Solid phase extraction of ultra trace amounts of cobalt and nickel on octadecyl bonded silica membrane disk modified with Cyanex272 and determination by inductively coupled plasma-optical emission spectrometry

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ABSTRACT

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 Cyanex272(bis(2,4,4-trimethyl pentyl) phosphinic acid). The retained ions on the prepared solid phase was eluted with 10ml of 0.01M nitric acid 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 Cyanex272and the effect of other ions on extraction efficiency were investigated. The limits of detection of the method were 0.3 and 0.1µg 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 1.8 and 1.7% 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.   © 2008 Trade Science Inc. - INDIA

KEYWORDS

INTRODUCTION

Cobalt is an essential micronutrient for life. Determination of low levels of cobalt by flame atomic absorption spectrometry(FAAS) often demands separation and precon-centration 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] 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 opportune 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].

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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.

When multielemental 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.

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]. Cobalt is known to be essential at trace levels to man, animals and plants for metabolic processes[27]. It is clear that the determination of the trace amounts of cobalt in biological and environmental samples is important in the fields of environmental analysis, process control and medicine. The determination of trace amounts of cobalt in natural waters is of great interest because cobalt is important for living species as complexed Vitamin B_{12}. The deficiency of cobalt in ruminants usually results in different types of anemia. Toxicological effects of large amounts of cobalt include vasodilation, flushing and cardiomyopathy in humans and animals. Investigations have been extended to the biochemistry of cobalt in animals, microorganisms and enzymes[28]. The maximum recommended concentration of toxic ions such as nickel and cobalt in drinking water for livestock is: Co-1.0mg l^{-1} and Ni-2.5mg l^{-1}[29]. For drinking water for human consumption the upper limits are even less. It is therefore

clear that a reliable analytical method must be established to test waters and soils on a regular basis. Previously, trace elements in natural waters were typically analyzed using flame atomic absorption techniques, which although almost interference free, were labor intensive owing to their one element at a time analytical mode. At the present time, even the furnace atomic absorption technique, for years the standard bearer of low-level trace metal analysis is giving way to inductively coupled plasma-optical emission spectrometry (ICPOES) techniques.

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 [30,31]. 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. Silica with chemically bounded alkyl chains modified by the use of suitable ligands has been an excellent and widely used extractor of metal ions[32–36]. Some works 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[37,38]. 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[39].

8-aminoquinoline derivatives are known as chromogenic reagents for spectrophotometric determina-

tion of micro-amounts of gold[40] and palladium[41], and for the fluorimetric determination of iron[42] and gold[43]. Cyanex272, has been used as a selective chelating agent for the simultaneous spectrophotometric determination of cobalt and nickel ions[44,47-49]. In this work, Cyanex 272 is synthesized and 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

Apparatus

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. Solid phase extractions were carried out by glassy membrane disks, ENVI-18DISK™ 47mm diameter ×0.6mm thickness containing octadecyl silica bonded phase(30μm particles, 70Å pore size) obtained from Supelco in conjunction with a standard Millipore 47mm filtration apparatus equipped with a vacuum pump. The pH measurements were carried out by an ATC pH meter (EDT instruments, GP 353).

Reagents

All metal salts, acids and solvents and Cyanex272 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 100μg ml⁻¹ was prepared by dissolving Co and Ni in appropriate amounts of nitrate salts. Single standard solutions of Co and Ni at 1000μg ml⁻¹ were also used (Merck). Phosphate buffer was prepared by dissolving 1.179g of potassium dihydrogen phosphate and 4.30g of disodium hydrogen phosphate in deionized double distilled water to give 1000ml of solution.

Preparation of modified extraction disks

Extractions were carried out by glassy membrane disks, ENVI-18DISK™ 47mm diameter ×0.6mm

thickness containing octadecyl silica bonded phase (30μm particles, 70Å pore size) obtained from Supelco in conjunction with a standard Millipore 47mm 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, 10ml 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 5min to dry it. After drying the disk, a 5ml solution of chloroform containing 6mg of Cyanex272 was introduced onto the disk and allowed to penetrate inside the disk completely. Then, the solvent was evaporated at 60⁰C and the modified disk was washed and preconditioned by passing a 20ml 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

TABLE 1 : Instrumental parameters

Plasma	Argon
Frequency of RF generator	40MHz
RF power	1.5 kW
Plasma gas flow rate	15 0min⁻¹
Nebulizer flow rate	0.8 3l min⁻¹
Sample uptake time	20 s
Integration time	0.5 s
Sample integration number	3
Sample solution flow rate	3ml min⁻¹
Integration time	1 s
High waveleng	1 s
Low wavelength	3
Sample integration number	
Analysis wavelength	
Co	228.629nm
Ni	231.598nm

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The general procedure for the extraction and determination of cobalt and nickel ions was as follows: A 250.0 ml volume of solution containing 0.5µg of each metal was adjusted to the pH=6.0 by the addition of 5ml phosphate buffer and then passed through the modified disk at 20ml min^{-1} flow rate. The disk was dried completely by passing air through it for 5min. After the extraction, a 25×200mm test tube was then placed under the extraction funnel. The extracted ions were stripped from the modified disk using 10ml solution of 0.01M of nitric acid at 7ml 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. 1000ml aliquot of water samples was first passed through 2.5m pore size filter paper(Whatman) to remove suspended particulate matter and was stored at 6^0C in the dark. Then complete the determination as discussed in section 2.4.

