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Air-assisted Liquid Liquid Microextraction Combined with Graphite Furnace Atomic Absorption Spectrometry for Preconcentration and Determination of Trace Amount of Co(II) and Ni(II) Ions in Water Samples

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A simple, rapid and efficient method has been developed for the extraction, preconcentration and determination of cobalt(II) and nickel(II) ions in water samples by air-assisted liquid-liquid microextraction (AALLME) coupled with graphite furnace atomic absorption spectrometry (GFAAS). In the proposed method, much less volume of an organic solvent was used as the extraction solvent in the absence of disperser solvent. Fine organic droplets were formed by sucking and injecting of the mixture of aqueous sample solution and extraction solvent with a syringe for several times in a conical test tube. After extraction, phase separation was performed by centrifugation and the enriched analytes in the sedimented phase were determined by GFAAS. Several variables that could affect the extraction efficiency were investigated and optimized. Calibration graphs were linear in the range of 6.5-100 ng l⁻¹. Detection limits for Co and Ni were 2.3 ng l⁻¹ and 3 ng l⁻¹, respectively. The accuracy of the developed procedure was checked by analyzing NRCC-SLRS4 Riverine water as a certified reference material. Finally, the proposed method was successfully applied for the determination of cobalt(II) and nickel(II) ions in tap, surface and river water samples.

Keywords: Air-assisted liquid-liquid microextraction, Cobalt, Graphite furnace atomic absorption spectrometry, Nickel, Water samples

INTRODUCTION

Trace metals are widely spread in environment and may enter the food chain from the environment. Some trace metals are essential elements and play an important role in human metabolism. On the other hand, at high concentrations all metals are recognized as potentially toxic [1]. The toxicity of cobalt is relatively low and it is considered as an essential element, which is required in the normal human diet in the form of vitamin B12 (cyanocobalamin). For this reason, cobalt has been used in the treatment of anemia [2]. However, the ingestion of large doses of cobalt may lead toxic effects [3,4]. High levels of cobalt may affect several health troubles such as paralysis, diarrhea, low blood pressure, lung irritation and bone

defects [5]. Since one of the routes of incorporation of cobalt into the human body is by ingestion [6], its determination in water would be of particular importance. The maximum admissible limit of cobalt in drinking water is not mentioned by world health organization (WHO, 2008), however, it has been reported 100 µg l⁻¹ by United States environmental protection agency (USEPA, 2008) [7]. The toxic effects of nickel are well known and it is also considered as one of the most common causes of allergic contact dermatitis and respiratory system diseases [8-10]. The maximum admissible limit of nickel in drinking water is 70 µg l⁻¹ (WHO, 2008) [11]. In spite of great improvements in the sensitivity and selectivity of modern instrumental analysis such as inductively coupled plasma mass spectrometry (ICP-MS), inductively coupled plasma optical emission spectrometry (ICP-OES) and graphite furnace atomic absorption spectrometry (GFAAS),

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difficulties still lie in the analysis of trace heavy metals because of their low abundance levels in the samples as well as the high complexity of the sample matrices [12]. Thus, extraction and preconcentration procedures are required for elimination or minimization of matrix effects and concomitants, lowering the detection limit of many metals with different techniques and enhancing the detect ability for many metals [13]. Several sample preparation methods have been developed for the determination of trace cobalt and nickel from various sample matrices, including liquid-liquid extraction (LLE) [14], co-precipitation [15], cloud point extraction (CPE) [16,17] and solid phase extraction (SPE) [18-20]. Nevertheless, these methods are time-consuming, tedious and often require large amounts of samples and toxic organic solvents. Recently, much attention is being paid to the development of miniaturized, more efficient and environmentally friendly extraction techniques which could greatly reduce the organic solvent consumption [21]. Therefore, liquid phase microextraction (LPME) methods [22] such as single drop microextraction (SDME) [23], hollow fiber liquid-phase microextraction (HF-LPME) [24] and dispersive liquid-liquid microextraction (DLLME) [25-27] have been developed for the extraction and preconcentration of heavy metals. DLLME is a sample preparation technique introduced by Assadi and co-workers [28]. It is a simple and fast microextraction technique. In this extraction method, the very large surface area between the fine droplets of an extraction solvent and an aqueous sample is achievable, and the accordingly fast extraction kinetic that results in the rapid achieving of a state of equilibrium; and the high enrichment factors are usually obtained [29,30]. This method has been applied for the determination of trace metallic ions in the environmental samples [31-33]. In the conventional DLLME, the extraction solvent is dispersed into the aqueous sample solution with the aid of a disperser solvent. The presence of a disperser solvent in aqueous sample solution makes it relatively non-polar leading to increase solubility of the target lipophilic analytes into aqueous sample solution, and consequently relatively low extraction efficiency. Farajzadeh *et al.* reported a new LPME method in which air was used to assist in dispersion of the extraction solvent into aqueous sample [34] and called air-assisted liquid-liquid microextraction method

(AALLME).

