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Solid Phase Extraction of Ultra Trace Amounts of Cobalt and Nickel on Octadecyl Bonded Silica Membrane Disk Modified with N,N′-*Bis*(3,5-di-*tert*-butylsalicylidene)-1,2-diaminoethane and Determination by Inductively Coupled Plasma-Optical Emission Spectrometry

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A highly sensitive and accurate method for preconcentration and determination of ultra trace amounts of cobalt and nickel ions in water samples is proposed. The preconcentration is achieved using C_{18}-silica extraction disks modified with N,N′-*bis*(3,5-di-*tert*-butylsalicylidene)-1,2-diaminoethane (H_2L_1). The retained ions on the prepared solid phase was eluted with 10 mL of nitric acid (0.01 M) and measured by inductively coupled plasma-optical emission spectrometry (ICP-OES). The influence of the type and amount of eluent used, pH, sample and eluent flow rates, amount of H_2L_1 and the effect of other ions on extraction efficiency were investigated. The limits of detection of the method were 0.2 and 0.09 μg L^{-1} for cobalt and nickel, respectively and provide an enrichment factor of 100. The results obtained on 10 successive extractions and elution cycles revealed relative standard deviations of 1.9 and 1.8 % for cobalt and nickel, respectively. The proposed method has been applied to the determination of ultra trace amounts of cobalt and nickel ions in natural and synthetic water samples with satisfactory results.

Key Words: Solid phase extraction, Cobalt, Nickel, N,N′-*bis*(3,5-di-*tert*-butylsalicylidene)-1,2-diaminoethane, Octadecyl bonded Silica membrane disk.

INTRODUCTION

Determination of low levels of cobalt by flame atomic absorption spectrometry (FAAS) often demands separation and preconcentration steps because of insufficient sensitivity or matrix interference. Several procedures of enrichment have been developed for cobalt determination involving different analytical techniques, such as coprecipitation[1] or liquid-liquid[2], cloud point[3]

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or solid-phase[4] extraction. Processes involving solid-phase extraction[5] show several advantages, like availability and easy recovery of sorbent, attainability of high preconcentration factors and facility of handling. Therefore, these procedures avoid or minimize the use of organic solvents that are generally toxic.

Online preconcentration systems using solid-phase extraction are favourable for metal determination, due to their flexibility, simplicity, high sample throughput and versatility. These characteristics permit the use of online systems coupled with different detectors. Many online procedures using solid-phase extraction can be found in the literature. The materials generally used are ion-exchangers[6,7], silica[8,9], activated alumina[10,11], carbon[12], fullerene[13], polyurethane foam[14,15] and chelating resins[16].

There is continued interest in development of chelating sorbents for use in metal preconcentration systems. To produce these matrices, chelating ligands can be loaded on solid supports[17-20] or can be covalently bonded to a polymeric matrix through an azo[21,22] or methylene group[23]. Coupling by covalent bond reduces problems of leaching of the ligand from the column.

Nickel can be found in many environments and has been shown to be essential for the human body. It is generally accepted that nickel concentrations below the 0.1 $\mu g\ mL^{-1}$ level in natural waters are harmless to aquatic organisms and irrigated plants[24]. However, it has been classified as one of the 13 priority metal pollutants by US EPA for its widespread use[25]. It is the metal component of the enzyme urease and as such is considered to be essential to plants and some domestic animals. The essentiality of nickel to man has not been demonstrated. More attention has been focused on the toxicity of nickel in low concentrations, such as the fact that nickel can cause allergic reactions and that certain nickel compounds may be carcinogenic[26].

When multi-elemental determinations are required, such as systems that use inductively coupled plasma-atomic emission spectrometry (ICP-AES) as the detection technique, the use of unselective ligands is convenient. However, in some determinations in which the goal is reduction of interference problems, the use of selective reagents is more suitable.

The ability of the ICP-OES system to perform multi-element trace metal analysis of environmental samples provided commercial laboratories with the needed incentive to enter into the business of trace metal analysis. Despite the selectivity and sensitivity provided by this technique, there is a crucial need for the preconcentration of ultra trace elements before their analysis due to their frequent low concentrations in numerous samples. Additionally, since ICP emission is normally subjected to high levels of interferences that usually accompany analytes; a cleanup step is often required. Many methods have been developed for the preconcentration of trace heavy metals from various samples. These include coprecipitation, electrodeposition, liquid-liquid extraction and solid phase extraction. Solid phase extraction (SPE) has received much attention in recent years for the analysis of trace concentrations in samples. This technique reduces the use of solvents, which reduces disposal costs and extraction times[27,28]. Many solid phases, such as activated carbon, polymeric fibers, Amberlite XAD, silica gel and modified alkyl-bonded silica gel have been used to preconcentrate trace metal ions from various media. Some works[29,30] dealing with the adsorption of trace metal chelates on C_{18}-silica adsorbent materials packed into columns or cartridges and their determination by ICP-OES can be found in literature. The use of extraction disks with a high cross-sectional area may largely prevent all the problems encountered with columns, cartridges and tubes and usually offer higher breakthrough volumes[31].

