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Application of a New Schiff Base as Modifier of Octadecyl Silica Membrane Disk for Solid Phase Extraction and Determination of Ultra Trace Nickel(II) from Natural Water and Food Additives

MOHAMMAD HOSSEIN MASHHADIZADEH*, TAYEBEH SHAMSPUR
and IRAN SHEIKH SHOAIE
Chemistry Department, Shahid Bahonar University of Kerman, Kerman 76169-1411, Iran
Fax: (98)(341)3221452; E-mail: mashhadizadeh@yahoo.com

A simple, rapid and cost effective pre-concentration method is described for the determination of trace amount of nickel(II) in water and food samples by flame atomic absorption spectrometry. The method is based on sorption of nickel(II) ions on octadecyl bonded silica membrane disk modified with a new Schiff base bis[5-((4-nitrophenyl)azo salicylaldehyde)] and then eluted with HCl and determined by flame atomic absorption spectrometry. Extraction efficiency and the pH of sample, optimum amount of Schiff base, type and optimum amount of eluent and flow rates of sample and eluent were evaluated. The analytical figures of merit for the determination of nickel(II) are as follows: pre-concentration factor 100, detection limit (3s) 0.5 ng/mL and precision (RSD) 1.4%. The method has been used for the determination of nickel in natural water samples and in baking powder and soda powder.

Key Words: **Nickel, Solid phase extraction, Atomic absorption spectrometry, Octadecyl bonded silica membrane disk, Baking powder, Soda powder.**

INTRODUCTION

Nickel is an important element, not only for industry but for biological systems as well. For many decades, nickel was regarded as a potentially toxic element, since its concentration in various foods was higher than that needed for living organisms. More recently, it is now considered a possible essential element for plants, although deficiencies can occur under certain circumstances. However, nickel can be toxic at high concentrations and can be a problem in some soils[1]. Hence, the need for nickel ion determination in clinical and food analysis and environmental monitoring has led to a number of methods for the measurement of this analyte[2, 3]. Many conventional methods, such as gravimetry with dimethylglyoxime[4], are time consuming and/or require use of reagents.

The atomic spectrometry techniques are extensively employed for the quantification of metallic species. In this way, flame atomic absorption spectrometry presents desirable characteristics, such as low costs, operational facilities, high analytical frequency and good selectivity. However, this technique presents some limitations, mainly those related to sensitivity[5,6]. According to these limitations, it is evident that despite recent advances in analytical instrumentation, the use of separation and preconcentration procedures is still often necessary before the determination step[7,8].

Solid phase extraction (SPE) is an attractive technique that reduces consumption of and exposure to solvent, disposal costs and extraction time[9,10]. Recently, the SPE disks modified by suitable ligands are successfully used for the separation and sensitive determination of metal ions[11-14].

The Schiff bases derived from salicylaldehyde (salen) polydentate ligands are known to form very stable complexes with transition metal ions. The resulting salen complexes have attracted increasing attention, mainly due to their peculiar properties and their reactivity mainly in the area of binding small molecules. As is known, Schiff bases are reagents, which are becoming increasingly important in the pharmaceutical, dye and plastic industries as well as for liquid-crystal technology and mechanistic investigations of the drugs used in pharmacology, biochemistry and physiology. In addition, there are potential applications as metallomesogens and their use in development of photonic devices[15-22]. However, despite extensive scientific reports on the synthesis, characterization and crystalline structure of the transition metal-salen complexes, there have been only limited reports on the use of salen molecules on analytical applications[11,12,23]. Recently, the synthesis of some Schiff bases and their use as ion carrier for the construction of liquid membrane electrodes[24-26] has been reported.

The aim of this work was the development of an efficient, highly selective, rapid and highly sensitive method for the selective extraction and pre-concentration of trace amount of Ni^{2+} ions from aqueous solutions using octadecyl silica membrane disks modified with Schiff base bis[5-((4-nitrophenyl)azo salicylaldehyde)] (Fig. 1) and its determination by flame atomic absorption spectrometry.