The present work describes the development of AALLME for the extraction and preconcentration cobalt and nickel in water samples. In the proposed method, a few microliters of an extraction solvent is transferred into aqueous sample solution, and then the mixture is repeatedly sucked into a glass syringe, and then injected into a tube to achieve a cloudy solutions resulted in dispersion of the extraction solvent into aqueous solutions. After centrifuging the cloudy solution, the extractant is settled down in the bottom of the centrifuge tube and used for GFAAS analysis. Compared to DLLME, it is a disperser solvent-free technique.

EXPERIMENT

Reagents and Solutions

Mix stock standard solution of Co(II) and Ni(II) (10 mg l^{-1}) was prepared from analytical reagent grade $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Merck, Darmstadt, Germany) by dissolving an appropriate amount of each salt in double deionized water. Working solution (20 ng l^{-1}) was prepared daily by diluting the mix stock solution with deionized water (Ghazi Company, Tabriz, Iran). Aqueous standard solutions used to construct calibration graphs were obtained by diluting the mix stock standard solution. A mix standard solution with a concentration of $15 \text{ } \mu\text{g l}^{-1}$ was also prepared and injected into GFAAS each day (three times) for quality control and the obtained signal was also used to calculate enrichment factors (EFs) and extraction recoveries (ERs) of the analytes. Sodium phosphate monobasic (NaH_2PO_4), sodium phosphate dibasic (Na_2HPO_4), ammonium chloride, ammonia, acetone, methanol and sodium chloride were also purchased from Merck. Sodium dimethyldithiocarbamate (SDDTC) was purchased from Fluka. The tested extraction solvents were obtained from the following sources: Chloroform, carbon tetrachloride, and 1,2-dibromoethane (1,2-DBE) were from Merck, and 1,1,2-trichloroethane (1,1,2-TCE) was from Janssen Chimica (Belgium).

Real Samples

Tap water was collected from our laboratory just before analysis. Surface water was picked up from local area

Table 1. Instrument Settings and Furnace Programs for Analysis of Co and Ni by GFAAS

Conditions	Co	Ni
Wavelength (nm)	242.5	232.0
Lamp current (mA)	20	25
Ar flow (ml min ⁻¹)	250	250
Injection volume (μl)	10	10
Heating program temperature °C [ramp time (s), hold time (s)]		
Drying 1	110 (2, 20)	110 (2, 20)
Drying 2	130 (5, 20)	130 (5, 20)
Pyrolysis	1300 (10, 10)	1100 (10, 10)
Atomization	2300 (0, 5)	2200 (0, 5)
Cleaning	2800(1, 3)	2700 (1, 3)

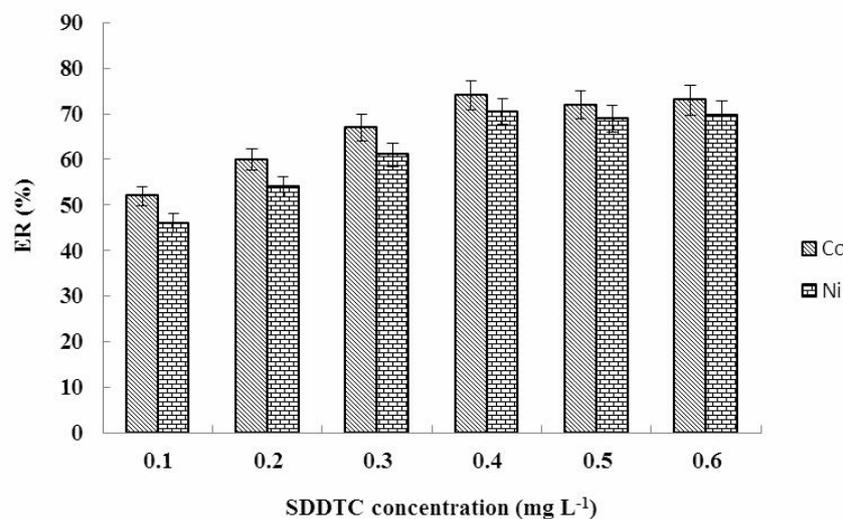


Fig. 1. The influence of SDDTC concentration on the extraction recovery of Co²⁺ and Ni²⁺. Extraction conditions: sample, 5 ml deionized water containing 20 ng l⁻¹ of Co²⁺ and 20 ng l⁻¹ of Ni²⁺; extraction solvent; 1,2-DBE (40 μl); extraction numbers, 6 times; centrifuge rate, 5000 rpm; and centrifuge time, 5 min. The error bars represents standard deviations (n = 3).

