

1-1-2010

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HOSSEINI, MAHDI; DALALI, NASSER; KARIMI, ALI; and DASTANRA, KOUROSH (2010) "Solid phase extraction of copper, nickel, and cobalt in water samples after extraction using surfactant coated alumina modified with indane-1,2,3-trione 1,2-dioxime and determination by flame atomic absorption spectrometry," *Turkish Journal of Chemistry*. Vol. 34: No. 5, Article 11. <https://doi.org/10.3906/kim-1002-22>

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Solid phase extraction of copper, nickel, and cobalt in water samples using surfactant coated alumina modified with indane-1,2,3-trione 1,2-dioxime and determination by flame atomic absorption spectrometry

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Received 04.02.2010

A simple method for simultaneous pre-concentration of Cu, Ni, and Co metal ions prior to their determination by flame atomic absorption spectrometry is reported. The method is based on the extraction of target ions via complexation with indane-1,2,3-trione 1,2-dioxime immobilized on sodium dodecyl sulfate (SDS) coated alumina. The metal content on the adsorbent was eluted with 4.5 mL of 2 mol L⁻¹ nitric acid. The influences of the analytical parameters including pH, sample volume and flow rate, and eluent type and flow rate were investigated. The effect of matrix ions on the retentions of the analytes was also examined. The recoveries of analytes were generally higher than 96% with a low relative standard deviation (R.S.D. < 3%). The presented method was successfully applied for determination of these metals in water samples.

Key Words: Solid phase extraction; surfactant coated alumina; atomic absorption spectrometry; indane-1,2,3-trione 1,2-dioxime

Introduction

The emphasis on the removal of toxic metal ions has led to a considerable growth in the development of new methods in analytical chemistry for extraction, separation, and determination of various metal ions. Accurate and precise analyses of trace amount heavy metal ions by instrumental techniques including inductively coupled plasma-mass spectrometry (ICP-MS), inductively coupled plasma-atomic emission spectrometry (ICP-AES), and flame atomic absorption spectrometry (FAAS) are an important part of analytical chemistry,¹⁻⁴ because ecological and health problems associated with environmental contamination continue to rise. The direct determination of the trace metals in solid or powder sample solutions with a complicated matrix by atomic

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spectroscopic methods, such as flame atomic absorption spectrometry (FAAS) and inductively coupled plasma atomic emission spectrometry (ICP-AES), is often difficult due to their extremely low concentrations and matrix interferences; therefore, a separation/pre-concentration step is required.^{5–8} The solid-phase extraction (SPE) technique has become increasingly popular in comparison with the more traditional liquid-liquid extraction methods because of its several major advantages, such as: (i) simple to operate; (ii) high pre-concentration factor; (iii) rapid phase separation; and (iv) the ability to combine with different detection techniques. Various solid phases including Chelex 100, Amberlite XAD resins, synthetic polymers, polyurethane foam, and activated carbon have been used for the solid phase extraction of trace heavy metals in environmental samples prior to their instrumental analysis.^{9–15} Among solid-phase adsorbents, SDS coated alumina is very useful for pre-concentration and separation of metal complexes^{16–18} because of its good physical properties such as porosity, uniform pore size distribution, high surface area as chemical homogeneous non-ionic structures, and good adsorbent properties for great amounts of uncharged compounds. Generally, the design of stable and selective solid phase sorbents for separation and pre-concentration of a target metal ion depends on different factors related to the nature of solid support, its surface area and activity¹⁹ as well as other important factors related to the organic complexing agent bound to the solid substrate. These factors include the structure of the immobilized organic compound as a whole, the nature of the incorporated donor atoms (O, N, P, and S), the positioning of the functional groups along the surface of the solid support, and the steric requirements of the complex formed after uptake of the desired metal ion.²⁰ The most successful solid phase extractors for soft metal ions are those immobilized basically: sulfur and nitrogen or phosphorous containing compounds.²¹ Nevertheless, the inorganic sorbents have the advantages of no swelling, fast kinetics, and good mechanical stability as well.²² Recent studies on the use of surfactant-coated mineral oxides columns for SPE have demonstrated these new sorbent materials to be a promising tool for the extraction/pre-concentration of organic compounds in a wide polarity range.²³ The most prominent among the supports used are activated carbon,²⁴ SDS coated alumina,²⁵ and modified chromosorb and octadecyl bonded silica (C₁₈).²⁶ The purpose of this work was to investigate the feasibility of adsorption of copper, nickel, and cobalt ions on SDS coated alumina modified with indane-1,2,3-trione 1,2-dioxime. In order to obtain the maximum signal for evaluation of these ion contents, the effective parameters, viz. pH of sample solution, amount of indane-1,2,3-trione 1,2-dioxime and sorbent, type of eluting agent and flow rate (sample and eluent), were optimized.

