307-314.

10. Maheswari MA and Subramanian MS. A new chelating resin for preconcentration and determination of Mn(II), Ni(II), Cu(II), Zn(II), Cd(II) and Pb(II) by FAAS. JAOAC Int. 2003; 86(6):1218-24.

11. Yamini Y, Hosseini MH and Morsali A. Solid Phase Extraction and Flame Atomic Absorption spectrometric determination of trace amounts of Zinc and cobalt ions in water samples. Microchim Acta. 2004;146:67-72.

12. Karatepe AU, Soylak M and Elci L. Separation/ preconcentration of copper, lead and iron in natural water samples on Chromosorb-105 resin. Analytical Letters. 2003;36(4):797-812.

13. Tuzen M, Narin I, Soylak M and Elci L. XAD-4/PAN solid phase extraction system for FAAS determination of some trace metals in environmental samples. Analytical Letters. 2004;37(3): 473-489.

14. Tuzen M, Soylak M, Elci L and Dogan M. Column solid phase extraction of copper, iron and zinc ions at trace levels in environmental samples on Amberlite XAD-7 for their FAAS determinations. Analytical Letters. 2004;37(6):1185-1201.

15. De Alcantara IL, Dos Santos Roldan P, Margionte MAL, Castro GR, Padilha CCF, De Oliveira Florentino A and De Magalhaes Padilha P. Determination of Cu, Ni and Pb in aqueous medium by FAAS after preconcentration on 2-Aminothiazole modified silica gel. Journal of the Brazilian Chemistry Society. 2004;15(3):366-371.

16. Duran C, Gundogdu A, Bulut VN, Soylak M, Elci L, Senturk HB and Tufekci M. Solid phase extraction of Mn (II), Co(II), Ni (II), Cu(II), Cd (II) and Pb(II) ions from environmental samples. Journal of Hazardous Materials. 2007;146(1-2):347-355.

17. Liu Y, Guo Y, Chang X, Meng S, Yang D and Din B. Column Solid-Phase Extraction with 2-Acetylmercaptophenyldiazoaminoazobenzene (AMPDAA) Impregnated Amberlite XAD-4 and Determination of Trace Heavy Metals in Natural Waters by Flame Atomic Absorption Spectrometry. Microchim Acta. 2005;149:95-99.

18. Tuzen M, Saygi KO and Soylak M. Novel solid phase extraction procedure for Gold (III) on Dowex M 4195 prior to its FAAS determination. J Haz Mater. 2008;156:591-595.

19. Grembecka M and Szefer P. Comparative assessment of essential and heavy metals in fruits from different geographical origins. Environ monit Assess. 2013;185(11):9139-60.

20. Ghaedi M, Mortazavi K, Montazerozohori M, Shokrollahi A and Soylak M. Flame atomic absorption spectrometric (FAAS) determination of copper, iron and zinc in food samples after solid-phase extraction on Schiff base-modified duolite XAD 761. Mater Sci Eng C Mater Biol Appl. 2013;33(4):2338-44.

21. Karimipour G, Ghaedi M, Sahraei R, Daneshfar A and Bivareh MN. Modification of gold nanoparticle loaded on activated carbon with bis(4-methoxysalicylaldehyde)-1,2-phenylenediamine as new sorbent for enrichment of some metal ions. Biol Trace Elem Res. 2012;145(1):109-17.

22. Ghaedi M, Tavallali H, Shokrollahi A, Zahedi M, Montazerozohori M and Soylak M. Flame atomic absorption spectrometric determination of zinc,

nickel, iron and lead in different matrixes after solid phase extraction on sodium dodecyl sulfate (SDS)-coated alumina as their bis (2-hydroxyacetophenone)-1, 3-propanediimine chelates. J Hazard Mater. 2009;166(2-3): 1441-8.

23. Ghaedi M, Niknam K, Taheri K, Hossainian H and Soylak M. Flame atomic absorption spectrometric determination of copper, zinc and manganese after solid-phase extraction using 2,6-dichlorophenyl-3,3-bis(indolyl)methane loaded on Amberlite XAD-16. Food Chem Toxicol. 2010;48(3):891-7.