(Tabriz, Iran). River water was collected from Mehranrood River (Tabriz, Iran). They were directly subjected to the extraction by the proposed AALLME method.

Instrumentation

The measurements were performed with a Shimadzu 6800 atomic absorption spectrometer (Japan) equipped with

a heated graphite tube atomizer. The instrument settings and furnace programs for determination the extracted amount of each element are described in Table 1. An ASC 6100 autosampler (Shimadzu, Japan) was used to deliver standard solutions and samples from the cup to the graphite tube. The Hettich centrifuge, model D-7200 (Germany), was used for acceleration of phase separation.

AALLME Procedure

A 5.0 ml of mix standard solution of Co^{2+} and Ni^{2+} (20 ng l^{-1}) or real sample with pH 8 (adjusted by 100 mM phosphate buffer) was poured into a 10-ml glass centrifuge tube with conical bottom. 1,2-DBE (40 μl) as extraction solvent and 4% (w/v) NaCl were added to the above solution. The mixture was sucked into a 10-ml glass syringe, and then injected into the tube for seven times via the syringe needle. The mixture was centrifuged at 6000 rpm for 4 min. The extraction solvent droplets were sedimented at the bottom of the conical test tube and its volume was measured using a 50- μl microsyringe (zero dead volume, Hamilton, Switzerland). It was $27 \pm 1 \mu\text{l}$. To investigate the extraction amount of the analytes, two 10- μl aliquots of the settled phase were removed and separately injected into GFAAS.

Calculation of EF and ER

EF is defined as the ratio between the analyte concentration in the sedimented phase (C_{sed}) and the initial concentration of analyte (C_0) in the sample:

$$EF = C_{\text{sed}}/C_0 \quad (1)$$

C_{sed} is obtained from a calibration graph. ER is defined as the percentage of the total analyte amount (n_0) which is extracted to the sedimented phase (n_{sed}),

$$ER = \frac{n_{\text{sed}}}{n_0} \times 100 = \frac{C_{\text{sed}} \times V_{\text{sed}}}{C_0 \times V_{\text{aq}}} \times 100 = EF \times \frac{V_{\text{sed}}}{V_{\text{aq}}} \times 100 \quad (2)$$

where V_{sed} and V_{aq} are the volumes of sedimented phase and aqueous solution, respectively.

RESULTS AND DISCUSSION

The parameters being effective on the extraction process, namely, amount of chelating agent, nature and level of extraction solvent, extraction numbers, salting out effect, sample volume, pH, centrifuge rate and time and coexisting ions were investigated and optimized.

Effect of the Concentration of SDDTC

SDDTC is a suitable chelating reagent that can react with many metallic ions, and form stable complexes. The amount of SDDTC can markedly effect on the extraction efficiency. Therefore, different concentrations of SDDTC ($0.1\text{-}0.6 \text{ mg l}^{-1}$) were investigated and the results are shown in Fig. 1. According to the results, ER increased up to 0.4 mg l^{-1} , and then it reached a plateau and no considerable difference was observed beyond that, so it was selected as the optimum concentration.

Effect of Type and Volume of the Extraction Solvent

The selection of an appropriate extraction solvent is of great importance for the optimization of an AALLME process. The extraction solvent has to fulfill some requirements: heavier or lighter than water, low volatility and solubility in water and high extraction efficiency toward the analytes. For this purpose, several extracting solvents including chloroform, carbon tetrachloride, 1,2-DBE and 1,1,2-TCE were investigated. To achieve the same volume of precipitated phase ($27 \pm 1 \mu\text{l}$), different volumes of the selected extraction solvents were used. The obtained volumes were 57, 55, 40 and 50 for chloroform, carbon tetrachloride, 1,2-DBE, and 1,1,2-TCE, respectively. The results in Fig. 2A showed that the best extraction efficiency for the target analytes is obtained when 1,2-DBE is used as the extraction solvent. In a microextraction procedure, the volume of extraction solvent is also a crucial parameter that has an important effect on the analytical signals. To evaluate the effect of extraction solvent volume on the extraction performance, different volumes of 1,2-DBE (40 to 60 μl) were tested. Analytical signals decreased by increasing volume of 1,2-DBE due to dilution effect. However, as shown in Fig. 2B, ERs of the analytes remain the same for various extractant volumes in the range of 40-

