



DETERMINATION OF TRACE OF HEAVY METALS IN WATER SAMPLES BY ATOMIC SPECTROMETRY BY PRECONCENTRATION WITH SOFT HUSK OF PISTACHIO

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This study uses solid phase extraction method to measure trace amount of metal ions of Cd²⁺, Pb²⁺, Cu²⁺, Ni²⁺ and Zn²⁺ in aqueous samples by using herbal absorbent called soft husk of Pistachio. To do so, aqueous solution of these metal ions was passed through a column containing adsorbent. Meanwhile, existing metal ions in solution were adsorbed, and then preconcentrated via eluting by nitric acid. Finally, they were measured by Flame Atomic Absorption Spectrometry (FAAS). Effective parameters such as pH, amount of adsorbent, volume and concentration of eluent, velocity of solution and interfering ions were examined. Calibration curve related to metal ions: lead, nickel, cadmium, copper and zinc in the range of 30-800, 10-400, 5-90, 10-350 and 5-90 µg L⁻¹ was linear and the limits of detection for metal ions lead, nickel, cadmium, copper and zinc were respectively: 2.581, 0.988, 0.139, 0.527 and 1.385 µg L⁻¹. The proposed method was applied to measure metal ions in real samples with acceptable accuracy.

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It consumes less time and solution than other methods such as LLE.²² The aim of the present paper is to optimize the various experimental working conditions in the processes of preconcentration of analytical ions from water samples collected from different locations followed by AAS determinations.

Introduction

Industrial sewerages resulting from different factories are among the main pollution sources of heavy metal.¹⁻⁴ Due to toxicity and damaging effects of heavy metals, removing their ions is a concern for many of environmental studies.³ Lead is the most common toxic heavy element in the environment.⁶ Cadmium compounds in mines, galvanizing, paint making are of its polluting sources in environment.⁷ Over-absorption of copper in human body causes intense mucus corrosion, extensive capillary, digestion system, and central neural system damages, and lead to depression.⁸ Over-absorption of zinc makes skin urticarial, vomit, nausea, and anemia.⁹ Nickel sources include fossil fluids burned in power plants, mines, and refineries.^{10,11} Due to harming effects of heavy metals, various methods are presented to remove them including chemical sedimentation, reverse osmosis ion exchange, adsorption etc.¹²⁻¹⁵ One of the most applicable methods is adsorption.¹⁶ There is a need for sample preparing methods because direct measurement of heavy metal ions in complex matrices is limited due to low concentrations and matrix disruption,^{17,18} which extracting method is one of the most basic methods. Specimen values are used for separating and pre-concentrate from the sample blank. Common extracting methods, such as Soxhlet, liquid-liquid extraction (LLE), are usually time consuming and require a large volume of toxic solution.^{19, 20} It is emphasized on limited use of these solutions because of their destroying effects on environment.²¹ According to these facts, SPE is a proper and effective technic in which extracting is easy and fast, and is capable of being automate.

Materials and methods

Preparation of adsorbent

After collecting soft husk pistachio from Damghan City, we eluted it with natural water and then triple-distilled water. Then, we dried it in oven at 100 °C, and next we pulverized it with mill. The powder is used as adsorbent after sieving the powder with mesh-16 sieve. Fig. 1 shows scanning electron microscopy (SEM) images of adsorbent before adsorption.

Chemicals and apparatus

All solutions for experiments were prepared using metal ions nitrate salts (Merck, Darmstadt, Germany) by dissolving the analytical grade sample in distilled water. The buffer solutions were prepared from formic acid for pH 2-4, from acetic acid for pH 5-6, from phosphate for pH 7, and from ammonium for pH 8-10. The pH measurements were made with a pH-meter (W3B, Italy) and analysis of Cd (II), Pb(II), Ni(II), Cu(II) and Zn(II) was performed by SHIMADZU AA-680 flame atomic absorption spectrophotometer. A Thermoelectric Auto Sampling pump model AS-21P was used for passing sample solutions through a column containing adsorbent.

A syringe tube (58 mm × 8 mm i.d.) with a fine bore packed with cotton was used as a preconcentration column. The column loaded with adsorbent was lightly compressed with the flat end of a plastic rod so that its height would be about 18 mm.