N,N′-*bis*(3,5-di-*tert*-butylsalicylidene)-1,2-diaminoethane (H_2L_1) has been used as a selective chelating agent for the simultaneous spectrophotometric determination of cobalt and nickel ions[32-35]. In this work, H_2L_1 is used to modify the C_{18}-silica extraction disks. Using these disks, a highly efficient and simple method for the preconcentration of ultra trace amounts of cobalt and nickel in natural water samples is developed and the simultaneous determination of these elements is achieved using ICP-OES.

EXPERIMENTAL

All metal salts, acids and solvents used were purchased from Merck (Darmstadt, Germany) and were of analytical reagent grade. Deionized double distilled water was used throughout. Multi-elemental standard solution containing Co and Ni at 100 μg mL^{-1} was prepared by dissolving Co and Ni in appropriate amounts of nitrate salts. Single standard solutions of Co and Ni at 1000 μg mL^{-1} were also used (Merck). Phosphate buffer was prepared by dissolving 1.179 g of potassium dihydrogen phosphate and 4.30 g of disodium hydrogen phosphate in deionized double distilled water to give 1000 mL of solution.

An inductively coupled plasma-optical emission spectrometer (ICP-OES, Varian Vista-Pro, Australia) coupled to a V-groovenebulizer and equipped with a charge-coupled device (CCD) detector was used. The operating parameters are listed in Table-1. The pH measurements were carried out by an ATC pH meter (EDT instruments, GP 353).

Synthesis of H_2L_1: Ligands were prepared by refluxing 0.02 mol of 3,5-di-*tert*-butylsalicylaldehyde and 0.011 mol of the appropriate diamine in 60 mL of methanol/ethanol mixture (v/v = 3:1) for *ca.* 1 h. The products were recrystallized from methanol/$CHCl_3$ mixture (v/v = 5:1) and dried in air (Yield: 92-95 %)[36].

TABLE-1
INSTRUMENTAL PARAMETERS

Plasma	Argon
Frequency of RF generator	40 MHz
RF power	1.5 kW
Plasma gas flow rate	150 min^{-1}
Nebulizer flow rate	0.831 min^{-1}
Sample uptake time	20 s
Integration time	0.5 s
Sample integration number	3
Sample solution flow rate	3 mL min^{-1}
Integration time	1 s
High wavelength	1 s
Low wavelength	3 s
Sample integration number	
Analysis wavelength	
Co	228.629 nm
Ni	231.598 nm

Preparation of modified extraction disks: Extractions were carried out by glassy membrane disks, ENVI-18DISK^{TM} 47 mm diameter × 0.6 mm thickness containing octadecyl silica bonded phase (30 μm particles, 70 Å pore size) obtained from Supelco in conjunction with a standard Millipore 47 mm filtration apparatus equipped with a vacuum pump. In order to remove potential interferences and to ensure optimal extraction of the analytes, disk cleaning and conditioning should be performed before use. Thus, after placing the disk in the filtration apparatus, 10 mL of methanol was poured onto the disk and immediately drawn through it by applying a slight vacuum to remove all contaminants arising from the manufacturing process and the environment. This procedure is especially important for the disks, which are used for the first time. After all of the solvent passed through the disk, air was drawn through it for 5 min to dry it. After drying the disk, a 5 mL solution of chloroform containing 6 mg of H_2L_1 was introduced onto the disk and allowed to penetrate inside the disk completely. Then, the solvent was evaporated at 60 °C and the modified disk was washed and preconditioned by passing a 20 mL portion of the buffer solution to pre-wet the surface of the disk prior to the extraction of ions from aqueous samples. In order to ensure complete wetting of the disk with the buffer solution it is preferable to leave extra buffer above the disk rather than to allow any air to come in contact with the surface of the disk.

