Preconcentration of Ni(II) on Silica gel Loaded with New Synthesized Schiff base and Their Determination by FAAS

HAMED MASOUDINIA[1], MOHAMMAD REZA NATEGHI[1]* and TAHEREH KHOSOUSI[2]

[1]Department of Chemistry, Yazd Branch, Islamic Azad University, Yazd, Iran.
[2]Department of Chemistry, Neyriz Branch, Islamic Azad University, Neyriz, Iran.
*Corresponding author E-mail: mnateghi@iauyazd.ac.ir

ABSTRACT

A preconcentration method was developed for the determination of trace amounts of Ni(II) by atomic absorption spectrometry. The method is based on the retention of the metal cations by modified silica gel adsorbent. The adsorbed metals were then eluted with nitric acid and the Ni(II) was determined by flame atomic absorption spectrometry. The optimal extraction and elution conditions were studied. The effects of diverse ions on the preconcentration were also investigated. A preconcentration factor of 100 can easily be achieved. Calibration graph was obtained and the detection limit of the method for Ni(II) was 1.3 ng mL^{-1}. The relative standard deviation (*RSD*) of 0.66–1.32 % was obtained. The method was applied successfully to the determination of Ni(II) in water samples.

Key words: Schiff base; Solid–liquid extraction; Silica gel; Ni(II).

INTRODUCTION

Flame atomic absorption spectrometry (FAAS), is often used for the determination of trace metal ions. The direct determination of metal ions at trace level is limited due to their low concentration and matrix interferences. Therefore, a preconcentration or separation step is frequently necessary to improve the detection limit and sensitivity. For this purpose, several separation and preconcentration procedures such as solvent extraction, co-precipitation or solid phase preconcentration technique can be applied. Solid phase extraction is a sensitive, fast and economic preconcentration method for traces of analyte ions in various materials, including natural waters, ores, biological samples, *etc*. Of all separation-enrichment separation procedures, solid phase extraction possesses several advantages: large preconcentration factors, simplicity of phase separation and suitability for automation[1–3].

Of the many types of solid phase used in SPE, silica gel immobilized by various organic and inorganic compounds that use a metal chelating agent to remove, extract, separate and preconcentrate metal ions from different matrices display high thermal, chemical and mechanical stability[4] and is less susceptible to swelling, shrinking, and microbial and radiation decay[5-8].The selectivity of the modified silica gel mainly depends on the structure of the immobilized organic compound as a whole, the nature of the incorporated donor atoms (O, N, P and S), the positioning of the functional groups along the surface of the silica, and the steric requirements of the complex formed after uptake of the desired metal ion[9-11]. A variety of chelating ligands have been used to modify a silica gel surface. It is then possible to immobilize new molecules with a variety of organic functions, including chelating agents[5,12-19]. Silica gel functionalized with 1,8-dihydroxyanthraquinone[19], 2-aminomethylpyridine[20], *p*-dimethyl amino benzaldehyde,[21] 4-(8-hydroxy-5-quinolyazo) naphthalene,[22] 2,4,6-trimorpholine-1,3,5-triazin[23], benzophenone-4-aminobenzoyl-hydrazine[17], 4-amino-2-ercaptopyrimidine[11], ethyl-2-benzothi -azolylacetate[24] have been used to enrich for metal ions, Cd(II), Co(II), Cu(II), Ni(II), Pb(II) and Zn(II). The modified silica have been used in various areas, most notably in metal ion preconcentration[25], ion exchange,[26-27] biotechnology[28], sensors[29], catalysis[30-32], pesticides removal[33] and green chemistry[34].

In this study, ethylendiamin-2-hydroxy-3-methoxy benzaldehyde was immobilized on the surface of a silica gel to create a new solid-phase extractant. The new sorbent was successfully applied to the preconcentration and determination of Ni(II) in aqueous solutions and environmental samples.

EXPERIMENTAL

Apparatus

A Varian model AA240FS flame atomic absorption Spectrophotometer (FAAS) equipped with hollow cathode lamp (HCL) was used for determinations. The optimum conditions for FAAS are given in Table 1.

Metrohm pH meters (model 827) with a combined glass pH electrode, calibrated against standard buffer solutions at pH 4.0, 7.0 and 9.0, were used for pH measurements. All measurements were made at atmospheric temperature and pressure.

