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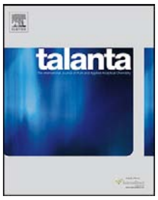

Silica gel–polyethylene glycol as a new adsorbent for solid phase extraction of cobalt and nickel and determination by flame atomic absorption spectrometry

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ABSTRACT

In this paper a novel solid phase extraction method to determine Co(II) and Ni(II) using silica gel–polyethylene glycol (Silica–PEG) as a new adsorbent is described. The method is based on the adsorption of cobalt and nickel ions in alkaline media on polyethylene glycol–silica gel in a mini-column, elution with nitric acid and determination by flame atomic absorption spectrometry. The adsorption conditions such as NaOH concentration, sample volume and amount of adsorbent were optimized in order to achieve highest sensitivity. The calibration graph was linear in the range of 0.5–200.0 ng mL^{-1} for Co(II) and 2.0–100.0 ng mL^{-1} for Ni(II) in the initial solution. The limit of detection based on $3S_b$ was 0.37 ng mL^{-1} for Co(II) and 0.71 ng mL^{-1} for Ni(II). The relative standard deviations (R.S.D.) for ten replicate measurements of 40 ng mL^{-1} of Co(II), and Ni(II) were 3.24 and 3.13%, respectively. The method was applied to determine Co(II) and Ni(II) in black tea, rice flour, sesame seeds, tap water and river water samples.

1. 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 higher concentrations all metals are recognized as potentially toxic [1]. Therefore, determination of trace heavy metals in different environmental samples is of great interest to analytical chemists. Flame atomic absorption spectrometry (FAAS) is one of the most widely used instruments for determination of heavy metals at trace levels due to its simplicity and lower cost than other instruments. However, there are some limitations in direct determination of heavy metals in environmental samples by FAAS because of matrix interferences and insufficient sensitivity of instrument [2]. Therefore, an initial preconcentration procedure is often required prior to determination of trace metal ions by FAAS. Many preconcentration techniques such as ion-exchange [3], coprecipitation [4], solvent extraction [5], cloud point extraction [6] and solid phase extraction [7–11] have been reported for determination of heavy metals at trace levels in various environmental samples such as natural waters, soil and food.

Solid phase extraction is an attractive separation and preconcentration technique for trace metal ions with advantages such as simplicity, flexibility, and high enrichment factor. Various solid phase materials have been introduced for the preconcentration and separation of heavy metal ions. These include chemically modified silica gel with aminothioamidoanthraquinone [2], polyurethane foam functionalized with α-naphthol [12], cellulose functionalized with 8-hydroxyquinoline [13], zeolite [14], Amberlite XAD.4 coated with dithiocarbamates [15], carboxylic acid (COOH) bonded to silica gel [16], 8-hydroxyquinoline anchored to silica gel [17], silica gel modified by 2,4,6-trimorpholino-1,3,5-triazin [18], 4,6-dihydroxy-2-mercaptopyrimidine (DHMP) loaded on activated carbon [19] and naphthalene loaded with tetraoctylammonium bromide [20].

The aim of the present work is to establish a new solid phase extraction method for determining Co(II) and Ni(II) at trace levels in environmental and food samples prior to their flame atomic absorption spectrometric determinations. The method is based on the retention of Co(II) and Ni(II) by silica gel–polyethylene glycol (Silica–PEG) in a mini-column, elution by nitric acid solution and measurement by FAAS.

2. Experimental

2.1. Apparatus

A Varian Spectra AA 220 atomic absorption spectrometer (Australia) equipped with cobalt and nickel hollow cathode lamps and air-acetylene flame was used for the analysis. All instrumental settings were those recommended by the manufacturer. The selected

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wavelengths for determination of cobalt and nickel were 240.7 and 232.0 nm, respectively. Lamp current of 5 mA was used for both cobalt and nickel. The spectral band pass was 0.1 and 0.2 nm for cobalt and nickel, respectively. A deuterium back ground correction was also used for both cobalt and nickel. FT-IR spectra were recorded on a Bomem FT-IR spectrophotometer (Canada). A digital pH-Meter model 632, Metrohm (Switzerland) with a combined glass electrode was used for pH adjustments. A Teb Azma vacuum pump (Iran) was used for pumping the solutions.