Experimental

Apparatus

The measurements of metal ions were performed with a Varian SpectrAA 220 atomic absorption spectrometer equipped with a hollow cathode lamp and a deuterium background corrector, at respective wavelengths (the used resonance wavelengths are 324.8 nm for copper, 232.0 nm for nickel, and 240.7 nm for cobalt) using an air-acetylene flame. A Metrohm 692 pH/Ion meter with a combined glass-calomel electrode was used for measurement of test solution pH.

Chemicals

Acids and bases were of the highest purity available from Sigma (St. Louis, MO, USA) and merck (Darmstadt, Germany) and were used as received. Doubly distilled deionized water was used throughout. The stock standard

solutions (1000 mg L^{-1}) Cu, Ni, and Co were supplied by Merck. The pH adjustment was done by addition of dilute hydrochloric acid, acetic acid/sodium acetate buffer, phosphoric acid/phosphate buffer, and sodium hydroxide to prepare the desired pH solution. The $\gamma\text{-Al}_2\text{O}_3$ mesh 20-50 was purchased from Merck and used as received. The surfactant, sodium dodecyl sulfate was purchased from Merck. Indane-1,2,3-trione 1,2-dioxime was synthesized by our laboratory as described in the literature²⁷⁻³² and a 0.75% (w/v) solution of indane-1,2,3-trione 1,2-dioxime was prepared in ethanol.

Immobilization of indane-1,2,3-trione 1,2-dioxime on surfactant-coated alumina

About 200 mg sodium dodecyl sulfate (SDS) added to 100 mL of water solution containing 3.0 g of γ -alumina particles and pH was adjusted to 2.0 with 2 mol L^{-1} nitric acid to form ad-micelles on alumina particles. Then 7.5 mg of indane-1,2,3-trione 1,2-dioxime dissolved in ethanol were mixed and pH adjusted 7.0 to form indane-1,2,3-trione 1,2-dioxime-impregnated on ad-micelles on alumina particles while shaking the suspension with a stirrer. After mixing for 20 min, the supernatant solution was discarded and the remaining was packed into a column. The column was washed by passing 5 mL of 0.2 mol L^{-1} nitric acid and then the column was neutralized with 0.1 mol L^{-1} aqueous sodium hydroxide. If kept in a refrigerator the sorbent is a stable at least for 1 week.

Extraction procedure

The modified adsorbent (indane-1,2,3-trione 1,2-dioxime-impregnated on ad-micelles on alumina) was washed with 25 mL of water. Then the sample (100 mL) containing trace amounts of metal ions was passed through the modified adsorbent at a flow rate of 2 mL min^{-1} with the aid of a suction pump. The analyte was then eluted from the adsorbent (in column) with 4.5 mL of 2 mol L^{-1} nitric acid at a flow rate of 3 mL min^{-1} . The metal ions content of the effluent was then analyzed by flame atomic absorption spectrometer using a standard solution of metal ions in a similar matrix.