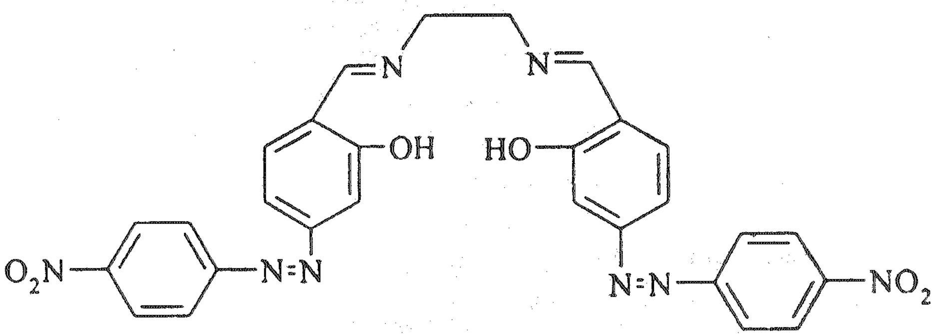

Fig. 1. Structure of bis[5-((4-nitrophenyl)azo salicylaldehyde)]

EXPERIMENTAL

All chemicals were of analytical reagent grade and were provided by Merck (Darmstadt, Germany). Doubly de-ionized water was used throughout. Working standard solutions of nickel were prepared by appropriate stepwise dilution of a 1000 mg L^{-1} stock standard solution with a 5% hydrochloric acid stock standard solution (Titrisol, Merck) to the required concentration levels just before use and their pH was adjusted with dilute NaOH. Ligand bis[5-((4-nitrophenyl)azo salicylaldehyde)] was synthesized and purified as described elsewhere[25].

The determination of nickel was carried out on a Varian Spectra AA220 atomic absorption spectrometer (AAS) with a nickel hollow cathode lamp and a deuterium background corrector, at a wavelength 232.0 (resonance line) using air-acetylene flame and slit 0.2 nm. AAS determination of all other cations was performed under the recommended conditions for each metal ion in the manual of the instrument. A digital pH-meter, Metrohm model 632, equipped with a combined glass calomel electrode, was used for the pH adjustments.

Extractions were performed with 47 mm diameter × 0.5 mm thickness 3 M Empore^{TM} membrane disks containing octadecyl (C_{18})-bonded silica (8 μm particle size, 60 Å pore size) distributed by Varian. The disks were used in conjunction with a standard Sartorius 47 mm filtration apparatus. After placing the membrane disk in the filtration apparatus, it was washed with 10 mL methanol and 10 mL acetonitrile to remove all contaminants arising from the manufacturing process and the environment. After drying the disk by passing air through it for several minutes, it was dried inside an oven at 60°C. Then, a solution of 7 mg ligand bis[5-((4-nitrophenyl)azo salicylaldehyde] dissolved in 2 mL DMF was introduced into the reservoir of the apparatus and was washed with 25 mL water and then 5 mL methanol and finally dried by passing air through it. In this step, the membrane disk modified by the Schiff base ligand was ready for sample extraction.

The general procedure for the extraction of Ni^{2+} ions on the membrane disk was performed as follows: The modified disk was first washed with 2 mL methanol followed by washing with 25 mL water. This step pre-wets the surface of the disk prior to the extraction of Ni^{2+} ions from water. It was practically important to wet the surface of the disk with methanol when the extraction of nickel ions was underway. Then 500 or 1000 mL of the sample solutions containing μg amounts of Ni^{2+} was passed through the membrane at a flow rate of 15–20 mL/min. With this procedure, Ni^{2+} ions in water samples were quantitatively adsorbed on the modified disk and consequently were eluted by two 5.0 mL portions of 0.5 M hydrochloric acid solution at a flow rate of 10 mL/min. Each portion was collected in a 5 mL volumetric flask and diluted to the mark with water (if necessary) and the amount of nickel was then determined by FAAS.

Sample preparation: Samples of wastewater and river water were collected from the Sarcheshme (near the copper mine of Sarcheshme) and Karoun river. Recovery experiments were also conducted by spiking the samples with appropriate amounts of nickel and its nickel content determined by this method. A sample of 1.00 g baking powder or soda powder was dissolved in a mixture of 0.5 mL concentrated HNO_3 and 20 mL distilled water. The solution was neutralized by using 1.0 M NH_3 and then separation/preconcentration procedures given above were separately applied and its nickel content determined by FAAS method. Recovery experiments were also conducted by spiking the samples with appropriate amounts of nickel and its nickel content determined by this method.