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 0.1M either nitric acid or ammonia solutions to a fixed pH and passed through modified octadecyl silica disks at a flow rate of 20ml 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. Figure 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>6.0. Thus for subsequent experiments, pH=6.0 was chosen as working pH. Addition of 5.0 ml phosphate buffer was sufficient for achieving this pH.

TABLE 2 : Percent recovery of cobalt and nickel from modified octadecyl silica extraction disks using varying amounts of different 0.01M of acid solutions[a]

Recovery (%)				Volume (ml)
Hydrobromic acid	Hydrochloric acid	Nitric acid	Acetic acid	
26.9	54.7	45.7	26.6	Co 2.5
32.7	47.5	45.6	32.5	Ni
43.5	85.8	60.5	35.6	Co 6.0
53.3	72.6	65.6	44.5	Ni
61.5	93.4	81.5	52.3	Co 10.0
76.7	98.0	73.8	62.8	Ni
80.0	98.7	95.4	70.6	Co 15.0
97.6	97.5	84.4	83.5	Ni

[a]Sample solution: 250ml of multi-elemental solution containing 0.5µg of cobalt and nickel ions (pH = 6.0) at 25ml min^{-1} flow rate. Eluent flow rate: 7mlmin[-1]. Amount of ligand: 10mg.
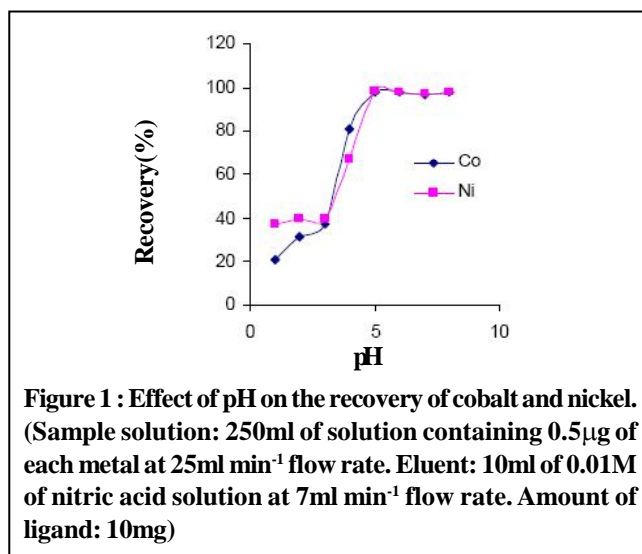

Figure 1 : Effect of pH on the recovery of cobalt and nickel. (Sample solution: 250ml of solution containing 0.5µg of each metal at 25ml min^{-1} flow rate. Eluent: 10ml of 0.01M of nitric acid solution at 7ml min^{-1} flow rate. Amount of ligand: 10mg)

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 0.01M 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 10.0ml of 0.01M nitric acid, while this could not be done even if greater than 10.0ml 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 quantitative stripping of the cations. Thus, 10ml portions of 0.01M nitric acid were used for further studies. It is noteworthy that when nitric acid of concentrations higher than 0.01M was used, there was some leaching of Cyanex272 from the disk.

Effect of the amount of ligand

In order to investigate the optimum amount of Cyanex272on the quantitative extraction of metal ions by the modified extraction disks, extraction from 250ml solutions containing 0.5μg of cobalt and nickel ions under the optimal conditions was conducted by varying the amounts of ligand from 5 to 20mg. In all cases, the extraction of metal ions found to be quantitative. Hence, subsequent experiments were carried out with 10mg 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 30ml min^{-1}. Adsorption of cations was quantitative and reproducible in this range and not considerably affected by the sample solution flow rate. Similar results for the extraction of organic[45] and inorganic[32–36] materials by octadecyl silica extraction disks have been reported in the literature. Thus, the flow rate of the sample solution was maintained at 20ml min^{-1} throughout the experiment. Quantitative stripping of metal ions from the modified disk was achieved in a flow rate range of 2-10ml min^{-1}, using 10ml of 0.01 M HNO$_3$ 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 7ml 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™ 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 10replicates. These observations are represented in figure 2.