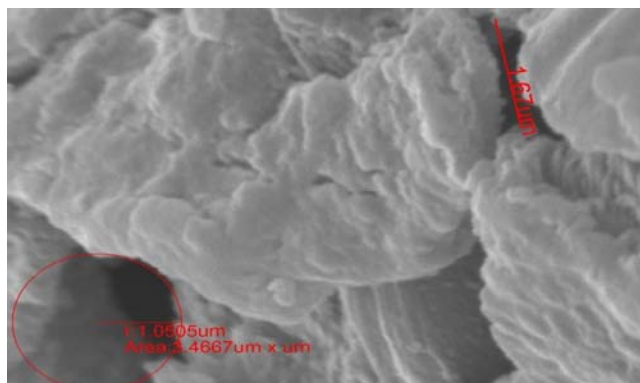


Figure 1. scanning electron microscopy (SEM) images of adsorbent before adsorption.

Recommended procedure

Initially, for column conditioning, distilled water was passed through the column. To measure negligible amounts of heavy metal ions of lead, copper, cadmium, zinc, and nickel, an aqueous solution is prepared with volume of 50 mL and concentration of $50 \mu\text{g L}^{-1}$ for each ion, containing 5 mL buffer solution to stabilize pH=6. Then, this solution is passed through a column containing 0.3 g of adsorbent, which its bottom is closed by some cotton, by a pump with flow rate of 5 mL min^{-1} . Next, the column is washed by 3 mL of nitric acid of 1.5 molar. Finally, adsorption of considered ions in recovery solution is measured by Atomic Absorption Spectrometer.

Results and Discussion

Effect of solution pH

pH is among effective factors in adsorption process.²³ Particularly, pH influences adsorption capacity. Amount of ion adsorption on adsorbent's surface is affected by adsorbent's surface charge, which is influenced by pH of solution.²⁴ In this study, pH of metal ions solution is adjusted by Buffer solutions, and effect of pH on adsorption of metal ions is studied in the range of pH=2 to 10. Figure 2 shows that maximum recovery is for pH=6. According to competitiveness between H^+ ion and cations, more basic pH leads to more recovery in lower ranges of pH. In other hand, in basic pH range recovery reduces, due to formation of metallic cation compounds, adsorbed not very well on the surface of adsorbent.

Effect of mass of adsorbent

In order to study the effect of this parameter, six solution samples with volume of 50 mL is prepared, containing 5 mL of Buffer to stabilize pH in the optimum state (pH=6). They contain metal ions with concentration of $50 \mu\text{g L}^{-1}$. These solutions pass a pump in flow rate of 3.5 mL min^{-1} through

prepared columns containing different values of adsorbent (0.05 - 0.3g). After eluting it with 3 mL of nitric acid of 1.5 mol L⁻¹ concentration, it is measured by atomic absorption spectrometer. As shown in Figure 3, adsorption and recovery increase by increasing adsorbent amount because of enhancing area of adsorbent surface and adsorption sites. Amount of 0.3g adsorbent is chosen as optimum value.

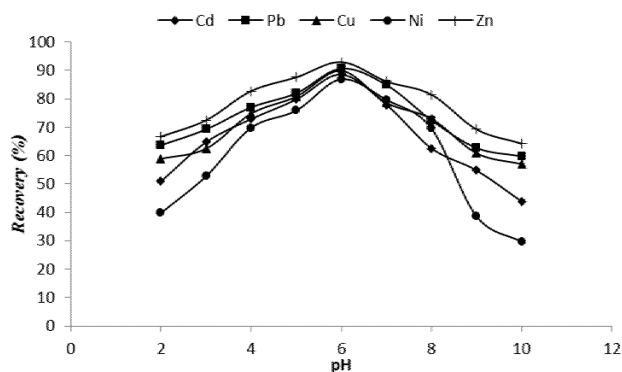


Figure 2. Effect of solution pH. *Experimental conditions:* 50 mL of sample containing $50 \mu\text{g L}^{-1}$ metal ions, sorbent, 0.2 g, eluent 3 mL of $1.5 \text{ mol L}^{-1} \text{ HNO}_3$ and flow rate 3.5 mL min^{-1} .