RESULTS AND DISCUSSION

Before the application of octadecyl silica membrane disk modified with ligands bis[5-((4-nitrophenyl)azo salicylaldehyde)] to solid phase extraction of nickel ion, the effects of several experimental parameters on the preconcentration and determination of Ni^{2+} was studied by spiking 50 mL of distilled water with 2.5 μg of nickel and using the procedure described in the general procedure. These parameters comprise the nature and concentration of eluent, pH of sample, eluent and sample flow rate and sample volume.

In order to choose a proper eluent for the retained Ni ions, after the extraction of 2.5 μg Ni from 50 mL of aqueous solution, the Ni ions were stripped from the modified disk with varying volumes of different stripping agents including sodium thiosulfate ($Na_2S_2O_3$), thiourea ($(NH_2)_2CS$), potassium thiocyanate (KSCN), ethylene diamine tetraacetic acid (Na_2EDTA), nitric acid and hydrochloric acid. The results are summarized in Table-1. It is obvious that elution is quantitative with KSCN, EDTA and HCl solutions; subsequent studies were carried out with 0.5 M hydrochloric acid solution. The influence of varying concentration of HCl on the recovery of nickel was also investigated in the range of 0.01–1.0 M. The results revealed that 10 mL of 0.5 M hydrochloric acid solution can accomplish the quantitative elution of nickel from the modified membrane disk. However, the elution was found to be 98% of nickel ions using 5 mL of 0.5 M HCl solution.

TABLE-1
PER CENT RECOVERY OF NICKEL FROM THE MODIFIED MEMBRANE DISK AS A FUNCTION OF STRIPPING SOLUTIONS AND VOLUME OF ELUENT[a]

Stripping agent	Percentage of recovery				
	First 5 mL	Second 5 mL	Third 5 mL	Fourth 5 mL	Total
$Na_2S_2O_3$ (0.1 M)	50	14	7	5	76 (±1)[b]
Thiourea (0.1 M)	52	15	8	4	79 (±1)
KSCN (0.1 M)	95	5	—	—	100 (±1)
EDTA (0.1 M)	89	14	—	—	103 (±1)
HNO_3 (0.1 M)	30	18	5	3	56 (±1)
HCl (0.01 M)	86	9.7	3	2	100.7 (±0.8)
HCl (0.05 M)	89	10.3	1.5	—	100.8 (±0.6)
HCl (0.1 M)	95	3.4	2	—	100.4 (±0.5)
HCl (0.3 M)	96	4.1	—	—	100.1 (±0.8)
HCl (0.5 M)	98	2.2	—	—	100.2 (±0.7)
HCl (1 M)	98	2.1	—	—	100.1 (±0.8)

[a] Initial samples contained 2.5 μg Ni^{2+} ion in 50 mL water.
[b] Values in parentheses are RSDs based on three replicate analyses.

Effect of pH of sample solution and flow rates: Most chelating ligands are conjugate bases of weak acid groups and accordingly, have a very strong affinity for hydrogen ions. The pH, therefore, will be a very important factor in the separation of metal ions by chelation, because it will determine the values of the conditional stability constants of metal complexes on the surface of sorbent[28]. Due to the presence of OH and NH groups on the ligand bis[5-((4-nitrophenyl)azo salicylaldehyde)] structure, it is expected that the extent of its complexation is sensitive to pH. Thus, the effect of pH on the extraction of nickel ions was investigated.

In order to study the effect of pH on the solid phase extraction of Ni^{2+} ion, the membrane disk was modified with 7 mg of bis[5-((4-nitrophenyl)azo salicylaldehyde)] and the pH of aqueous samples containing 2.5 μg Ni^{2+} was varied from 1.0–7.5, using appropriate acid or base solutions. The resulting per cent recovery *vs.* pH plot is shown in Fig. 2. As seen, the per cent recovery of Ni^{2+} ion increases with increasing pH of solution until a pH of 6.0 is reached. Quantitative extraction of nickel ion occurs at a pH range 6.0–7.5. The pH values higher than 7.5 were not tested because of the possibility of the hydrolysis of octadecyl silica in the disks[13, 14]. Furthermore, at high pH deprotonation of —OH groups will occur and the solubility of ligand in water will largely increase. Thus, before the quantitative retention of nickel, the ligand will be eluted from the disk. The pronounced decrease in the Ni^{2+} recovery in solutions of low pH is due to the protonation of Schiff base in acid solution.