Analytical figures of merit

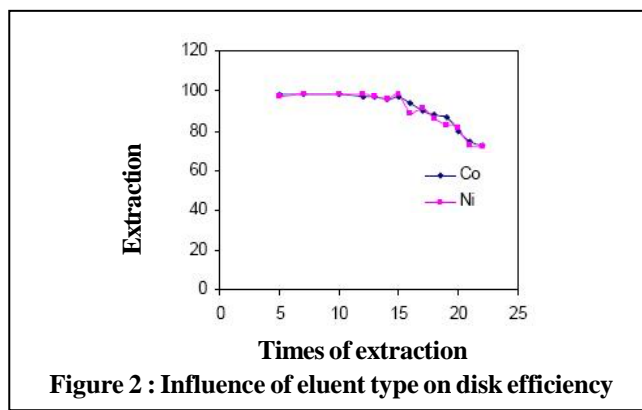The measurement of breakthrough volume is important in solid phase extraction because breakthrough

Times of extraction
Figure 2 : Influence of eluent type on disk efficiency

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 0.5μg of cobalt and nickel ions in 500, 750 and 1000ml 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 1000ml. Consequently, by considering the final elution volume of 10ml and the sample solution volume of 1000ml, an enrichment factor of 100 was easily available. The maximum capacity of the modified disk for each ion was determined by passing 250ml portions of buffered aqueous solutions through the disk in which each of the solutions contains 500μg of one of the ions. The conditions were as recommended procedure. The maximum capacities of the disks obtained from three replicate measurements were 0.035±7 and 0.048±5μg 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 0.3and 0.1μg l^{-1} for cobalt and nickel, respectively. The reproducibility of the proposed method for the extraction and determination of 0.5μg of analyte ions from 250 ml buffered solution at pH=6.0 was also studied. The results obtained on 10 successive extractions and elution cycles revealed relative standard deviations of 1.8 and 1.7% for cobalt and nickel, respectively.

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TABLE 3 : Effect of foreign ions on the recovery of cobalt and nickel ions[a]

Recovery (%)		Concentration (ppm)	Ions
Ni	Co		
97.5	98.9	0.7	Zn^{+2}
98.8	97.7	0.09	Cu^{+2}
97.7	–	0.5	Co^{+2}
–	97.0	0.5	Ni^{+2}
95.9	97.8	0.7	Fe^{+3}
96.6	98.8	0.5	Al^{+3}
98.9	95.8	0.4	Mn^{+2}
97.8	97.6	300	Mg^{+2}
98.3	96.4	1200	Na^{+}
97.7	98.4	1200	K^{+}
96.5	98.7	450	Ca^{+2}
97.6	98.4	0.7	Hg^{+2}
96.6	96.8	0.8	Cd^{+2}
98.4	97.3	0.6	Cr^{+3}
96.8	98.4	8	Ag^{+}
94.7	97.6	0.6	Pb^{+2}
96.7	97.8	49	Ba^{+2}
97.4	97.8	48	As^{+3}

[a]Sample solution: 250ml of multi-elemental solution containing 0.5μg of cobalt and nickel (pH = 6.0) at 25ml min^{-1} flow rate. Eluent: 10ml of 0.01M of nitric acid solutions at 7ml min^{-1} flow rate. Amount of ligand: 10mg, [a]Concentration values are confidence intervals based on three replicate analyses at 95%; n.d.: not determined.

TABLE 4 : Determination of cobalt and nickel ions in 1000ml of different water samples and recovery test[a]

Recovery (%)	Concentration (μgl^{-1}), X ts± $\sqrt{n}$		Added (μg)	Element	Sample
	Proposed method	Reference method			
–	12.26±0.35	12.32±0.67	–	Co	Sea water
87.8	–	16.64 ±0.54	5		
94.9	–	21.75 ±0.67	10		
–	14.90±0.63	17.26±0.67	–	Ni	
96.8	–	20.09 ±0.56	5		
94.7	–	24.65±0.58	10		
–	1.30±0.37	1.23 ±0.58	–	Co	Tap water
109.3	–	6.73 ±0.48	5		
102.5	–	11.55 ±0.55	10		
–	2.28±0.74	2.18 ±0.57	–	Ni	
93.3	–	8.86 ±0.65	5		
95.4	–	13.78 ±0.57	10		
–	n.d.	n.d.	–	Co	Synthetic water (K^+,Na^+,Li^+, Mg^{2+},Ba^{2+},Na^+, Ag^+,Ca^{2+},Fe^{3+}, Mn^{2+}, 0.0mg of eachcation)
95.5	–	4.50 ±0.77	5		
97.6	–	9.64 ±0.68	10		
–	n.d.	n.d.	–	Ni	
94.6	–	4.59 ±0.68	5		
96.4	–	9.56 ±0.64	10		

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 250ml aliquot of aqueous solution(pH=6.0) containing 0.5μg 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 the aforementioned procedure. The accuracy of the results given in TABLE 4was demonstrated by the use of a cloud point extraction procedure[46]. According to the 95% confidence level, there was no significant difference between the results obtained from the two methods.

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 Cyanex272 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 0.09μg 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 conclusion, the developed method can be applied in order to simultaneously determine ultra trace amounts of these elements in various natural water samples.

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