2.2. Reagents

Analytical reagent-grade chemicals and doubled distilled water were used throughout the study. A stock solution of 1000 μg mL^{-1} of Ni(II) was prepared by dissolving 0.4780 g of $NiSO_4 \cdot 7H_2O$ (Merck) in water and diluting to 100 mL in a volumetric flask. A stock solution of 1000 μg mL^{-1} of Co(II) was prepared by dissolving 0.4037 g of $CoCl_2 \cdot 6H_2O$ (Merck) in water and diluting to 100 mL in a volumetric flask. The above stock solutions were standardized by EDTA titration [21] and the working solutions were prepared by appropriate dilution of these stock solutions. A 0.10 mol L^{-1} solution of NaOH was prepared by dissolving 2.0 g of sodium hydroxide (Merck) in water and diluting to 500 mL in a volumetric flask. Silica gel (Aldrich 70–270 mesh, 60 Å and surface area > 500 m^2/g) was activated by treatment with HCl (5 mol L^{-1}) and dried in vacuum at 120 °C. polyethylene glycol, PEG (Merck) was heated at 80 °C under vacuum for 30 min before use to remove traces of moisture.

The Silica–PEG adsorbent was prepared by immobilization of polyethylene glycol on silica gel as previously reported in the literature [22].

2.3. Sample preparations

2.0 g of dry black tea, sesame and rice flour samples was each separately weighed into 100 mL beakers, 10 mL of 1:1 (v/v) nitric acid solution was added and gently heated at 150 °C for 3 h. After cooling at room temperature, the residue was dissolved in water and the pH of the final digest was adjusted by the addition of 10% (w/v) sodium hydroxide solution. This solution was finally transferred to a 250 mL volumetric flask and was subjected to the general procedure.

Tap and river water samples were acidified with 5 mL of nitric acid, stored in polyethylene bottles, kept in the refrigerator before use and filtered prior to analytical procedure.

2.4. Recommended procedure

A glass tube (10 cm length and 7 mm i.d.) with a very fine bore was packed with 0.3 g of the Silica–PEG adsorbent and used for simultaneous preconcentration of Co(II) and Ni(II). 250 mL of the solution containing 0.5–200.0 ng mL^{-1} of Co(II), 1.0–100.0 ng mL^{-1} of Ni(II) and 5×10^{-4} mol L^{-1} of NaOH was passed through the mini-column at a flow rate of 20 mL min^{-1}. The adsorbed metal ions were eluted with 3.0 mL of 2.0 mol L^{-1} of nitric acid and the concentration of each element in the eluent was determined by FAAS separately. A blank solution was also run under the same analytical conditions without adding any Co(II) or Ni(II).

3. Results and discussion

Silica-grafted polyethylene glycol has been successfully applied as a solid–liquid phase-transfer catalyst by organic chemists. It seems that this polymeric catalyst could form complexes with cations much like crown ethers [22]. Therefore, polyethylene glycol was easily immobilized on silica gel and used as a new adsorbent for preconcentration of cobalt and nickel ions. In order to improve the recovery of preconcentration, the effect of various variables was studied and optimized. The percent of metal ions adsorbed on the column was calculated from the amounts of metal ions in the starting sample and the amounts of metal ions eluted from the column.

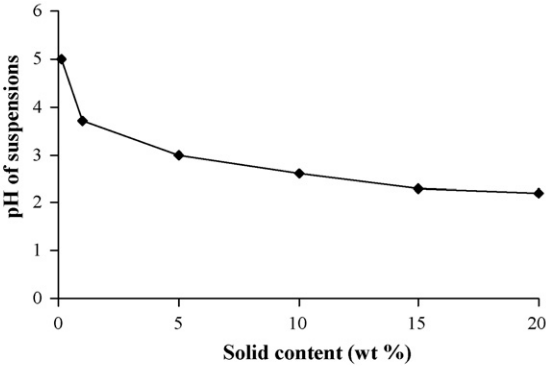

Fig. 1. Determination of PZC for Silica–PEG adsorbent.