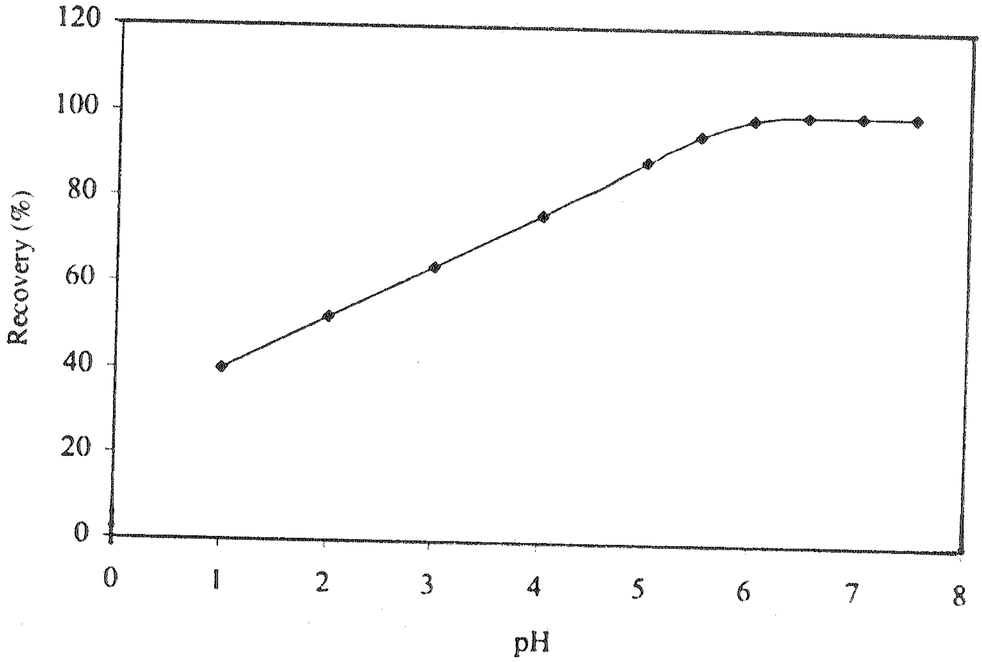

Fig. 2. Effect of pH on recovery of nickel(II) ion from membrane disks modified with bis[5-((4-nitrophenyl)azo salicylaldehyde)]. Initial samples contain 2.5 μg Ni in 50 mL aqueous sample

The influence of flow rates of the sample and stripping solutions from the modified membrane disk on the retention and recovery of nickel ions was investigated by passing 500 mL sample solutions containing 2.5 μg Ni^{2+} followed by stripping with 10 mL of a hydrochloric acid (0.5 M) solution. As shown in Fig. 3, it was found that in the range of 5–20 mL min^{-1}, the retention of nickel by the modified disk is not affected by the sample solution flow rate considerably. On the other hand, quantitative stripping of the retained nickel ions from the modified disk was achieved in a flow rate range of 5–10 mL min^{-1}. It is interesting to note that the Schiff base bis[5-((4-nitrophenyl)azo salicylaldehyde)] is protonate in acidic media, so that HCl can easily release the retained nickel ions from the modified disks.