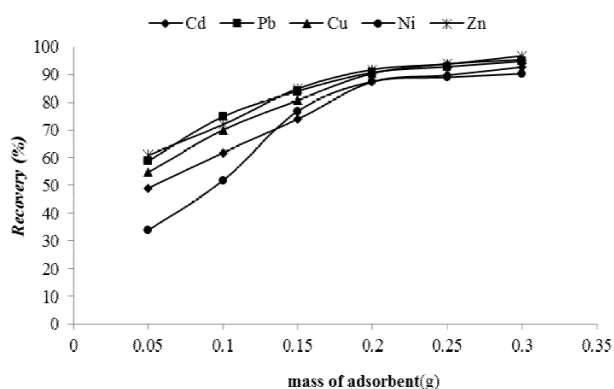


Figure 3. Effect of mass of adsorbent. *Experimental conditions:* 50 mL of sample containing $50 \mu\text{g L}^{-1}$ metal ions, eluent 3 mL of $1.5 \text{ mol L}^{-1} \text{ HNO}_3$ and flow rate 3.5 mL min^{-1} .

Elution

Selecting appropriate eluent is so important, because it should have three features: efficiency, selectivity, and compatibility. To select proper eluent for desorption of metal ions from adsorbent surface, effect of 3 mL of eluents, such as nitric acid, hydrochloric acid, and sulfuric acid with concentration of 1.5 M is examined. Using nitric acid, as an eluent, leads to formation of metal cations nitrates. Nitrate has more solubility than sulfates and chlorides of metal cations, formed because of elution with hydrochloric and nitric acids. As seen in Figure 4 and Table 1, nitric acid has the most recovery extent, and so, this solvent is chosen as proper eluent for next steps.

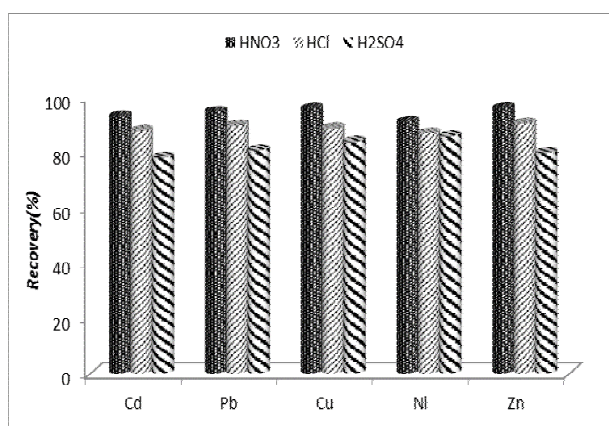
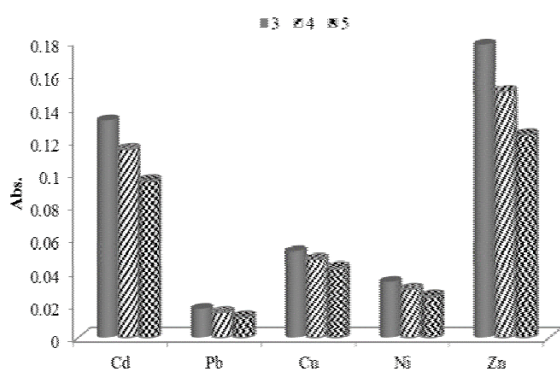
In one side, volume of eluent should reach an amount that is able to desorb analyte ions, in the other hand, enhancing volume of eluent reduces concentrate factor. Thus, this parameter is investigated.

Table 1. Effect of different eluent on recovery of analytes.

Eluent	Recovery, %				
	Pb	Zn	Cu	Ni	Cd
HNO ₃	94.7989	96.0866	95.9643	91.0964	93.0643
HCl	89.7432	90.5434	88.7532	86.9653	87.8654
H ₂ SO ₄	80.8542	79.7439	83.9653	85.9654	78.0755

Experimental conditions: 50 mL of sample containing 50 µg L⁻¹ metal ions at pH 6, sorbent, 0.3 g, eluent 3 mL of 1.5 mol L⁻¹ different eluent and flow rate 3.5 mL min⁻¹.