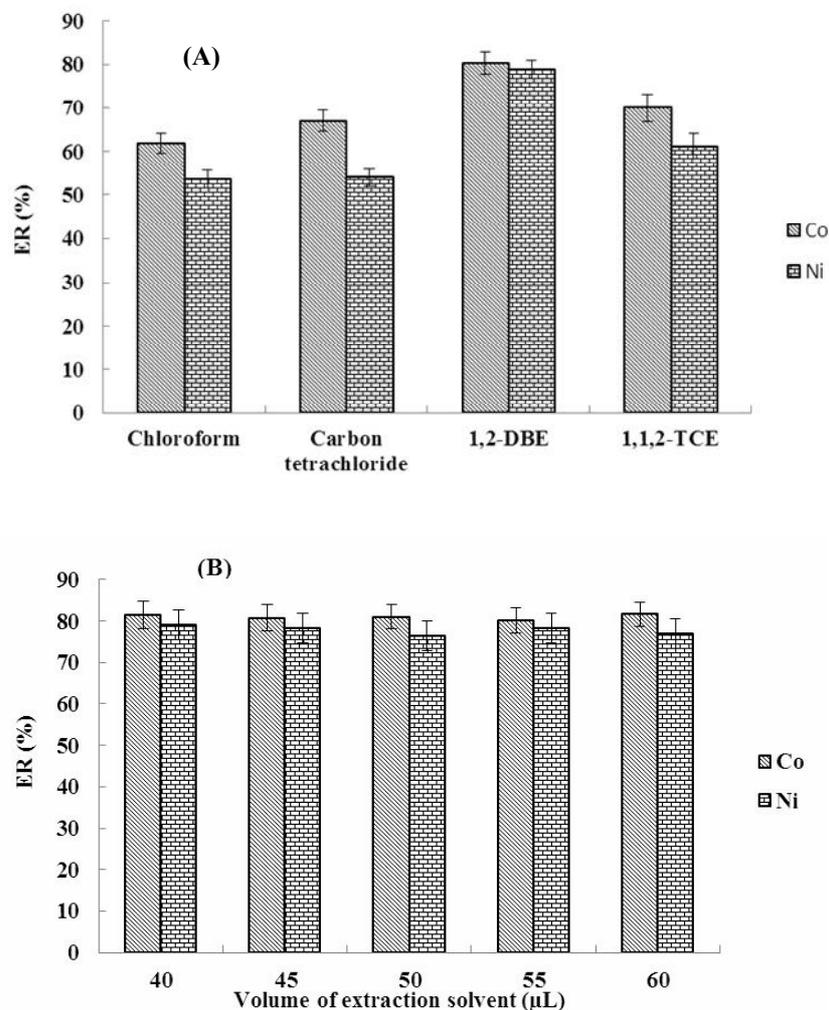


Fig. 2. A) Effect of the chemical identity of extraction solvent in ERs of the selected elements. Extraction conditions: SDDTC concentration, 0.4 mg l^{-1} ; and other experimental conditions were as given as for Fig. 1. B) Effect of extraction solvent (1,2-DBE) volume on the analytical signals of Co^{2+} and Ni^{2+} . Extraction conditions: the same as used in Fig. A. The error bars represents standard deviations ($n = 3$).

60 μl .

It is noted that, based on Eq. (3), by increasing V_{org} while V_{aq} is constant, ER % should be increased.

$$ER\% = \frac{D}{D + \frac{V_{\text{aq}}}{V_{\text{org}}}} \quad (3)$$

[D: partition coefficient of the analyte; V_{aq} : volume of aqueous phase; V_{org} : volume of organic phase]

However, when D is very high with respect to V_{org} , increasing V_{org} does not affect the ER%. It was observed that by increasing volume of the extraction solvent from 40 to 60 μl , volume of the sedimented phase increases from 27 to 42 μl . Therefore, use of low volume of the extractant leads to high EFs and low detection limits. In the case of $<40 \mu\text{l}$ of 1,2-DBE, the volume of sedimented phase was less than 27 μl , by which the analysis of analytes was impossible (10 μl was required for analysis of each analyte).