3.1. Adsorbent characterization

The PEG-grafted silica particles are special type of branched inorganic–organic copolymer which has polyether functional groups in the side chains that has been found to be stable to acid, base, high temperature and oxygen. Its FT-IR spectrum shows the presence of OH and ethylene oxide groups on the surface of the adsorbent.

One of the most important characteristics of an oxide surface is the point of zero charge (PZC) which corresponds to the pH value of the liquid surrounding oxide particles when the sum of surface positive charges balances the sum of surface negative charges [23]. The surface charge depends on the pH of the surrounding electrolyte [24]. Noah and Schwarz have proposed a method for evaluation of the PZC of the surface [25]. This method was carried out to estimate the pHPZC of the adsorbent. Accordingly, suspensions with the weight percentages of 0.1, 1, 5, 10, 15 and 20% of the adsorbent prepared in 0.1 mol L^{-1} of NaCl solutions [23] were sealed under nitrogen and kept at constant temperature under nitrogen atmosphere. The pH value of each suspension was measured after 24 h contact time. The suspension pH values were plotted as a function of solid mass content. It has been considered that the PZC value is the pH value of the suspension having the higher solid content. As shown in Fig. 1 the pHPZA value derived from experimental measurements was found to be 2.2.

3.2. Effect of NaOH concentration

The adsorption of metal ions was performed in both acidic and alkaline media. The preliminary investigation showed that the metal ions are retained by the adsorbent in the alkaline solution. When pH of the solution is higher than pHPZC, the negative charge on the surface provides electrostatic interactions that are favorable for adsorbing cationic species. The decrease of pH leads to neutralization of surface charge, thus, the adsorption of cations should decrease [23]. Since pHPZC was found to be 2.2, it is expected that adsorption of metal ions is performed better in alkaline media and it was for this reason that the effect of sodium hydroxide concentration was studied. As presented in Fig. 2 the highest recoveries are obtained for both metal ions at sodium hydroxide concentration of 5×10^{-4} mol L^{-1}. Therefore, concentration of 5×10^{-4} mol L^{-1} was selected for further investigations.

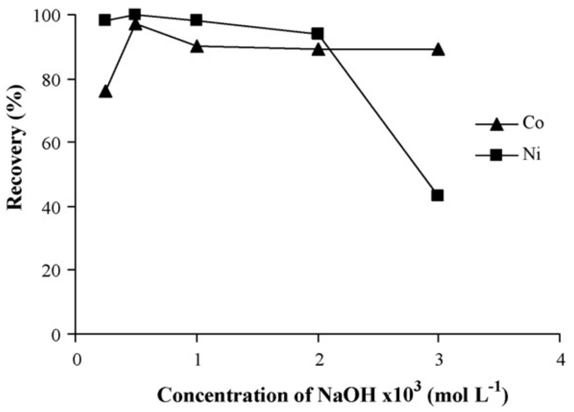

Fig. 2. Effect of NaOH concentration on the recovery of 100 ng mL^{-1} Co(II) and Ni(II).

3.3. *Effect of elution parameters*

A satisfactory eluent should effectively elute the adsorbed metal ions with small volume in order to achieve high enrichment factor. Various acids and organic solvents such as acetone, hexane, ethanol, HCl and HNO_3 were tested as the eluent for desorbing metal ions from the adsorbent surface. Among the solvents studied, nitric acid provided higher recovery compared to other solvents. Therefore, the effect of nitric acid concentration was studied. As the results in Fig. 3 show, the highest recoveries were obtained when 0.10–0.25 mol L^{-1} of nitric acid was used as an eluent. The effect of the volume of the eluent was also studied and 3.0 mL of 0.2 mol L^{-1} of nitric acid was selected as the optimum value because it was sufficient for quantitative recovery of the metal ions.

3.4. *Effect of the amount of adsorbent*

The amount of solid phase material is another important factor on the column studies for quantitative recovery. In order to estimate the optimum adsorbent quantity, the recoveries of Co(II) and Ni(II) were examined by using the adsorbent quantities in the range of 0.1–0.4 g. The results shown in Fig. 4 indicate that quantitative recoveries were achieved when adsorbent quantity was greater than 0.2 g. In the proposed procedure, 0.3 g of the adsorbent was used in further experiments.