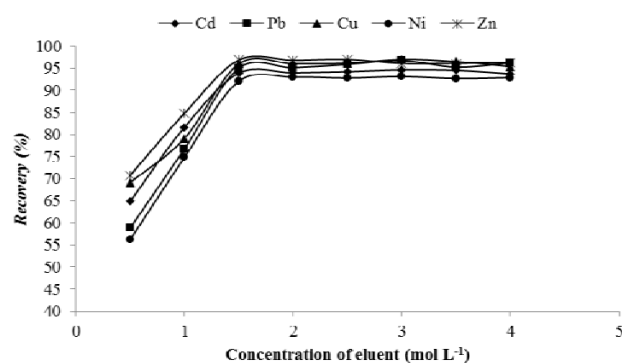
To optimize eluents' volume, regarding to simultaneous measuring of 5 metal ions, volumes of 3, 4, and 5 mL is studied. According to Fig.5, the maximum adsorption extent is observed for 3 mL of eluent volume. However, the recovery is same for all three volumes. Hence, volume of 3 mL is used as optimum value for next stages, in a view that enhancing volume of eluent decreases the concentrate factor.

**Figure 4.** Effect of different eluent on recovery of analytes. Experimental conditions: 50 mL of sample containing 50 µg L⁻¹ metal ions at pH 6, sorbent, 0.3 g, eluent 3 mL of 1.5 mol L⁻¹ different eluent and flow rate 3.5 mL min⁻¹.**Figure 5.** Effect of eluents' volume on recovery of analytes. Experimental conditions: 50 mL of sample containing 50 µg L⁻¹ metal ions at pH 6, sorbent: 0.3 g, eluent: different volum of 1.5 mol L⁻¹ HNO₃ and flow rate 3.5 mL min⁻¹.

Concentration effect of nitric acid, on recovery level of metal cations, is examined. In this study, desorption is tested by 3 mL of HNO₃ with different concentrations (0.5-4 M), and concentration of 1.5 M is picked out as optimum eluent concentration considering the results (Fig. 6).

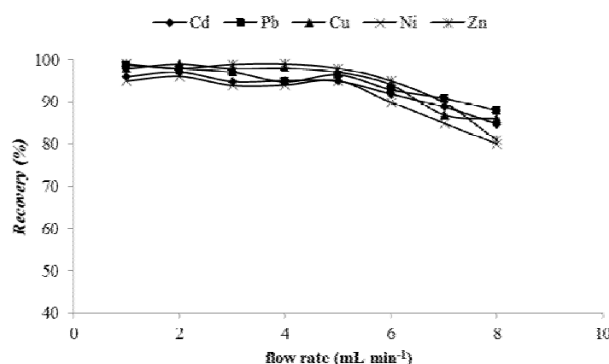
Effect of flow rate of sample

In the SPE method, rate of sample solution is one of the most important parameters affecting both return efficiency of analytes and extracting time.²⁵

**Figure 6.** Effect of eluent concentration. Experimental conditions: 50 mL of sample containing 50 µg L⁻¹ metal ions at pH 6, sorbent, 0.3 g, eluent 3 mL of different concentration HNO₃ and flow rate 3.5 mL min⁻¹.

Effect of sample solution rate is examined in the range of 1-8 mL min⁻¹. To do this, solutions with size of 50 mL are passed through columns in optimum conditions with different rates. After elution and desorption of analytes by 3 mL nitric acid of 1.5 Molar, Atomic absorption spectrometer measures them.

As shown in Figure 7, rates more than 5 mL min⁻¹ cause to reduce in recovery of considered cations. Therefore, we choose flow rate of 5 mL min⁻¹ as optimum rate for next steps.

**Figure 7.** Effect of flow rate of sample. Experimental conditions: 50 mL of sample containing 50 µg L⁻¹ metal ions at pH 6, sorbent, 0.3 g, eluent 3 mL of 1.5 mol L⁻¹ HNO₃.

Effect of interfering ions

In this section, interfering effect of other ions, as well as interfering effect of considered cations extracted simultaneously, on recovery of analyte on adsorbent is examined in optimum conditions. Allowed error for ion's concentration is determined less than ±5% for pre-concentrate and measuring analytes. Interfering ion refers to an ion that makes a change more than allowed error in recovery extent. Table 2 lists the results.

Due to results, mentioned ions have no interfering effect on recovery of analyte ions.

Table 2. Tolerance limits for coexisting ions in adsorption of 50 µg L⁻¹ of Zn, Pb, Cu, Cd and Ni.