Results and discussion

Activated alumina can function as either a cation or as an anion pre-concentrator depending on the pH. The SDS concentration was maintained below the critical micellar concentration to avoid formation of micelles in the aqueous solution. The adsorption of SDS is highly dependent on the solution pH. Negatively charged SDS was more effectively and almost quantitatively adsorbed on the positively charged alumina surfaces at pH 1-3, so that organic compounds could be adsorbed on SDS-coated γ -alumina. This phenomenon is greatly increased by decreasing the pH due to the higher charge density on the mineral oxide surface. The anionic surfactant (SDS) is effectively adsorbed on positively charged γ -alumina surfaces via formation of self aggregates over a wide pH range (1-5), whereas very small amounts of SDS could be adsorbed on the inert surface of α -alumina. Therefore, γ -alumina is essential for the preparation of surfactant-coated sorbents. The purpose of this work was to investigate the possibility of immobilization of indane-1,2,3-trione 1,2-dioxime as complexing agent on SDS coated alumina for sorbent extraction/pre-concentration of Cu, Ni, and Co ions.

Influence of pH

The effect of pH on the pre-concentration of metal ions on SDS coated alumina modified with indane-1,2,3-trione 1,2-dioxime was studied by determination of individual elements. For this, $10 \mu\text{g}$ of each element (in 100 mL)

was pre-concentrated in the pH range of 1-9. The results are shown in Figure 1. The results obtained indicated that the target ions could be retained quantitatively by the adsorbent at pH 8-9. The decrease in signal at pH < 4 may be due to competition of hydronium ion toward complexation with indane-1,2,3-trione 1,2-dioxime, which leads to the decrease in the extraction yield. To achieve high efficiency and good selectivity, a pH of 5; 7, and 9 was selected for Cu, Ni, and Co ions, respectively. With the results shown in Figure 1, if the extraction is carried out for each element at different pHs, it is very time consuming. Thus the best pH (optimum) was 9 for extraction of the 3 elements.

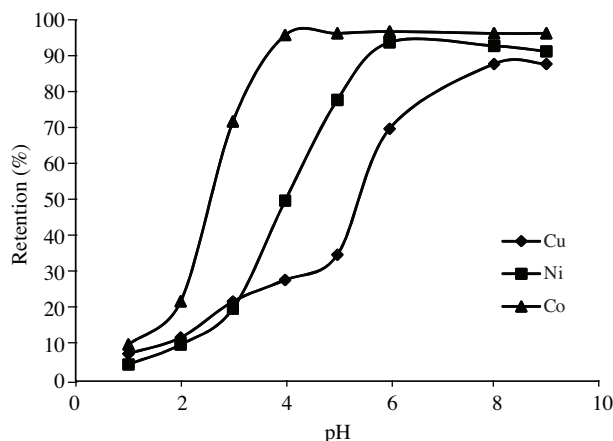


Figure 1. Effect of pH on the retention of metal ions (N=3).

Eluent type and volume

The choice of a suitable eluent is another important task in the recovery of analytes. As can be seen from Figure 1, the extraction of these metal ions was negligible at pH < 3, in the presence of dilute HCl and HNO₃. The elution of the adsorbed metal-chelates on the solid phases is an important step for solid phase extraction studies. Due to this point, various eluent solutions, given in Table 1, were used for desorption of ions complexed with indane-1,2,3-trione 1,2-dioxime chelates from SDS coated alumina. Quantitative recoveries for copper, nickel, and cobalt ions were obtained only with 1 mol L⁻¹ HNO₃. Recoveries were not quantitative for other eluents used in the present study. For this reason, HNO₃ is the best eluent and was chosen as eluent and various concentrations and volumes of HNO₃ were attempted to elute the analytes retained in the modified column. The results obtained are given in Table 1. The effect of eluent volume on the recoveries of the analytes was also studied by using 1 mol L⁻¹ HNO₃; it was found that quantitative recoveries could be obtained with 6.0 mL of 1 mol L⁻¹ HNO₃. To achieve a higher concentration factor a lower volume of eluent was required; hence 4.5 mL of 2 mol L⁻¹ HNO₃ was selected for the further experiment.