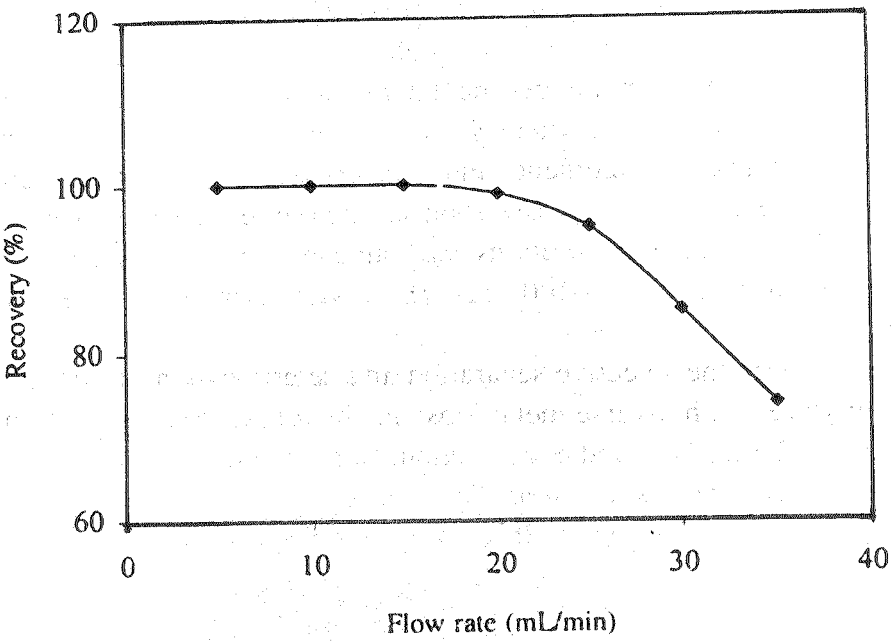

Fig. 3. Effect of flow rate of sample solution on the recovery of Ni^{2+} ion; each sample contains 2.5 μg Ni in 500 mL aqueous sample at pH *ca.*6.0

Analytical performance: When solution containing 2.5 μg of nickel in 50, 100, 250, 500, 1000, 1500 and 2000 mL water were passed through the modified disks, the Ni^{2+} was quantitatively retained from 1000 mL and smaller volumes (Fig. 4). Thus, the breakthrough volume for the method was 1000 mL. Consequently, by considering the final elution volume of 10 mL 0.5 M hydrochloric acid and the breakthrough volume of 1000 mL, an enrichment factor of 100 was easily achievable.

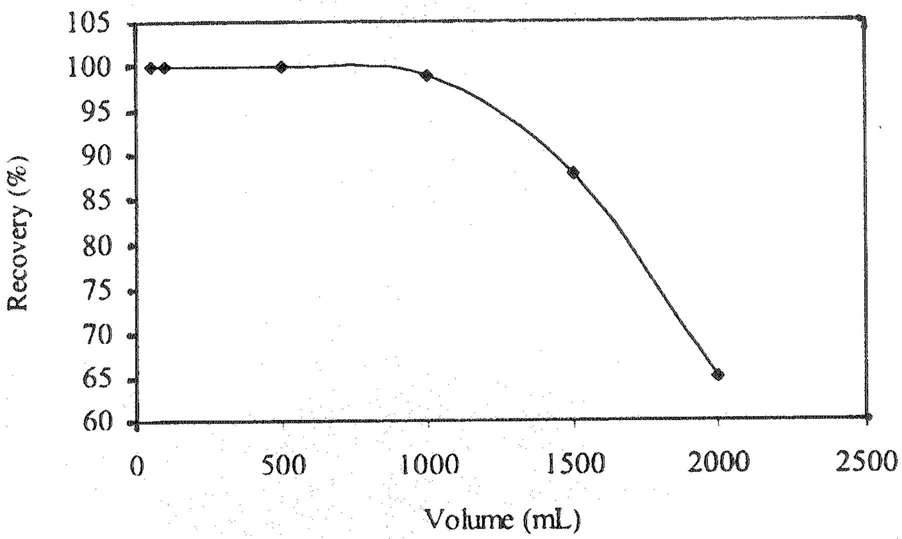

Fig. 4. Effect of sample volume on the recovery of nickel ion; each sample contains 2.5 μg Ni at pH *ca.*6.0

The maximum capacity of the membrane disk modified by 7 mg ligand bis[5-((4-nitrophenyl)azo salicylaldehyde)] was determined by passing varying portions of an aqueous 0.5 ppm nickel solution at pH about 6.5, followed by the determination of retained nickel ions using FAAS. The maximum capacity of the membrane disk was found to be 90 ± 2 μg of nickel ion on the disk.