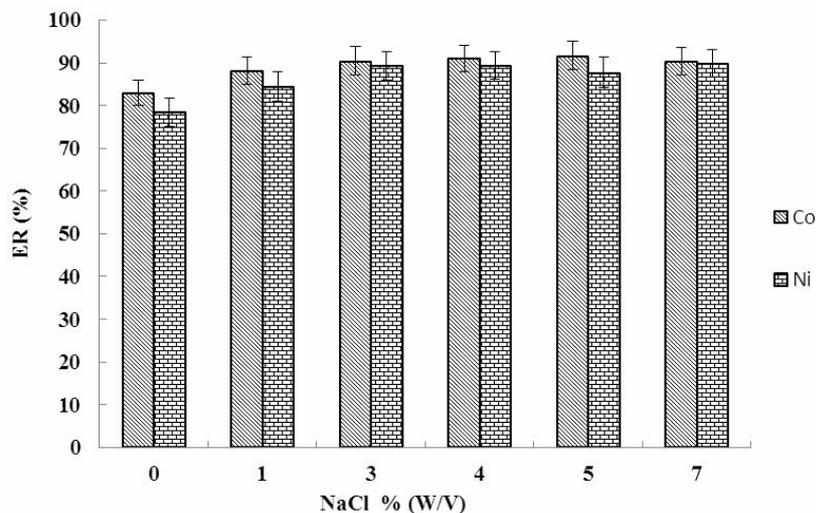


Fig. 3. Effect of NaCl addition on the ERs of Co^{2+} and Ni^{2+} . 1,2-DBE volume was selected different in the presence of various concentrations of NaCl in order to reach a constant volume of the sedimented phase (27 μl). Extraction conditions are the same as used in Fig. 2. The error bars represent standard deviations ($n = 3$).

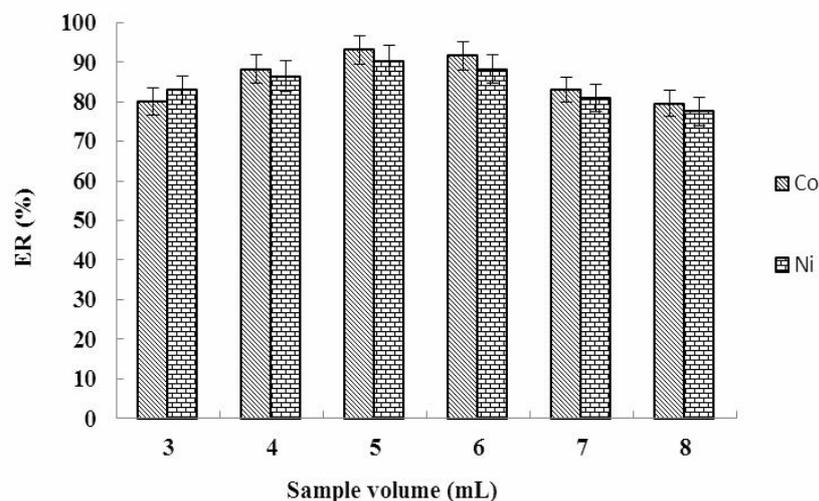


Fig. 4. Effects of sample volume on the ER of Co^{2+} and Ni^{2+} . Extraction conditions: NaCl, 4% (w/v); and other conditions are the same as used in Fig. 3. The error bars represent standard deviations ($n = 3$).

Thereby, 40 μl of 1,2-DBE was used as the extraction solvent in the subsequent experiments to obtain 27 μl sedimented phase volume.

Effect of Salt Addition

In most cases, addition of a salt plays an important role

in the conventional extraction procedures. By increasing ionic strength of aqueous sample, solubility of organic compounds in the aqueous phase is decreased and more analyte molecules are transferred into the organic phase. So, ER is often increased in the presence of a salt. The experiments were performed using different volumes of

extraction solvent to achieve 27 μl of the sedimented phase volume (40, 40, 37, 34, 32 and 30 μl for 0, 1, 3, 4, 5 and 7%, w/v, NaCl concentration, respectively), while other experimental parameters were constant. The extraction efficiencies relating to the extracted amount of the analyte against NaCl concentration are presented in Fig. 3. The results showed that with increasing the concentration of NaCl up to 4%, ER increased and then reached a plateau after that. Regarding the extraction efficiency increasing with NaCl concentration, the salting-out effect is thought to be responsible. Therefore, 4% (w/v) NaCl was used to ensure obtaining analyte responses at the highest possible level. Addition of salt increases the ionic strength of the samples and makes complexes (Co/Ni-SDDTC) less soluble and forces it to migrate into the organic phase. Therefore, 4% (w/v) NaCl concentration was chosen as the optimum salt concentration for the further experiments.