Amount of SDS

The concentration (hemi-micelles or ad-micelles) of surfactant aggregates on mineral oxides mainly depends on the surfactant/oxide weight ratio. Their influence on the percentage of complexed ions adsolubilized was investigated by passing 100 mL of a solution containing 10 μg of each ion through solid phase containing various amounts of SDS, 150 mg of γ-Al₂O₃, and 7.5 mg of indane-1,2,3-trione 1,2-dioxime at pH 5, 7, and

9, respectively. The results obtained are presented in Figure 2. In the absence of SDS, ions were not retained on γ -alumina. The retention of metal ions on hemi-micelles, which have a hydrophobic surface, was clearly dependent on analyte complex polarity. Therefore, addition of SDS is necessary. The formation of minute amounts of ad-micelles was essential to achieve complete adsolubilization of these ions as a respective complex. At surfactant concentrations higher than about 50 mg/g alumina, a decrease in the percentage of ions retained was observed as a result of the formation of micelles.

Table 1. Effect of type and concentration of eluting agent on recovery of analytes.

Eluent	Recovery (%)		
	Cu	Ni	Co
4.5 mL HNO ₃ (0.5 mol L ⁻¹)	94.7 ± 2	92.7 ± 4	94.2 ± 4
4.5 mL HCl (0.5 mol L ⁻¹)	82.3 ± 4	81.7 ± 5	85.8 ± 5
4.5 mL H ₂ SO ₄ (0.5 mol L ⁻¹)	42.3 ± 2	45.5 ± 2	50.7 ± 4
4.5 mL CH ₃ COOH (0.5 mol L ⁻¹)	24.6 ± 4	41.4 ± 3	46.5 ± 2
4.5 mL Na ₂ S ₂ O ₄ (0.5 mol L ⁻¹)	29.1 ± 5	30.8 ± 2	32.2 ± 2
4.5 mL EDTA (0.5 mol L ⁻¹)	46.1 ± 3	57.1 ± 5	48.2 ± 3
4.5 mL HNO ₃ (1 mol L ⁻¹)	94.5 ± 4	96.5 ± 2	94.8 ± 4
4.5 mL HNO ₃ (2 mol L ⁻¹)	100.5 ± 4	98.0 ± 2	102 ± 5
6 mL HNO ₃ (1 mol L ⁻¹)	99.0 ± 2	101.0 ± 5	101.8 ± 4
6 mL HNO ₃ (2 mol L ⁻¹)	100 ± 4	101.0 ± 5	102.8 ± 4
4.5 mL HCl (1 mol L ⁻¹)	84.4 ± 4	80.7 ± 4	85.0 ± 3
4.5 mL HCl (2 mol L ⁻¹)	90.1 ± 5	85.4 ± 2	84.0 ± 2
6 mL HCl (1 mol L ⁻¹)	90.5 ± 3	89.2 ± 2	86.4 ± 3
6 mL HCl (2 mol L ⁻¹)	80.7 ± 2	78.7 ± 3	71.0 ± 5

Effects of amounts of alumina

The influences of the amounts of alumina in the column were also investigated in Figure 3. The results display that with up to 150 mg of alumina the efficiency of extractions increase and further addition has no significant change on recoveries. The recoveries of analytes above 150 mg of solid phase were below 96% with 4.5 mL of the eluent. In the proposed procedure 150 mg of alumina is recommended.

Sample volume and flow rate

Experiments to determine the maximum sample loading volume were performed by passing increasing volumes between 25 and 2000 mL (at increments of 250 mL until 1500 mL and at increments of 50 mL up to 2000 mL) of aqueous solutions at pH 5, 7, and 9 containing 10 μ g of all ions, through the solid phase column filled with 150 mg of γ -alumina, 200 mg of SDS (hemi-micellar/admicellar region), and 7.0 mg of indane-1,2,3-trine 1,2-dioxime, and then determining the amount of all analyte ions eluted with nitric acid. Table 2 shows the feasibility of determination of the sample with different analyte concentration levels. However, it should be pointed out that the larger amount of the sample solution, the more time (for passing it through solid phase) was required in the procedure. To trade off the enrichment factor and analytical time, \sim 2000 mL of sample and 4.5 mL of HNO₃ were used; therefore, an enrichment factor of 444.4 was obtained. In order to study the effect of sample flow rate, 50 mL portions of sample solution were passed through the column at different flow rates. The percent retention of the target ions as a function of sample flow rate is shown in Figure 4. As can be seen