The limit of detection (LOD) of the method for the determination of nickel was studied under the optimal experimental conditions. The LOD obtained from 3s of blank[29] ($C_{LOD} = K_bS_b/m$, where K_b is a numerical factor of 3, S_b is the S.D. of ten replicate blank measurements and m is the slope of calibration graph) is 0.5 ng/mL. The relative standard deviation for the ten replicate recoveries of 2.5 μg Ni^{2+} from 100 mL aqueous solutions was found to be ±1.4%. Linear calibration range of the method is 5.0–100 ng mL^{-1} with correlation coefficient of $r^2 = 0.9991$.

In order to study the selective separation and determination of Ni^{2+} ion from its binary mixtures with diverse metal ions, an aliquot of aqueous solutions (500 mL) containing 2.5 μg Ni^{2+} and excess amounts of diverse cations was taken and the proposed procedure was followed. The results are summarized in Table-2. The results clearly indicate that the modified membrane disk, even in the presence of mg amounts of diverse ions retains 2.5 μg of nickel(II) ions in the binary mixtures almost completely. Meanwhile, the retention of other cations by the modified disk, with the exception of Ag^+, Hg^{2+} and Cu^{2+}, is quite low and most of them can be separated almost completely from the Ni^{2+} ion.

TABLE-2

SEPARATION OF NICKEL FROM BINARY MIXTURES[a]

Diverse Ion	Amount taken (μg)	% Recovery	
		Foreign ion	Ni
Co^{2+}	600	1.1 (0.5)[b]	100.1 (1.1)[b]
K^+	200	0.0 (0.4)	100.1 (0.5)
Na^+	500	0.0 (0.2)	99.8 (0.8)
Cd^{2+}	700	1.1 (0.6)	99.5 (1.2)
Ag^+	50	25.5 (0.5)	99.4 (0.7)
Zn^{2+}	200	1.1 (0.6)	100.0 (0.8)
Mg^{2+}	200	0.5 (0.6)	101.5 (0.8)
Ca^{2+}	500	0.0 (0.7)	99.6 (1.1)
Cu^{2+}	700	1.5 (0.5)	100.5 (1.3)
Fe^{2+}	500	0.8 (0.2)	99.5 (1.2)
Fe^{3+}	500	8.5 (0.8)	99.5 (1.3)
Pb^{2+}	500	1.5 (0.5)	101.2 (1.1)

[a] Initial samples contained 2.5 μg Ni^{2+} and different amounts of diverse ions in 500 mL water.

[b] Values in parentheses are RSDs based on four replicate analyses.

Applications

In order to assess the applicability of the method to real samples with different matrices containing varying amounts of a variety of diverse ions, it was applied to the separation and recovery of Ni ions from two water samples that spiked with different amounts of Ni and the results are summarized in Table-3. As is obvious, the nickel ions added can be quantitatively recovered from water matrices.

TABLE-3
DETERMINATION OF NICKEL IN WATER SAMPLES AND FOOD SAMPLES

Sample	Ni^{2+} added	Found amount by standard addition method and AAS (mg/g)	Found by this method[a]	Recovery (%)
River water	5.1 μg L^{-1}	—	5.05 (0.02) μg L^{-1}	99.0 (0.5)
Sarcheshme water	3.5 μg L^{-1}	—	3.52 (0.01) μg L^{-1}	100.6 (0.4)
Baking powder 1	0	17.35	17.36 (0.7) mg/g	—
" "	5	22.34	22.40 (0.7) mg/g	100.2 (0.6)
Baking powder 2	0	24.48	25.10 (0.8) mg/g	—
" "	6	30.48	30.65 (0.7) mg/g	100.5 (0.5)
Baking soda 1	0	3.13	3.19 (0.08) mg/g	—
" "	1.2	4.32	4.41 (0.05) mg/g	101.7 (0.6)
Baking soda 2	0	3.24	3.21 (0.06) mg/g	—
" "	1.5	4.75	4.68 (0.07) mg/g	98.0 (0.5)

[a]Values in parentheses are RSDs based on five replicate analyses

The analytical system was used for nickel determination in some food additive samples obtained from supermarkets in Kerman, Iran. As can be seen from Table-3, recovery obtained by the standard addition method proved that the developed procedure is not affected by matrix interferences and can be applied satisfactorily for natural food additives.

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