Procedure of extraction, elution and determination: The general procedure for the extraction and determination of cobalt and nickel ions was as follows: A 250 mL volume of solution containing 0.5 μg of each metal was adjusted to the pH = 6 by the addition of 5 mL phosphate buffer and then passed through the modified disk at 20 mL min^{-1} flow rate. The disk was dried completely by passing air through it for 5 min. After the extraction, a 25 mm × 200 mm test tube was then placed under the extraction funnel. The extracted ions were stripped from the modified disk using 10 mL solution of 0.01 M of nitric acid at 7 mL min^{-1} flow rate. The analyte ion concentrations were then determined at recommended conditions by ICP-OES.

Analytical procedure for cobalt and nickel in water samples: Water samples were acidified with HNO_3 to 0.5 % (v/v) prior to storage in order to avoid metal adsorption onto the inner bottles walls. 1000 mL aliquot of water samples was first passed through 2.5 μm pore size filter paper (Whatmann) to remove suspended particulate matter and was stored at 6 ºC in the dark. Then complete the determination as discussed above.

RESULTS AND DISCUSSION

Effect of pH on the adsorption of metal ions: The pH of the sample solution is one of the influencing factors in solid phase extraction process. The analyte solutions were adjusted by the addition of appropriate amounts of 0.1 M either nitric acid or ammonia solutions to a fixed pH and passed through modified octadecyl silica disks at a flow rate of 20 mL min^{-1}. The pH range studied was between 2.0 and 8.0. Higher pH values (> 8) were not tested because of the possibility of the hydrolysis of octadecyl silica in the disks. Then the metal ions were eluted from the disks and their determination by ICP-OES gave the percentage recoveries of the eluted metal ions at various pHs. Fig. 1 shows the effect of pH on the retention of metal ions on the modified octadecyl silica extraction disks. Both cobalt and nickel ions have been quantitatively retained in the pH > 6. Thus for subsequent experiments, pH = 6 was chosen as working pH. Addition of 5 mL phosphate buffer was sufficient for achieving this pH.

Choice of eluent: In order to choose a proper eluent for the retained ions after their extraction, the analyte ions were stripped with varying amounts of 0.01 M concentrations of different acids and the results are summarized in Table-2. It is seen that their elution from the modified membrane disk was quantitative with 10 mL of nitric acid (0.01 M), while this could not be done even if greater than 10 mL volumes of the other acids tested. In other experiments, it was found that the lower the concentration of nitric acid, the larger the volume of the acid solution needed for the

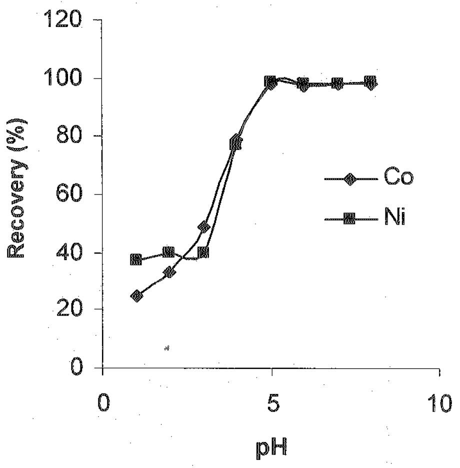

Fig. 1. Effect of pH on the recovery of cobalt and nickel. (Sample solution: 250 mL of solution containing 0.5 μg of each metal at 25 mL min^{-1} flow rate. Eluent: 10 mL of nitric acid solution (0.01 M) at 7 mL min^{-1} flow rate. Amount of ligand: 10 mg)

TABLE-2
RECOVERY PERCENTAGE OF COBALT AND NICKEL FROM MODIFIED OCTADECYL SILICA EXTRACTION DISKS USING VARYING AMOUNTS OF DIFFERENT 0.01 M OF ACID SOLUTIONS*

Metal ions	Volume (mL)	Recovery (%)			
		Hydrobromic acid	Hydrochloric acid	Nitric acid	Acetic acid
Co	2.5	26.6	53.5	41.3	26.3
Ni		32.8	47.8	43.8	33.5
Co	6.0	49.9	87.5	60.5	34.6
Ni		53.8	72.4	65.8	44.6
Co	10.0	61.7	97.5	81.7	52.5
Ni		72.7	99.0	72.7	61.6
Co	15.0	80.0	98.7	95.6	70.9
Ni		95.6	98.5	85.4	80.5

*Sample solution: 250 mL of multi-elemental solution containing 0.5 μg of cobalt and nickel ions; (pH = 6) at 25 mL min^{-1} flow rate.
Eluent flow rate: 7 mL min^{-1}; Amount of ligand: 10 mg.

quantitative stripping of the cations. Thus, 10 mL portions of nitric acid (0.01 M) were used for further studies. It is noteworthy that when nitric acid of concentrations higher than 0.01 M was used, there was some leaching of H_2L_1 from the disk.