Reagents and solutions

All chemicals used were of analytical-reagent grade and all solutions were prepared with doubly distilled deionized water. Stock solutions of iron and those used for the interference study (1000 mg L^{-1}) were prepared by dissolving appropriate amounts of their respective pure nitrate salts (Merck) in deionized water. Working standard solutions were obtained daily by suitable stepwise dilution of the stock solutions with deionized water and shaking them just prior to use. Sodium dihydrogen phosphate (NaH_2PO_4)-disodium hydrogen phosphate (Na_2HPO_4), hydrochloric acid (HCl), nitric acid (HNO_3), and sodium hyroxide (NaOH) were obtained from Merck Chemicals. In the elution work, HNO_3 1 M was used to extract the adsorbed Ni(II) from the Schiff base-loaded silica gel. The buffer solutions in the range of pH 2–10 were prepared using sodium dihydrogen phosphate (NaH_2PO_4)- and disodium hydrogen phosphate (Na_2HPO_4). The Schiff base solution was prepared by dissolving 0.7 g of ethylendiamin-2-hydroxy-3-methoxy benzaldehyde in 50 mL of aceton (Merck). Silica gel (bead size, 20–40 mesh) taken from Merck. All glass apparatus were washed with acid after use.

Preparation of Schiff base-loaded silica gel

Modified silica gel was prepared as follows: 0.7 g of Schiff base was suspended in 50 mL of aceton. Then, the prepared Schiff base solution was added to 35 g silica gel and the mixture was stirred to evaporate the acetone. The modified silica gel was dried and the prepared powder was ground and was kept for further studies.

Extraction procedure

The pH of the Ni(II) solution (700 mL; 12.5 ng mL^{-1}) was adjusted to the studied pH. 0.6 g of dried modified silica gel was added to Ni(II) solution. The mixture was mechanically stirred for 60 min and filtered through a filter paper by using a vacuum pump. For elution of the adsorbed Ni(II) on the modified silica gel, 7.0 mL of HNO_3 1M was used. The clear solution was measured using FAAS. The blank solutions were carried out in the same way.

RESULTS AND DISCUSSION

Modified silica gel has been used to preconcentrate Ni(II) after a chelating agent was adsorbed or bonded chemically on silica gel surface. Extraction of Ni(II) is probably due to proton exchange mechanism. Therefore for selection of desorption solvent, acidic solution with different concentration were used. The parameters that are thought to affect the preconcentration and measurement steps in the analytical scheme were examined using the model solutions of 12.5 ng mL^{-1}. The effect of each parameter was tested three times.

Metal extraction

The ability of modified silica gel to adsorb Ni(II) from aqueous solutions was studied by varying different parameters namely the pH, weight ratio of Schiff base/silica gel, stirring time, and type and concentration of eluent. The solid-liquid extraction of a metal ion may be described by the following equilibrium:

$$M^{n+} + nHL \leftrightarrow ML_n + n\,H^+$$

The extraction percentage of a metal may be expressed as:

$$E(\%) = \frac{[M]aq,i - [M]aq,e}{[M]aq,i}$$

where $[M]_{aq,i}$ and $[M]_{aq,e}$ are the concentrations in the aqueous phase before and after extraction, respectively[35].

Effect of the pH on recovery

The influence of pH on recovery was studied because the hydrogen-ion concentration plays an important role in the preconcentration of metals by SPE because it significantly affects the metal-ligand complex formation. The model Ni solutions was preconcentrated using various pH values ranging from 2 to 10. The obtained recoveries are given in Fig. 1. It was seen that the maximum recoveries (up to 95%) were found in the pH >8.0. Therefore, for subsequent studies, the pH 8.0 was used.

Test solutions were buffered in order to have stable pH values and avoid time-consuming dropwise addition of acid or base to obtain the desired pH. The influence of buffer was carried out by keeping all other experimental variables constant. The results showed that in the presence of buffer the recoveries were lower than aqueous solution (**Figure 2**). Thus all experiments were carried out in aqueous solution.

Effect of the weight ratio of schiffbase/silica gel on recovery

In order to determine the optimum weight ratio of schiffbase/silica gel, the recoveries of model solution of Ni(II) at the optimum pH (8.0) were examined using different weight ratio of 0.010, 0.015, 0.020, 0.025, and 0.030 Schiff base/silica

Table 1: Operating parameters for flame atomic absorption spectrometry

Method Parameters	Type or Value
Ni(II) Wavelength (nm)	232.0
Lamp Current (mA)	4
Slit Width (nm)	0.2
Flame type	Air / Acetylene
Optimum working range (ppm)	0.1-20

Table 2: Effect of interfering ions on the recovery of 50 ng mL^{-1} Ni(II) in water samples using SPE-FAAS method