Effect of Sample Solution Volume

To investigate the effect of sample solution volume on the extraction efficiency, it was investigated in the range of 3-8 ml. The results are shown in Fig. 4. They proved that analytical signals increase by increasing the sample volume up to 5 ml, and then decrease at higher volumes. This is due to the increase in EF of the analytes in the extract. However, more increasing of sample size is not reasonable, because it prevents the formation of organic phase drops. The volume of sedimented phase also decreased from 34 to 15 μl by increasing the volume of aqueous phase from 3 to 8 ml. To obtain high ER, 5 ml was selected for the future studies.

Effect of Sample Solution pH

Extraction of metallic ions by AALLME involves prior complex formation with sufficient hydrophobicity to be extracted into the small volume of the extraction solvent. The pH of aqueous phase is one of the most important factors in extraction of metallic ions from various media in terms of formation of the related complexes. The influence of the pH on the ER of cobalt and nickel ions was investigated in the pH range of 2.0-12.0 while the other experimental conditions were kept constant. The results are depicted in Fig. 5. At low value of pH, the extraction efficiency of the analytes is low. It may be attributed to the interaction of SDDTC with hydronium ions rather than with

the analytes. ER increased with increasing solution pH from 2.0 to 8.0 and was effective in pHs 8.0 and 9.0. Further increasing pH of aqueous solution led to decrease in ER of the analytes probably due to hydrolysis of Co^{2+} and Ni^{2+} . Therefore, the further works were performed for microextraction at pH 8.0.

Optimization of the Number of Extractions

In this study, the number of extractions is defined as the number of repeatedly sucking extraction solvent and sample solution mixture into a 10-ml glass syringe, and then its injecting into the test tube. Therefore, to reach the equilibrium status, the number of extractions was studied in the range of 4-9 times. The results in Fig. 6 show that by increasing the extraction numbers, ER is also increased till 7th extraction, and then remains almost constant. Hence, 7 times of extraction was selected as the optimum for the further studies.

Optimization of Centrifuging Rate and Time

Other parameters that may affect on the extraction efficiency are centrifuging rate and time. They were studied in the ranges of 1000-8000 rpm and 2-8 min, respectively. Therefore, two series of experiments were carried out. In one set of experiments a constant centrifugation time (5 min) was selected while its speed varied in the range of 1000-8000 rpm. Another set of experiments were performed at a constant centrifugation speed (6000 rpm) while the run time varied (2-8 min). According to the results, 6000 rpm and 4 min were selected as the centrifuge rate and time, respectively.

Effect of Coexisting Ions

The effect of common coexisting ions in natural water samples on the ER of cobalt and nickel was also studied. In these experiments, 5.0 ml of solution containing 20 ng l^{-1} of the analytes and various amounts of interfering ions was treated according to the recommended procedure. A given species was considered to interfere if it resulted in a $\pm 5\%$ variation in the absorbance signal. The tolerable concentration ratios of the interfering ions to the analytes were found to be as follows: 1000 for Ba^{2+} , Cd^{2+} , Al^{3+} , CH_3COO^- and NO_3^- ; 500 for Zn^{2+} and Mg^{2+} ; 5 for Cu^{2+} and Fe^{3+} .

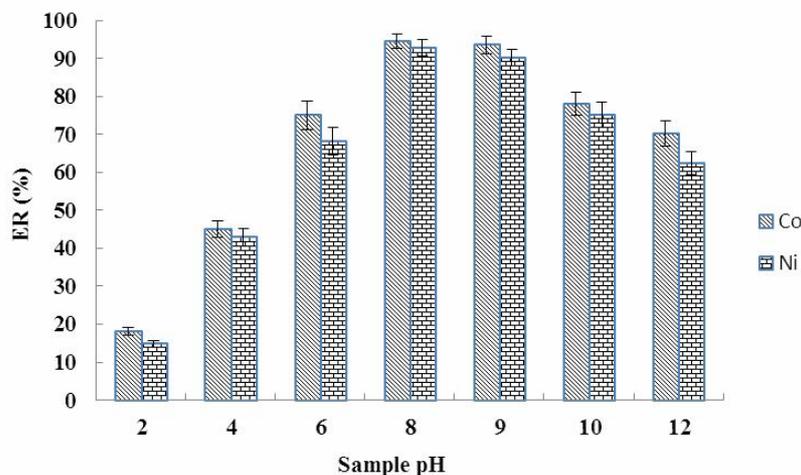


Fig. 5. Effect of sample pH on the enrichment performances. The conditions are the same as used in Fig. 4. The error bars represent standard deviations ($n = 3$).