Effect of the amount of ligand: In order to investigate the optimum amount of H_2L_1 on the quantitative extraction of metal ions by the modified extraction disks, extraction from 250 mL solutions containing 0.5 μg of cobalt and nickel ions under the optimal conditions was conducted by varying the amounts of ligand from 5 to 20 mg. In all cases, the extraction of metal ions found to be quantitative. Hence, subsequent experiments were carried out with 10 mg of the ligand.

Effect of flow rates: The dependency of uptake of the metal ions on the flow rate was studied. The flow rate of the solution through the modified disk was being varied from 10 to 30 mL min^{-1}. Adsorption of cations was quantitative and reproducible in this range and not considerably affected by the sample solution flow rate. Thus, the flow rate of the sample solution was maintained at 20 mL min^{-1} throughout the experiment. Quantitative stripping of metal ions from the modified disk was achieved in a flow rate range of 2-10 mL min^{-1}, using 10 mL of HNO_3 (0.01 M) as a stripping solution. At higher flow rates, a large volume of eluent was necessary for the quantitative stripping of ions. Hence, subsequent experiments were carried out with a flow rate of 7 mL min^{-1}.

Disk efficiency: Undoubtedly, one of the major parameters affecting in the SPE determinations is the efficiency of the used membrane disks. However, to the best of our knowledge this case has not been discussed elsewhere in similar reports. Under the optimum experimental conditions, it was found out that each ENV-18 DISK^{TM} disk could perform at least 15 replicate analyses if organic eluting solvents are used. On the other hand, acidic eluents practically decrease the number of time a disk could be used to 10 replicates. These observations are represented in Fig. 2.

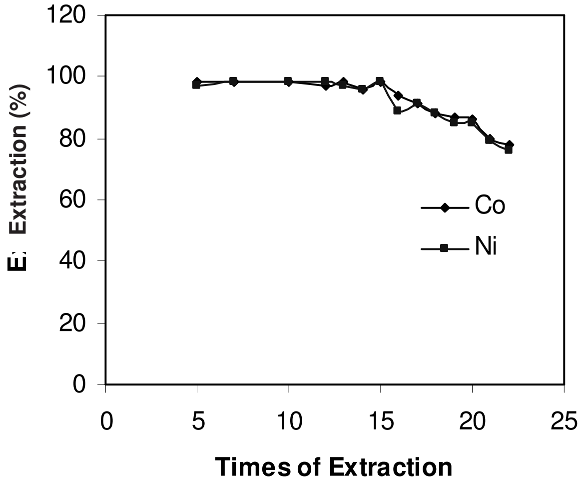

Fig. 2. Influence of eluent type on disk efficiency

Analytical figures of merit: The measurement of breakthrough volume is important in solid phase extraction because breakthrough volume represents the sample volume that can be preconcentrated without the loss of analyte during elution of the sample. The breakthrough volume of the sample solution was tested by dissolving 0.5 µg of cobalt and nickel ions in 500, 750 and 1000 mL of buffered solution and the recommended procedure was followed. In all cases, the extraction by modified disk was found to be quantitative. Thus, the breakthrough volume for the method should be around 1000 mL. Consequently, by considering the final elution volume of 10 mL and the sample solution volume of 1000 mL, an enrichment factor of 100 was easily available. The maximum capacity of the modified disk for each ion was determined by passing 250 mL portions of buffered aqueous solutions through the disk in which each of the solutions contains 500 µg of one of the ions. The conditions were as recommended procedure. The maximum capacities of the disks obtained from three replicate measurements were 0.034 ± 3 and 0.042 ±4 g per grams of loaded ligand for cobalt and nickel, respectively. The limits of detection (LOD) of the proposed method were studied under the optimal experimental conditions.

This parameter was calculated by $LOD = ks_b/m$, where k is equal to 3 according to the desired confidence level (95 %), s_b is the standard deviation of the blank signal and m is the slope of the analytical curve. The LODs were found to be 0.2 and 0.09 µg L^{-1} for cobalt and nickel, respectively. The reproducibility of the proposed method for the extraction and determination of 0.5 µg of analyte ions from 250 mL buffered solution at pH = 6 was also studied. The results obtained on 10 successive extractions and elution cycles revealed relative standard deviations of 1.9 and 1.8 % for cobalt and nickel, respectively.