Foreign ions	Interferent /ion ratio				
	Cu ²⁺	Pb ²⁺	Ni ²⁺	Zn ²⁺	Cd ²⁺
Zn ²⁺	500	1000	500	-	500
Pb ²⁺	500	-	1000	500	1000
Cu ²⁺	-	500	500	1000	500
Ni ²⁺	1000	1000	-	1000	1000
Cd ²⁺	1000	1000	500	1000	-
Ag ⁺ , Ca ²⁺ , Na ⁺ , Mn ²⁺ , Cr ³⁺ , Cl ⁻ , Li ⁺ , NO ₃ ⁻ , Fe ²⁺ , K ⁺ , Br ⁻ , CH ₃ COO ⁻	1000	1000	1000	1000	1000
S ₂ O ₃ ²⁻	500	250	1000	1000	1000
F ⁻	500	1000	1000	1000	1000
Co ²⁺	1000	1000	500	1000	1000
Mg ²⁺	1000	1000	1000	500	1000
Al ³⁺	500	1000	250	100	100
I ⁻	1000	500	1000	1000	1000

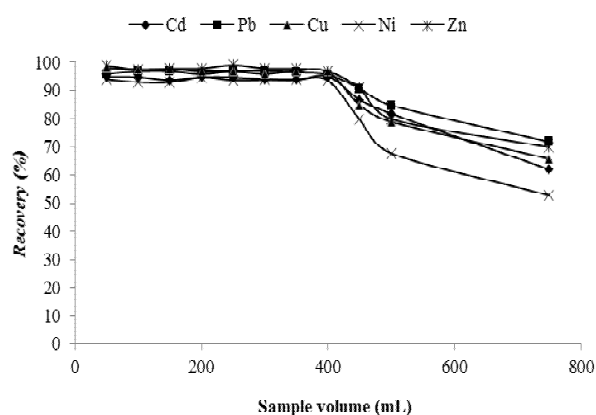
Table 3. Analytical characteristics of proposed method at the optimum conditions.

Ions	Linear range, µg L ⁻¹	Regression equation	Correlation coefficient (r)	LOD, µg L ⁻¹ (n = 10)	R.S.D., % (n = 10)
Ni ²⁺	10-400	y=0.0016x+0.0032	0.9996	0.988	1.682
Pb ²⁺	30-800	y=0.0006x+0.0031	0.9992	2.581	2.151
Zn ²⁺	5-90	y=0.0086x+0.206	0.9996	1.385	2.276
Cu ²⁺	10-350	y=0.0024x-0.0007	0.9995	0.527	0.928
Cd ²⁺	5-90	y=0.0104x+0.0045	0.9998	0.139	1.202

Effect of sample volume

To study concentrate capability of analyte, effect of sample volume on recovery of considered ions is examined by passing various sample volumes (50-750 mL) with optimum flow rate (5 mL) through columns containing 0.3 g of adsorbent, in which each pH of solution is stabilized by adding proper amount of Buffer in optimum condition.

According to Fig. 8, adsorption is done well, with up to 400 mL of solution containing heavy metal ions. Then, adsorbed ions are eluted by 3 mL of nitric acid 1.5 molar. The resulted pre-concentrate factor is 133.

**Figure 8.** Effect of sample volume. *Experimental conditions:*, sorbent, 0.3 g, eluent 3 mL of 1.5 mol L⁻¹ different eluent and flow rate 5 mL min⁻¹

Detection limit

Detection limit is the least concentration or amount, which is traceable by analytical method with a certain assurance. Based on IUPAC recommendation, signal of detection limit is average value of instance plus thrice of its standard deviation.

$$LOD = \frac{3S_b}{m} \quad (1)$$

where,

S is standard deviation, and
 m is calibration curve slope.²⁶

By this way, 10 solutions of triple-distilled water of 50 mL volume are pre-concentrated in optimum solution, and measured by atomic absorption spectrometer. Results are listed in Table 3.

Measuring metal cations in real samples

Based on obtained optimum conditions, proposed method is employed to measure considered metal cations in three real samples. To do this, columns containing 3 g of adsorbent is prepared, and 50 mL of real sample solution are passed through them with flow rate of 5 mL min⁻¹. Pre-concentrate method is used too. That is, after passing the solution, columns are eluted by 3 mL of 1.5 molar nitric acid and atomic absorption spectrometer measures concentration of metal cations.

Table 4. Comparing results of preconcentration factor and detection limit of current work with other works.