3.5. *Stability and reusability of the adsorbent*

The stability of the adsorbent was checked for several months and it was found that it is stable for at least six months. Each column containing 0.3 g of adsorbent can be used three times without any loss in the recovery. The used adsorbents can also be recovered by a simple procedure. Used Silica–PEG was stirred with 100 mL of 5% hydrochloric acid for 2 h, filtered and dried. The recycled adsorbent can be used three times again, thus the consumption of the adsorbent is too low because it can be recycled several times without any loss in the sensitivity.

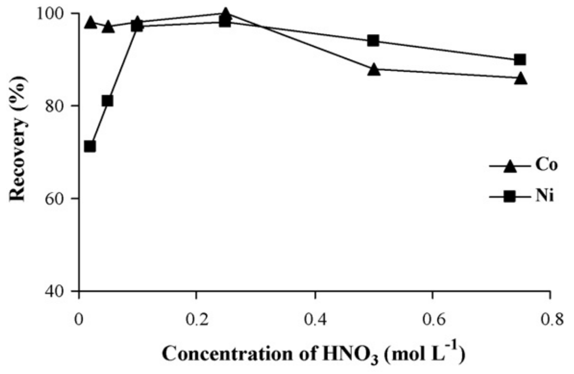

Fig. 3. Effect of nitric acid concentration as the eluent on the recovery of 100 ng mL^{-1} Co(II) and Ni(II).

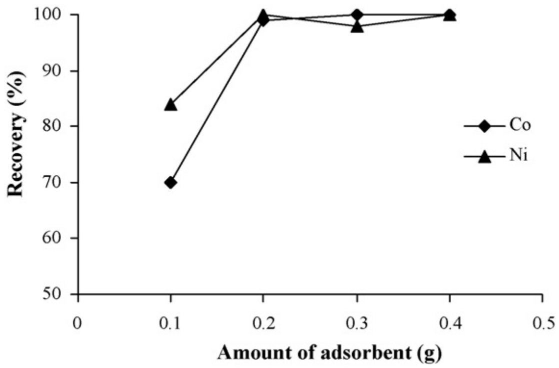

Fig. 4. Effect of amount of adsorbent on the recovery of 100 ng mL^{-1} Co(II) and Ni(II).

3.6. *Effect of sample flow rate*

One of the parameters affecting the recovery and preconcentration time is the sample flow rate whose effect on the adsorption of the metal ions was investigated. This study was conducted by pumping 250 mL of the solution containing 100 ng mL^{-1} Co(II) and Ni(II) at different flow rates. The results indicated that the analyte ions were quantitatively retained when the sample flow rate was in the range of 2–20 mL min^{-1}. In posterior experiments, the flow rate was kept constant at 20 mL min^{-1} in order to increase the sample throughput.

3.7. *The effect of sample volume*

For the preconcentration of trace elements in natural water samples, the method used must have high preconcentration factor. To obtain the preconcentration factors, maximum applicable sample volume must be established. For this purpose, Co(II) and Ni(II) were preconcentrated from sample volumes of 50–500 mL containing the same amounts of metal ions (25 μg of nickel and 25 μg of cobalt) and applying the general procedure. The recovery values for Co(II) and Ni(II) were very efficient (>95%) for sample volumes up to 500 mL. Thus, in this procedure, by using 3 mL of elution solution, a preconcentration factor of 166.6 could easily be obtained. However, in order to decrease the analysis time we used 250 mL for the preparation of calibration curves for which a preconcentration factor of 83.3 was employed.

3.8. *Adsorption capacity*

The adsorption phenomena at the solid–liquid interface are commonly described by Langmuir isotherms which are described by the equation given below:

$$\frac{C}{q} = \frac{1}{kq_m} + \frac{C}{q_m}$$

where q is the amount of metal adsorbed per unit weight of the adsorbent (mg g^{-1}) at equilibrium, C is the final concentration in the solution (mg L^{-1}), q_m is the maximum adsorption in monolayered adsorption systems (mg g^{-1}) and k is the adsorption equilibrium constant related to adsorption energy (L mg^{-1}). A plot of C/q versus C shows a linear relationship, and Langmuir constants q_m

Table 1
Effect of diverse ions on the determination of 100 ng mL^{-1} of Co(II) and Ni(II).