the percent retention decreased with increase in flow rate, which is due to the shorter contact time between the adsorbent and the metal ions and subsequently the decrease in complex formation. Therefore, a flow rate of 2 mL min⁻¹ was chosen to compromise between the analytical time and the quantitative adsorption.

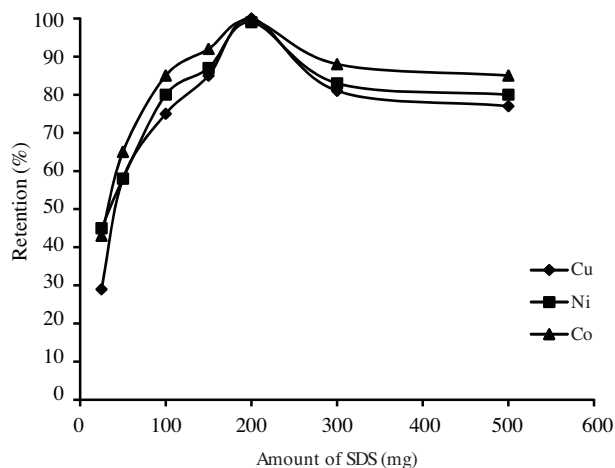


Figure 2. Effect of amount of SDS on the retention of metal ions (N=3).

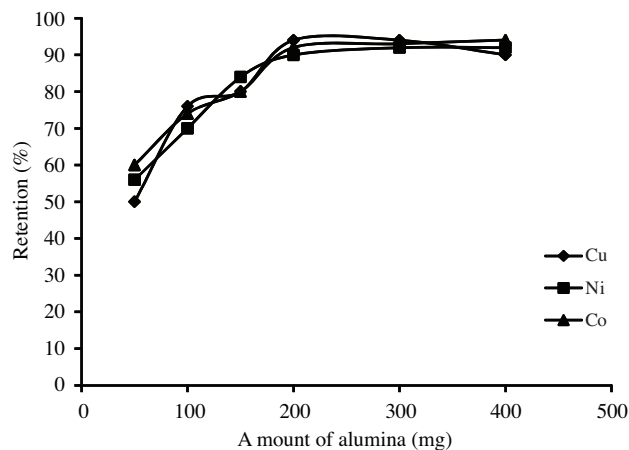


Figure 3. Effects amount of Al₂O₃ on the retention of examined metal ions

Table 2. Effect of sample volume on the retention of the examined metal ions (N = 3).

Sample volume (mL)	Cu (%R*)	Ni (%R)	Co (%R)
25	97.1 ± 1.1	95.6 ± 2.1	91.3 ± 2.0
50	97.4 ± 2.0	94.4 ± 1.3	89.6 ± 1.0
100	98.5 ± 2.0	95.0 ± 1.0	96.5 ± 3.1
250	98.3 ± 2.1	96.6 ± 1.0	88.2 ± 1.0
500	97.8 ± 1.2	94.7 ± 1.2	90.3 ± 1.3
1000	95.1 ± 1.1	95.5 ± 1.1	91.6 ± 2.2
2000	90.2 ± 1.2	87.2 ± 3.0	81.4 ± 2.0

*Percent of retention.