Ion	Mole ratio	Recovery(%)
Ca^{2+}	500	98
Mg^{2+}	500	101
Na^+	500	99
K^+	500	98
Hg^{2+}	500	93
Fe^{3+}	500	98
Ag^+	500	95
Al^{3+}	500	94
Fe^{2+}	200	97
Mn^{2+}	200	95
CH_3COO^-	200	98
NH_4^+	100	97
SO_4^{2-}	100	95
Co^{2+}	15	96

Table 3: Analytical results of Ni(II) determination in spiked natural water samples with the SPE-FAAS method (n = 3)

Sample	Ni^{2+} (ng mL^{-1})		Recovery
	Added	Determined	(%)
Tap Water	-	0	-
	20	1860	93
60	5700	95	
Well Water	-	0	-
	20	1920	96
	60	6180	103

gel. It is seen from Fig. 3 that the recoveries increase up to 95% with weight ratio of 0.020 Schiff base/ silica gel and have very little change by adding up to 0.030. Thus, weight ratio 0.020 was used in contact with 700 mL Ni(II) solution in the subsequent studies. This amount was increased according to the volume of Ni(II) solution, proportionally.

Effect of the stirring time on recovery

The kinetics of the Ni(II) sorption and desorption were investigated in a batch system. It was found that the stirring time of 60 min is sufficient for sorption of Ni(II) on silica gel (Fig. 4). The preconcentration procedure was applied to the model solutions using different stirring times with all other optimum conditions. It was found that the stirring time of 60 min was sufficient for maximum recovery in the first step (up to 95%). This stirring time is shorter compared to other studies where preconcentration time as long as 2–4 h was required for maximum recovery in the literature. So, the stirring time of 60 min was used for all studies.

Effect of the type and concentration of eluent on recovery

Extraction of Ni(II) is probably due to proton exchange mechanism. Therefore for elution purpose, acidic solutions with different concentration were examined. The efficiency of the two eluents (HCl and HNO$_3$) were studied by taking different concentrations (0.5-4.0 M). It was found that 7 mL of 1 M HNO$_3$ was sufficient for maximum recovery (up to 95%) of Ni(II) (Fig. 5). Therefore, 7.0 mL of 1 M HNO$_3$ was used for complete desorption of the nickel. HCl van be reach to this recovery at 4 M that indicated the HNO$_3$ is stronger eluent than HCl.

Effect of sample volume on recovery

One of the most important parameters for obtaining high preconcentration factors is the sample volume. The effect of sample volume on the recovery of Ni(II), was investigated in the range of 250-1500 mL volume of the model solutions containing 12.5 ng mL^{-1} at pH 8.0. The results in Figure 6 show that Ni(II) up to volume of 1000 mL were recovered quantitatively. When the volume of final solution was 7 mL, the preconcentration factors for Co(II) was found to be 143.In addition, volume of 1000 mL was used for determination of sorption capacity (Fig. 6). The sorbtion capacity was 14600 ng per g modified silica gel.

Effect of interfering ions

The effect of some major components present in natural samples such as Na(I), K(I), Ca(II), Mg(II), and SO$_4^{2-}$ ions on the recoveries of analyte ions was investigated by the proposed method. The interfering elements were added to the model sample solutions as their nitrate or chloride salts. 700 mL of model solutions containing 50 ng mL^{-1} and the matrix ions were prepared and the proposed procedure was applied. Table 2 shows the effect of the interfering ions on the recoveries of Ni(II). In the medium containing 500 times of alkaline and alkaline earth metals, the signal of Ni(II) was not affected from matrix components, the recovery values for cobalt are not quantitative.

Analytical performance

The calibration curve was observed to be linear at the concentration range of 5-100 ng mL^{-1} by taking 700 mL solution to final volume of 7.0 mL of 1 M HNO$_3$ (using 600 mg modified silica gel). The equations of the curves are as follows (Fig. 7):

Table 4: Comparison of the characteristic data between typical published methods and the propos method for separation/preconcentration and determination of Ni(II)

Soebent	Detection method	Preconcentration factor	RSD (%)	Linear range (ng mL⁻¹)	Detection limit (ng mL⁻¹)	Ref.
TiO_2 nanotubes	FAAS	N.R[a]	2.6	1-150	0.25	36
TiO_2 nanotubes /8-hydroxyquinoline	FAAS	66.7	2.6	1-150	1.0	37
Bacillus sphaericus/chromosorb 106	FAAS	250	N.R	N.R	1.46	38
SDS-alumina/indane-1,2,3-trione 1,2-dioxime	FAAS	444	1.5	5-1500	1.83	39
AC/DTO[b]	FAAS	330	0.9	17-850	0.75	40
MWCNT/D2EHPA[c] and TOPO[d]	FAAS	25	<10	N.R	40	41
Amberlit XAD-7/PDANP[e]	FAAS	125	2.8	0.2-4	0.44	42
Amberosrb-572/EDTA[f]	FAAS	50	N.R	N.R	1.42	43
Styrene-(EGDMA)/DCQ[g]	FAAS	200	2.25	0-500	2.0	44
DMC/SDS-ACMNPs[h]	FAAS	320	1.9	10-100	4.6	45
Silica gel/PEG[i]	FAAS	166.6	3.13	2-100	0.71	46
Silica gel/ aminothioanthraquinone	FAAS	N.R	<9	N.R	2.9	47
Silica gel/gallic acid	FAAS	100	5.8	1-5	0.92	48
Silica gel/ethylendiamin-2-hydroxy-3-methoxy benzaldehyde	FAAS	100	<1.32	5-100	1.3	This work