Interfering ion	Tolerance ratio	
	Co(II)	Ni(II)
Ca^{2+}, F^-, $CO_3{}^{2-}$ Cr^{3+}, I^-, $HCO_3{}^-$, SCN^-, Br^-	1000	1000
$SO_4{}^{2-}$, K^+	1000	500
Mg^{2+}, Cd^{2+}, Pb^{2+}	100	100
Mn^{2+}, Zn^{2+}, Cu^{2+}, Hg^{2+}	10[a]	100
Fe^{3+}	1[b]	1[b]

[a] 100, after the addition of 2 mL of 1000 μg mL^{-1} of oxalate solution.
[b] 50, after the addition of 4 mL of 1000 μg mL^{-1} of thiocyanate solution.

and k can be calculated from the slope and intercept of the plot [26].

In order to determine the adsorption capacity, 0.25–20 μg mL^{-1} of the analytes were loaded to the column containing 0.30 g of adsorbent to obtain C/q and C. Langmuir isotherms were plotted to determine the capacity. Adsorption capacity of the Silica–PEG was evaluated to be 6.49 and 8.33 mg g^{-1} of adsorbent for Co(II) and Ni(II), respectively.

3.9. *Analytical performance*

The calibration graphs were constructed using the general procedure under optimum conditions. Linear calibration graphs were obtained in the range of 0.5–200.0 ng mL^{-1} for Co(II) and 2.0–100.0 ng mL^{-1} for Ni(II) in the initial solution. The equations of the lines are $A = 6.2 \times 10^{-3}C + 0.0021$ and $A = 5.7 \times 10^{-3}C + 0.053$ for Co(II) and Ni(II), respectively where A is the absorbance and C is concentration of metal ions in ng mL^{-1}. The regression coefficients for the lines are 0.9985 and 0.9988 for Co(II) and Ni(II), respectively. The limit of detection based on $3S_b$ was 0.37 ng mL^{-1} for Co(II) and 0.71 ng mL^{-1} for Ni(II). The relative standard deviations (R.S.D.) for ten replicate measurements of 40 ng mL^{-1} of Co(II) and Ni(II) were 3.24 and 3.13%, respectively.

3.10. *Interference studies*

In order to examine the effect of different ions on determination of Co(II) and Ni(II), constant amounts of Co(II) and Ni(II) were taken with different amounts of ions and subsequently the general procedure was followed. Any deviation of ±5% or more from the absorbance value of the standard solution was considered as interference. The results presented in Table 1 show that a large number of ions tested have no effect on determining Co(II) and Ni(II). The tolerance ratio of Mn^{2+}, Zn^{2+}, Cu^{2+}, Hg^{2+} for Co(II) can be improved to 100 by adding 2 mL of 1000 μg mL^{-1} of oxalate solution and the tolerance ratio of Fe^{3+} can be improved to 50 by adding 4 mL of 1000 μg mL^{-1} of thiocyanate solution.

Table 2
Determination of Co(II) and Ni(II) in tap and river water samples.

Sample	Element	Added (ng mL^{-1})	Found (ng mL^{-1})[a]	Recovery (%)
Tap water	Co	–	2.3 ± 0.2	–
		5	7.3 ± 0.4	100
		10	12.4 ± 0.7	101
	Ni	–	8.7 ± 0.3	–
		5	13.8 ± 0.4	102
		10	18.9 ± 0.4	102
River water	Co	–	3.0 ± 0.2	
		5	8.0 ± 0.3	100
		10	13.3 ± 0.3	103
	Ni	–	12.7 ± 0.3	
		5	17.7 ± 0.4	100
		10	23.0 ± 0.8	103

[a] $\bar{x} \pm ts/\sqrt{n}$ at 95% confidence ($n = 5$).

Table 3
Determination of Co(II) and Ni(II) in black tea, rice flour and sesame seeds.