Effect of foreign ions

To assess the possible applications of the procedure, the effect of foreign ions that may interfere with the determination of Cu, Ni, and Co ions by the presented method and/or often coexisting in various real samples was examined with the optimized conditions presented above. A fixed amount of analytes was taken with different amounts of foreign ions and the recommended procedure was followed. The recoveries of analytes were higher than 95%. Tolerable limit was defined as the highest amount of foreign ions that produced an error not exceeding 5% in the determination of investigated analyte ions by the combination of the SDS coated alumina solid phase extraction procedure and the flame atomic absorption spectrometric determination methods. The results are summarized in Table 3. As can be seen, large numbers of ions used have no significant effect on the determination of analyte ions.

Table 3. Effects of the interference of diverse ions on the recoveries of the examined metal ions (N = 3).

Ion ^a	Tolerable limit	Recovery (%)		
		Cu	Ni	Co
Na ⁺ , K ⁺ , Ca ²⁺ , Mg ²⁺ , Ba ²⁺	> 1000	95.8	94.2	92.4
Fe ²⁺	200	95.5	94.8	91.5
Mn ²⁺	250	96.5	94.0	92.0
Cd ²⁺ , Pb ²⁺	100	94.4	94.7	91.7
Ni ²⁺	1	92.3	-	85.0
Zn ²⁺	100	95.0	93.7	91.7
Co ²⁺	1	92.2	93.6	-
NO ₃ ⁻ , Cl ⁻ , SO ₄ ²⁻	500	94.2	94.7	92.5
Br ⁻	1000	94.6	94.5	91.2
Cu	1	-	94.4	93.8

^aAll values of RSD are between 2.0% and 4.5%

Adsorption capacity

Adsorption capacity is an important factor to evaluate the sorbent, because it determines how much modified SDS coated alumina is required for a given solution. The adsorption capacity of the solid phase was studied. The adsorption capacity calculated for Cu, Ni, and Co was 2.41, 2.28, and 2.19 $\mu\text{g mg}^{-1}$, respectively.

Figures of merit

The sensitivity of the developed method is reflected by the limit of detection (LOD) studies, defined as the lowest concentration of metal ions below which quantitative sorption of the metal ion by basic alumina is not perceptibly seen. The limits of detection (LOD) of the present work were calculated under optimal experimental conditions after application of the pre-concentration procedure to blank solutions. The limits of detection (LOD) of the proposed method for the determination of investigated elements were studied under the optimal experimental conditions. The limits of detection based on 3 times the standard deviations of the blank ($N = 7$, $X_L = X_b + 3s$, where LOD is the limit of detection and X_b is the blank value) for copper, nickel, and cobalt ions were found to be 1.77, 1.83, and 1.93 mg L^{-1} , respectively. The precision of the determination of Cu, Ni, and Co was evaluated using model solutions containing 100 ng mL^{-1} of metal ions under the optimum conditions mentioned above. For this purpose, the procedure was repeated 7 times for ions. The sample volume was maintained at 100 mL. The relative standard deviation of the method was found to be below 3% (Table 4).

Table 4. Specification of presented method at optimum conditions for each element.

Parameter	Cu	Ni	Co
Linear range (ng mL^{-1})	5.0-2500.0	5.0-1500.0	5.0-1000.0
Limit of detection (ng mL^{-1})	1.77	1.83	1.93
Loading capacity (mg g^{-1})	2.41	2.28	2.19
RSD (%)	1.80	1.50	1.70
Retention (%)	98.7	96.2	95.0

Application to environmental samples

We have explored the feasibility of the methodology given in Section 2 using pre-concentration with SDS coated alumina for the determination of Cu, Ni, and Co in water samples (Zanjan city, Iran) by the standard addition method. The results for this study are presented in Table 5 for water samples. The recovery of spiked samples is satisfactory and was confirmed using the addition method, which indicates the capability of the system in the determination of Cu, Ni, and Co. A good agreement was obtained between the added and measured analyte amounts. The recovery values calculated for the added standards were always higher than 96%, thus confirming the accuracy of the procedure and its independence from the matrix effects. In order to establish the validity of the proposed procedure, the method has been applied to the determination of the content of the studied element in a standard reference material (GBW07602, Bush Twigs and Leaves). Portions (0.5 g) of GBW07602 Bush Twigs and Leaves were transferred into beakers, 10 mL of concentrated HNO₃ and 3 mL of H₂O₂ were added, heated until the solution became transparent, continuously heated to near dryness, and the residue dissolved in 0.1 mol L⁻¹ HCl. After adjustment of the pH to 9.0, the solution was made up to 50 mL with distilled water. The content of the studied elements was determined according to the recommended procedure. The results are presented in Table 6. As can be seen, the results are in agreement with the reference values.