[a] Not reported

[b] Activated carbon/dithiooxamide

[c] Multi-wlled nanotubes/Di-(2-ethyl hexyl phosphoric acid)

[d] Tri n-Octyl phosphine oxide

[e] Diamino-4-(4-nitro-phenylazo)-1H-pyrazole

[f] Ethylendiaminetetraacetic acid

[g] Ethylene glycol dimethacrylate/5,7-Dichloroquinoline-8-ol

[h] dimethylglyoxim/sodium dodecyl sulfate-immobilized on alumina-coated magnetite nanoparticles
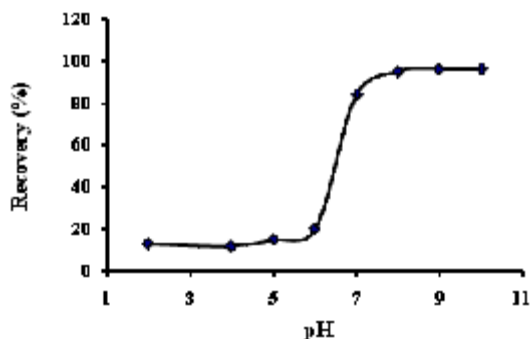
[i] polyrthylen glycol.

Fig. 1: Influence of sample pH on the recovery percentage of Ni(II) in aqueous solution. Experimental conditions: [Ni]=12.5 ng mL^{-1}, [Schiff base/silica gel]=0.02, stirring time = 60 min, HNO$_3$ 1M as eluent
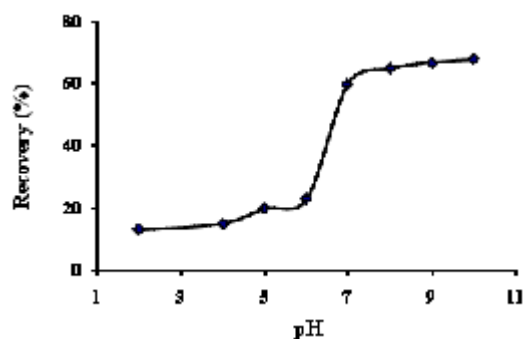

Fig. 2: Influence of sample pH on the recovery percentage of Ni(II) in phosphate buffer (0.01 M) solution. Experimental conditions: [Ni]=12.5 ng mL^{-1}, [Schiff base/silica gel] = 0.02, stirring time = 60 min, HNO$_3$ 1M as eluent
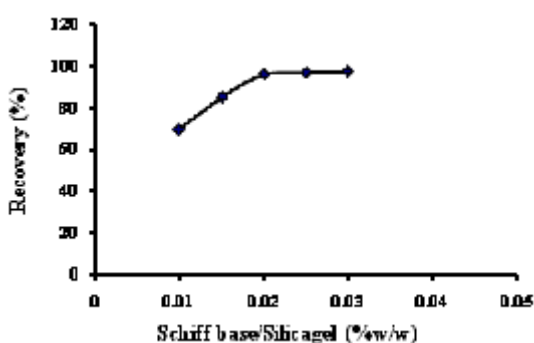

Fig. 3: Influence of schiffbase/silica gel weight percentage on the recovery percentage of Ni(II). Experimental conditions: [Ni]= 12.5 ng mL^{-1}, pH=8, stirring time = 60 min, HNO$_3$ 1M as eluent
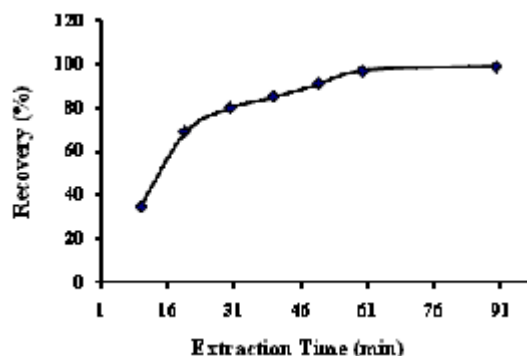