Sample	Element	Added (ng mL^{-1})	Found (ng mL^{-1})[a]	Recovery (%)	(μg g^{-1})
Black tea	Co	–	10.7 ± 0.4	–	1.30 ± 0.20
		5	15.9 ± 0.7	104	
		10	21.0 ± 0.8	103	
	Ni	–	32.7 ± 1.2	–	4.20 ± 0.30
		5	37.8 ± 1.2	102	
		10	42.9 ± 1.2	102	
Rice flour	Co	–	ND[b]	–	–
		5	5.1 ± 0.3	102	
		10	10.2 ± 0.4		
	Ni	–	17.2 ± 0.7	–	2.15 ± 0.20
		5	22.2 ± 0.8	100	
		10	27.5 ± 1.2	103	
Sesame seeds	Co	–	1.1 ± 0.2	–	0.14 ± 0.02
		5	6.2 ± 0.3	102	
		10	11.5 ± 0.4	104	
	Ni	–	2.2 ± 0.2	–	0.28 ± 0.03
		5	7.3 ± 0.4	100	
		10	12.1 ± 0.4	99	

[a] $\bar{x} \pm ts/\sqrt{n}$ at 95% confidence ($n = 5$).
[b] ND: not detected.

Table 4
Comparison of the results for the determination of Co(II) and Ni(II) in black tea and tap water with graphite furnace atomic absorption spectrometry.

Sample	Metal ion	Graphite furnace method[a] (ng mL^{-1})	This method[a] (ng mL^{-1})
Black tea	Co	11.1 ± 0.5	10.7 ± 0.4
	Ni	32.8 ± 1.2	32.7 ± 1.2
Tap water	Co	2.3 ± 0.2	2.3 ± 0.2
	Ni	8.8 ± 0.4	8.7 ± 0.3

[a] $\bar{x} \pm ts/\sqrt{n}$ at 95% confidence ($n = 5$).

Table 5
Comparison of the proposed method with some of the methods reported in the literature.

System	Preconcentration factor	LOD (ng mL^{-1})		Ref.
		Ni	Co	
Modified silica gel with aminothioamidoanthraquinone	50.0	2.90	0.95	[2]
Cloud point extraction	–	1.10	0.90	[6]
Activated carbon modified by dithioxamide	330.0	0.75	0.80	[8]
Cellulose functionalized with 8-hydroxyquinoline	90.0	1.61	1.09	[12]
Carboxylic acid (COOH) bonded to silica gel	–	2.10	3.10	[15]
8-Hydroxyquinoline anchored to silica gel	200.0	7.50	6.00	[17]
Modified silica gel by 2,4,6-trimorpholino-1,3,5-triazin	100.0	0.29	0.20	[18]
Activated carbon loaded by 4,6-dihydroxy-2-mercaptopyrimidine	260.0	3.50	3.40	[19]
Silica–PEG	83.3	0.71	0.37	This work

4. Application

The proposed solid phase extraction procedure was applied to determine cobalt and nickel ions in black tea, rice flour, sesame seeds, and tap and river water samples. The results are given in Tables 2 and 3. Different amounts of the investigated metal ions were also spiked to the samples and the resulting solutions were submitted to the preconcentration procedure. Good agreement was achieved between the added and found concentrations of analytes using the recommended procedure. The recovery values for the analyte ions were in the range of 99–104%. In order to estimate the accuracy of the procedure, the black tea and tap water samples were also run by graphite furnace atomic absorption spectrometry method, the results of which are given in Table 4. These values revealed that there is good agreement between the two methods and there was also no significant difference between the results by performing *t*-test at 95% confidence limit.

5. Conclusion

The results of this study manifest the capability of Silica–PEG as an adsorbent for simultaneous preconcentration of Co(II) and Ni(II) with an enrichment factor of 83.3-fold. To the best of our knowledge, this is the first application of Silica–PEG as an adsorbent for preconcentration of metal ions. Moreover the prepared adsorbent is eco-friendly and very economical because it can be recycled and used several times without any loss in the recovery. The method is highly sensitive and selective for determination of trace amounts of Co(II) and Ni(II) by flame atomic absorption spectrometry. The detection limits for cobalt and nickel ions are better than or comparable to some of the previously reported values. A comparison with some of the previous works is also given in Table 5. The method was successfully applied to the determination of Co(II) and Ni(II) in black tea, sesame seeds, rice flour, tap water and river water samples.

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