Effect of foreign ions: The effect of other cations on the determination of analyte ions was studied. Known quantities of the foreign ions were added to 250 mL aliquot of aqueous solution (pH = 6) containing 0.5 µg of cobalt and nickel ions and the recommended procedure was followed. As shown in Table-3, most of the cations examined did not interfere considerably with the extraction of analyte ions and their recoveries were quantitative in the presence of other cations.

Analysis of water samples: To test the applicability of the developed procedure, it was applied to the extraction and determination of cobalt and nickel contents from some water samples. Tap water (Saveh, 20 February, 2007), seawater (taken from the Caspian sea, Anzali port, 11 November 2006) and a synthetic sample were analyzed. As can be seen in Table-4, the added analyte ions can be quantitatively recovered from the water samples by aforementioned procedure. According to the 95 % confidence level, there was no significant difference between the results obtained from the two methods.

TABLE-3
EFFECT OF FOREIGN IONS ON THE RECOVERY OF COBALT AND NICKEL IONS*

Ions	Concentration (ppm)	Recovery (%)	
		Co	Ni
Zn^{2+}	0.20	98.9	97.2
Cu^{2+}	0.08	97.7	98.5
Co^{2+}	0.10	–	96.5
Ni^{2+}	0.10	97.0	–
Fe^{3+}	0.50	96.8	95.8
Al^{3+}	0.50	98.7	98.6
Mn^{2+}	0.40	97.8	98.6
Mg^{2+}	400	97.0	97.8
Na^{+}	1000	96.6	97.3
K^{+}	1000	99.1	97.7
Ca^{2+}	400	98.7	97.5
Hg^{2+}	0.5	98.4	97.4
Cd^{2+}	0.6	97.8	96.6
Cr^{3+}	0.7	97.3	98.4
Ag^{+}	5.0	99.4	96.8
Pb^{2+}	0.7	96.7	94.7
Ba^{2+}	47.0	97.5	96.7
As^{3+}	47.0	97.9	97.4

*Sample solution: 250 mL of multi-elemental solution containing 0.5 μg of cobalt and nickel (pH = 6) at 25 mL min^{-1} flow rate. Eluent: 10 mL of nitric acid (0.01 M) at 7 mL min^{-1} flow rate. Amount of ligand: 10 mg.

Conclusion

The results presented in this work well demonstrate the tremendous possibilities offered by the solid phase extraction of ultra trace amounts of cobalt and nickel in water samples using C_{18}-silica extraction disks modified by N,N′-*bis*(3,5-di-*tert*-butylsalicylidene)-1,2-diaminoethane (H_2L_1) and its determination by inductively coupled plasma-optical emission spectrometry (ICP-OES). This method is a rapid, simple, precise and accurate alternative to conventional procedures for determining these ions in natural water samples. Low detection limits, up to 0.2 and 0.09 μg L^{-1} for cobalt and nickel, respectively and an enrichment factor of 100 are the main advantages of this analytical procedure used in environmental ultra trace analysis. In concl-usion, the developed method can be applied in order to simultaneously determine ultra trace amounts of these elements in various natural water samples.

TABLE-4
DETERMINATION OF COBALT AND NICKEL IONS IN 1000 mL OF DIFFERENT WATER SAMPLES AND RECOVERY TEST*

Sample	Element	Added (μg)	Concentration (μg L^{-1}), X ts ± √n		Recovery (%)
			Reference method	Proposed method	
Sea water	Co	–	12.35 ± 0.58	12.26 ± 0.35	–
		5	16.62 ± 0.33	–	87.6
		10	21.73 ± 0.56	–	94.6
	Ni	–	17.26 ± 0.67	14.90 ± 0.63	–
		5	20.09 ± 0.58	–	96.8
		10	24.67 ± 0.57	–	94.5
Tap water	Co	–	1.25 ± 0.56	1.30 ± 0.37	–
		5	6.75 ± 0.43	–	109.4
		10	11.56 ± 0.59	–	102.7
	Ni	–	2.17 ± 0.59	2.28 ± 0.74	–
		5	8.83 ± 0.63	–	93.2
		10	13.74 ± 0.56	–	95.7
Synthetic water (K^+, Na^+, Li^+, Mg^{2+}, Ba^{2+}, Na^+, Ag^+, Ca^{2+}, Fe^{3+}, Mn^{2+}, 0.01 mg of each cation)	Co	–	n.d.	n.d.	–
		5	4.50 ± 0.74	–	90.0
		10	9.64 ± 0.63	–	96.6
	Ni	–	n.d.	n.d.	–
		5	4.59 ± 0.64	–	94.6
		10	9.56 ± 0.60	–	96.4

*Concentration values are confidence intervals based on three replicate analyses at 95%; n.d.: not determined.

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