Fig. 4: Influence of stirring time on the recovery percentage of Ni(II). Experimental conditions: [Ni]= 12.5 ng mL^{-1}, pH=8, [Schiff base/silica gel]= 0.02, HNO$_3$ 1M as eluent
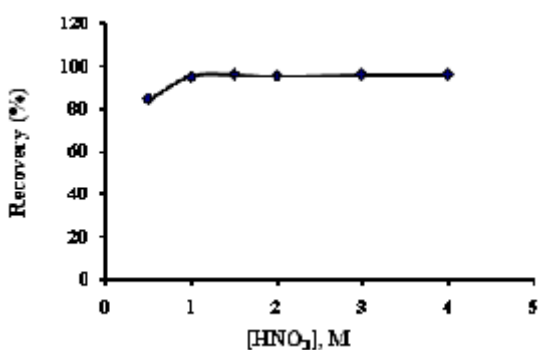

Fig. 5: Influence of eluent concentration on the recovery percentage of Ni(II). Experimental conditions: [Ni]=12.5 ng mL^{-1}, [Schiff base/silica gel]= 0.02, pH=8, stirring time = 60 min.
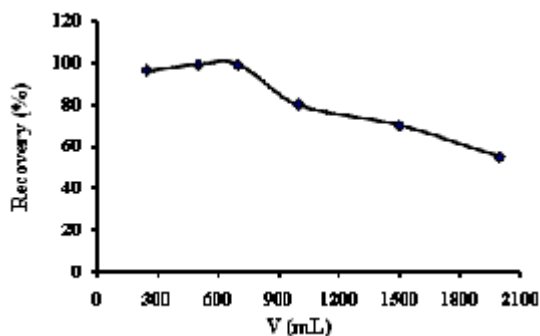

Fig. 6: Influence of volume of Ni(II) on the recovery percentage of Ni(II). Experimental conditions: [Ni]=12.5 ng mL^{-1}, [Schiff base/silica gel] =0.02, pH=8, stirring time = 60 min, HNO$_3$ 1M as eluent
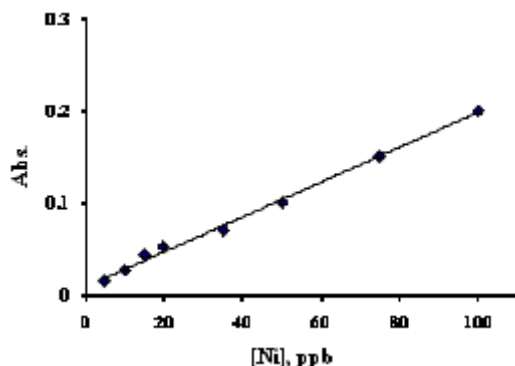
Fig. 7: Calibration curve for different concentration on Ni(II). Experimental conditions: [Schiff base/silica gel] = 0.02, pH=8, stirring time = 60 min, HNO$_3$ 1M as eluent, [Ni]=5, 10, 15, 20, 35, 50, 75, 100 ng mL^{-1}.

$$Y = 0.0103X + 0.0019, R^2 = 0.9965$$

The preconcentration factor of 100-times was required due to Ni(II) concentration as low as 12.5 ng mL^{-1} in water. Relative standard deviations (RSD) were 1.32, 0.6, and 1.01% for 700 mL of 5, 10, and 15 ng mL^{-1} of Ni(II) solution respectively. The detection limit (LOD) defined as three times the standard deviation of the blank was 1.3 ng mL^{-1}.

In addition, the accuracy of the method was studied by examining the recoveries of Ni(II) from mineral water samples fortified with this element. From the results of Table 3, it was found that up to 90% of the Ni(II) added to water samples was recovered.

CONCLUSION

The preconcentration method described by using Schiff base-loaded silica gel for the determination of Ni(II) in water samples has a good accuracy, repeatability, and sensitivity. The sensitivity of FAAS was increased up to 100-times using the optimized method. So, the detection limit was found to be 1.3 ng mL^{-1} when a sample volume of 700 mL was preconcentrated to a final volume of 7.0 mL. The RSD of the method was < 1.32. A comparison of the characteristic data between some existing reported methods and the proposed method for separation/preconcentration and determination of Ni(II) by FAAS [36-48] is given in Table 4. As Table 4 shows, the proposed method exhibits a comparable capacity factor, a low detection limit and a wide linear range, as well as being a convenient, safe, simple, and inexpensive method for the determination of trace quantities of Ni(II) in real samples giving satisfactory results.

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