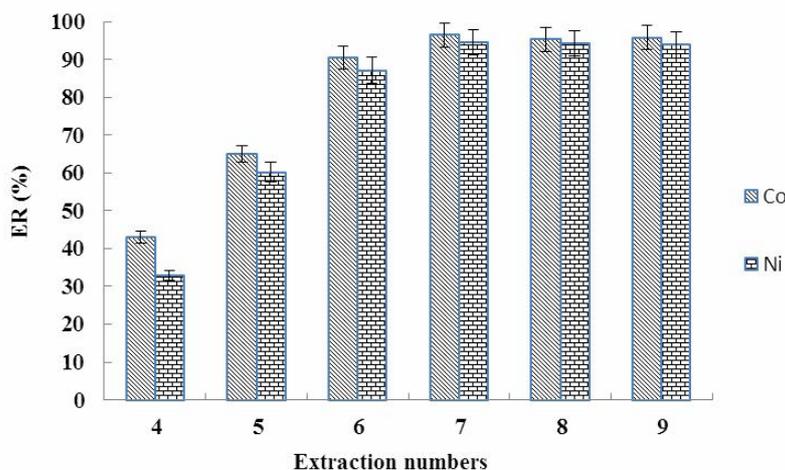


Fig. 6. Effect of extraction numbers on the ERs of Co^{2+} and Ni^{2+} . Extraction conditions: sample pH, 8.0; other conditions are the same as used in Fig. 5. The error bars represent standard deviations ($n = 3$).

Analytical Figures of Merit

Under the optimized conditions, quantitative characteristics, namely linear range (LR), squared correlation coefficient (r^2), precision, limit of determination (LOD) and limit of quantification (LOQ) of the analytes were evaluated, and are summarized in Table 2. The LODs were calculated by progressively reducing the concentration of analytes until the response had a peak height three times as large as the average noise around the peaks and the

values obtained for Co and Ni were 2.3 ng l^{-1} and 3 ng l^{-1} . To evaluate repeatability of the method, extractions were carried out on the six separate solutions at a concentration of 20 ng l^{-1} . High EFs, low LODs and LOQs are the main advantages of the proposed method. The accuracy of the proposed method was assessed with the measurement of the analytes in NRCC-SLRS-4 Riverine water as certified reference material. For analysis of Ni, the certified reference material was diluted till 10-fold, and then adjusted to the

Table 2. Quantitative Characteristic of the Proposed AALLME-GFAAS for the Analysis of Co and Ni

Analyte	Calibration curve equation	LR ^a (ng l ⁻¹)	r ^{2,b}	LOD ^c (ng l ⁻¹)	LOQ ^d (ng l ⁻¹)	RSD		ER±SD ^f	EF±SD ^g
						(%) ^e			
						Intra-day	Inter-days		
Cobalt	Y=0.0118X-0.0072	6.50-100	0.996	2.30	6.50	3.4	4.3	96±2	171±7
Nickel	Y=0.0112X+0.0049	8.50-100	0.995	3.00	8.50	3.9	4.9	94±3	168±8

^aLinear range. ^bSquare of correlation coefficient. ^cLimit of detection, S/N = 3. ^dLimit of quantification, S/N = 10. ^eRelative standard deviation (C = 20 ng l⁻¹, n = 6) for intra-day and (C = 20 ng l⁻¹, n = 4) for inter-days. ^fExtraction recovery ± standard deviation (n = 3). ^gEnrichment factor ± standard deviation (n = 3).

Table 3. Analysis of the Certified Water Reference Material (SLRS-4) for the Determination of the Selected Elements with Proposed AALLME-GFAAS Procedure

Element	Certified value (ng l ⁻¹)	Found (ng l ⁻¹)
	±SD (n = 3)	±SD (n = 3)
Cobalt	33±8	36.4±2.0
Nickel	670±80	622.2±32.3

proposed procedure. The certified and observed values were given in Table 3. It was found that the analyzed results were in a good agreement with the certified values.

Application of the Proposed Method to Analyze the Real Samples

To demonstrate the performance of the present method, it was utilized to determine cobalt and nickel concentrations in different real water samples. The results are listed in Table 4. Recovery studies were also carried out after the samples were spiked with known concentrations of the analytes at levels of 20 and 40 ng l⁻¹. The recovery values calculated for the added concentration were ranged from 90 to 97%, confirming the accuracy of the procedure and its independence from the matrix effects.