Table 5. Levels of analyte ions in tap water, mineral water, and rainwater samples (N = 3).

^a Ions	Added	Tap water			Mineral water			Rainwater		
		found	RSD (%)	Recovery	found	RSD (%)	Recovery	found	RSD (%)	Recovery
Cu	0	8.5	0.8	n.d. ^b	8	0.5
	10	18.7	0.5	101.0	11.5	0.4	115.0	19.2	0.9	106.6
	20	27.4	0.6	96.1	21.1	0.2	105.5	28.5	0.1	101.7
Co	0	6.3	0.4	n.d.	3.4	0.5
	10	16.7	0.5	102.4	10.8	0.7	108.0	12.8	0.2	95.6
	20	27.2	0.1	103.7	21.5	0.6	107.5	24.0	0.2	102.5
Ni	0	6.6	0.5	n.d.	5.5	0.5
	10	16.4	0.4	98.8	11.1	0.5	111.0	15.2	0.7	98.0
	20	27.5	0.9	103.3	21.5	0.6	107.5	25.8	0.7	101.1

^bn.d.: Not detected

^aAll values are in ng mL⁻¹

Table 6. The analytical results of standard reference material (GBW07602) (mg g⁻¹).

Element	Found ^a	Reference value
Cu	0.15 ± 0.05	0.14 ± 0.01
Ni	1.5 ± 0.2	1.7 ± 0.3
Co	40 ± 3	38 ± 2

^aThe value following "±" is the standard deviation (n = 3).

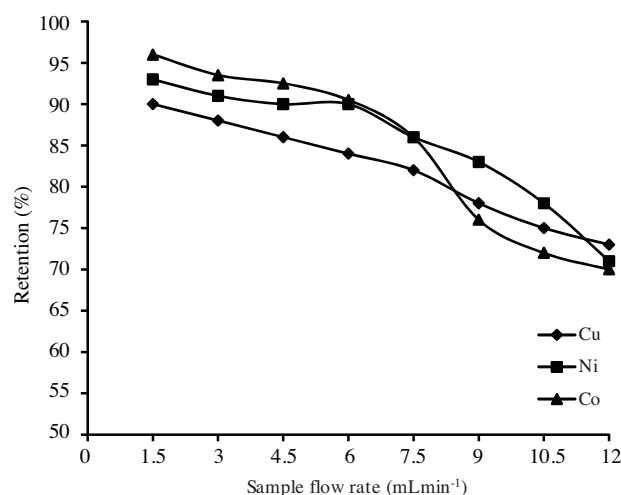


Figure 4. Effect sample flow rate on the retention of examined metal ions

Conclusions

In the presented study, a new solid phase extraction technique was developed based on the pre-concentration of copper, nickel, and cobalt on SDS coated alumina prior to the determination by FAAS. Under conditions given in Table 4, the determination of copper, nickel, and cobalt yields quantitative recoveries. Conditions for quantitative and reproducible pre-concentration, elution, and FAAS determinations were studied. The method is simple, accurate, and economical and can be applied for the determination of copper, nickel, and cobalt in environmental samples. The system showed reproducibility and reliability in analytical data, with an RSD value of lower than 3% in 7 experiments. Moreover, 0.2 g of SDS coated alumina can be used in as many as 12 experiments without any loss in its sorption behavior. The system was successful in pre-concentration of analytes from large sample volumes (~ 2000 mL).

Acknowledgement

The authors express their appreciation to the Graduate School and Research Council of Zanjan University for its financial support of this work.

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