Analytical ions	Method/Instrumental	Preconcentration factor	Detection limit $\mu\text{g L}^{-1}$	References
Ir(III)	SPE on naphthalene/spectrophotometry	40	20	27
Ni(II)	SPE on MIP/spectrometry	72.66	0.3	28
Cd(II)	SPE on naphthalene/DDP	40	70	29
Cu(II)	SPE on mini column of sisal fiber/FAAS	75	0.01	30
In(III)	SPE on naphthalene/DDP	25–50	200	31
Co(II)	SPE on surfactant-coated alumina/AAS	100	-	32
Cr(III)	SPE on activated carbon/FAAS	50	0.27	33
Cd(II), Pb(II), Cu(II), Ni(II), Zn(II)	SPE on soft husk of Pistachio/FAAS	133	0.13-2.58	Present work

SPE: solid phase extraction, MIP: molecularly imprinted polymers, DDP: differential pulse polarography, AAS: atomic absorption spectrometry

Table 5. Analytical result for determination of metal ions in tap water from Tehran city

Ions	Added, $\mu\text{g L}^{-1}$	Found, $\mu\text{g L}^{-1}$	RSD, %	Recovery, %
Cd ²⁺	-	n.d.	-	-
	50	52.14	2.141	104.28
	100	101	1.429	101.0
Pb ²⁺	-	8.98	3.978	-
	50	58.85	3.890	99.74
	100	109.0	2.561	100.02
Cu ²⁺	-	18.79	3.988	-
	30	48.1	3.521	97.70
	60	78.51	1.926	99.53
Ni ²⁺	-	n.d.	-	-
	75	75.42	3.951	100.56
	150	149.38	3.891	99.58
Zn ²⁺	-	16.05	1.091	-
	25	43.15	0.633	108.4
	50	66.12	0.581	100.14

Table 6. Analytical result for determination of metal ions in mineral water

Ions	Added, $\mu\text{g L}^{-1}$	Found, $\mu\text{g L}^{-1}$	RSD, %	Recovery, %
Cd ²⁺	-	-	-	-
	75	76.50	1.952	102.0
	150	155.21	1.614	103.47
Pb ²⁺	-	-	-	-
	75	76.10	3.921	101.46
	150	150.0	3.031	100.0
Cu ²⁺	-	7.512	4.012	-
	50	57.42	3.029	99.82
	100	107.55	3.321	100.04
Ni ²⁺	-	-	-	-
	75	75.03	4.258	100.04
	150	150.12	4.012	100.08
Zn ²⁺	-	23.20	1.234	-
	50	73.08	0.439	99.76
	100	124.5	0.331	101.3

Table 7. Analytical result for determination of metal ions in well water from Semnan city

Ions	Added ($\mu\text{g L}^{-1}$)	Found ($\mu\text{g L}^{-1}$)	RSD(%)	Recovery(%)
Cd^{2+}	-	0.654	3.152	-
	75	76.0	1.823	100.46
	150	150.98	1.021	100.22
Pb^{2+}	-	n.d.	-	-
	75	76.5	4.080	102.0
	150	149.4	3.120	99.60
Cu^{2+}	-	6.814	4.112	-
	50	56.94	3.021	100.26
	100	108.01	2.890	101.20
Ni^{2+}	-	n.d.	-	-
	75	74.10	4.150	98.80
	150	150.0	3.980	100.0
Zn^{2+}	-	14.701	2.354	-
	50	62.94	0.951	96.48
	100	115.01	0.873	100.31

Here, to verify results, we apply standard addition method. Hence, we add a certain amount of standard metal cations solution to sample solution, and pass it through column again. Tables 5 to 7 list the results. As results show, the observed value is almost equal to initial value of metal cation plus the added amount that demonstrates accuracy of method.

Conclusion

In this study, the wastage of soft husk of pistachio was used as an absorbent. Preparation of absorbent out of this wastage is easy and considering of the fact that the wastage of soft husk of pistachio has no function except being animals' food, its consumption is economical. Effective parameters were optimized and a high retrieval for metal ions from water solution was gained. The speed of optimal flow equaled 5 ml min; therefore we need a short time to analyze the samples. Concentration factor (133) was suitable and the result of examination of efficiency number and measurement of heavy metals in real samples approved the validity and accuracy of this method.

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