Comparison of the Proposed Method with other Methods

Table 5 summarizes the analytical characteristics of some other analytical methods along with those of the proposed AALLME-GFAAS method for the extraction and determination of Co²⁺ and Ni²⁺ in different real samples. Most of the analytical characteristics of the proposed method were good and comparable with those of the other reported methods. LODs and LOQs for the proposed method are lower than those of all mentioned methods. The repeatability of the method is good and RSD for the proposed method is lower than those of the others. This method has the higher EFs when compared with other methods of sample preparation in screening selected heavy metals in aqueous samples. These results reveal that the

Table 4. Results of Assays to Check the Samples Matrices Effect for the Cobalt and Nickel and Concentrations of the Detected Analytes

Analyte	Spiked amount (ng l ⁻¹)	Tap water		Surface water		River water	
		Found (ng l ⁻¹) ± SD (n = 3)	Recovery ± SD (n = 3)	Found (ng l ⁻¹) ± SD (n = 3)	Recovery ± SD (n = 3)	Found (ng l ⁻¹) ± SD (n = 3)	Recovery ± SD (n = 3)
Co	0	N.D.	-	10.5±0.4	-	7.1±0.3	-
	20	19.0±0.8	95±3	29.3±1.3	94±3	25.5±1.2	92±2
	40	38.8±1.7	97±3	48.5±2.1	95±2	44.3±2.1	93±3
Ni	0	N.D.	-	27.5±1.4	-	10.9±0.6	-
	20	18.8±0.8	94±3	45.9±2.2	92±2	28.9±1.5	90±3
	40	38.8±1.8	97±3	64.7±3.0	93±3	47.7±2.3	92±3

presented technique is sensitive, simple, rapid, and repeatable and can be used for the preconcentration of the heavy metal residues from aqueous samples.

CONCLUSIONS

In this study, a developed microextraction technique, namely AALLME, coupled with GFAAS was used for preconcentration and determination of cobalt and nickel in aqueous samples. The method is rapid, precise, efficient, and sensitive. In the proposed method, much less volume of an organic solvent was used as the extraction solvent in the absence of disperser solvent. Finally the proposed method was successfully applied in the determination of the target analytes in different real aqueous samples. The results indicated that this extraction procedure is noticeable due to its outstanding advantages, including minimum organic solvent consumption, simplicity, low cost, rapidness, high efficiency, high EF and environmentally friendly.

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Table 5. Comparison of the Proposed AALLME-GFAAS Method with other Methods Used in Pre-concentration and Determination of Co^{2+} and Ni^{2+}

Method	LR ($\mu\text{g l}^{-1}$)	LOD ($\mu\text{g l}^{-1}$)	LOQ ($\mu\text{g l}^{-1}$)	RSD (%)	EF	Ref.
SPE-HPLC ^a	0.1-100	0.04-0.05		6.21-9.14	200	[20]
DLLME-ICP-OES ^b	-	0.2	0.7	0.7-1.1	8-11	[26]
DLLME-SFO ^c -ICP-OES	1.2-250	0.2	-	3.4	76	[35]
SM-DLLME-FAAS ^d	10-280	4.2	-	2.1	58	[36]
IL-DLLME-FAAS ^e	6-500	4.4		3.1	51	[37]
HA-PUF ^f -FAAS	1.3-75	0.4	1.3	-	36	[38]
		$\mu\text{g g}^{-1}$	$\mu\text{g g}^{-1}$			
CPE ^g -FAAS	0-280	1.09-1.22	-	2.53-2.89	27	[17]
DLPME ^h -GFAAS	-	0.021-0.033		7.5-8.2	101-200	[39]
Emulsion-GFAAS	-	0.32	-	3.7	-	[40]
DLLME-FAAS	3-10	0.9	3	-	16	[41]
LL-USAEME-ICP-OES ⁱ	0.50-1000	0.13-0.28	-	3.4-6.1	18.3- 18.8	[42]
USAEME-FAAS ^j	-	0.23	0.77	2.3-4.1	190	[43]
AALLME-GFAAS	0.005-0.2	0.0016	0.005	2.9	274	This work

^aSolid phase extraction-high performance liquid chromatography. ^bDispersive liquid-liquid microextraction-inductively coupled plasma - optical emission spectrometry. ^cDispersive liquid-liquid microextraction based on the solidification of floating organic drop. ^dSupramolecular-based dispersive liquid-liquid microextraction-flame atomic absorption spectrometry. ^eIonic liquid-dispersive liquid-liquid microextraction-flame atomic absorption spectrometry. ^fHydroxyacetophenone-polyurethane foam. ^gCloud point extraction. ^hDispersive liquid phase microextraction. ⁱLigandless-ultrasound-assisted emulsification microextraction-inductively coupled plasma-optical emission spectrometry. ^jUltrasound-assisted emulsification microextraction-flame atomic absorption spectrometry.

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