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Determination of nickel in natural waters by FAAS after sorption on octadecyl silica membrane disks modified with a recently synthesized Schiff's base

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Abstract

A simple, highly sensitive, accurate and selective method for the determination of trace amounts of Ni^{2+} ions in water samples is proposed. The method is based on the separation and preconcentration of Ni^{2+} on an octadecyl-bonded silica (ODBS) membrane disk modified by a recently synthesized Schiff's base *N*,*N*′-bis (3-methylsalicylidene) ortho phenylene diamine (MSOPD) at pH 7. The synthesis of this extractant ligand is also described. The retained nickel on the membrane was eluted with 2×5 ml 0.5 M HNO_3 and measured by flame atomic absorption spectrometry (FAAS) at 232.0 nm. The extraction efficiency and the influence of the type and least amount of eluent for the stripping of Ni^{2+} from the disks, pH, flow rates of sample solution and eluent, amount of MSOPD, effect of other ions, and breakthrough volume were evaluated. The maximum capacity of the membrane disks modified by 3 mg of MSOPD was found to be 146 ± 4 μg Ni^{2+}. The 3σ limit of detection of the method was 30 ng per 1000 ml and also an enrichment factor of 250 was obtained. The proposed method has been applied to the determination of nickel in several water samples with satisfactory results.

Keywords: Nickel determination; SPE; Preconcentration; Separation; *N*,*N*′-bis (3-methylsalicylidene) ortho phenylene diamine; FAAS

1. Introduction

The importance of the determination of heavy metal ions, such as nickel, in environmental samples can hardly be overemphasized because they have undoubtedly a serious potential hazard to the human organism. The main sources of nickel in aquatic systems are from dissolution of rocks and soils, biological cycles, atmospheric fallout, and especially industrial processes and water disposal [1]. Nickel is the metal component of the enzyme urease and as such considered to be essential to plants. Evidence has also been presented nickel being essential to some domestic animals. Essentiality of nickel to man does not yet seem to have been demonstrated. More attention has been focussed on the toxicity of nickel in low concentrations, such as the fact that nickel can cause allergic reactions and that certain nickel compounds are carcinogenic [2]. The maximum recommended concentration of nickel ion in drinking water for livestock is 2.5 mg l^{-1} [3]. For drinking water for human consumption the upper limits are even less. The development of reliable, yet affordable, analytical approaches for the determination of Ni^{2+} in low concentration levels seems worthwhile.

Nickel determination in water samples could be carried out directly by electrothermal atomic absorption spectrometry (ETAAS) or by inductively-coupled plasma mass spectrometry (ICP-MS), which have usually enough limit of detection [4,5]. Flame atomic absorption spectrometry (FAAS), which is an available technique in most laboratories and is normally less subjected to interferences than ETAAS or ICP-MS, requires the use of a preconcentration step in order to reach an appropriate level of sensitivity. Preconcentration of the nickel ion prior to analysis can not only concentrate the analyte but also simplify the matrix of the sample. Solid-phase extraction (SPE) has received much attention in recent years for the analysis of trace con-

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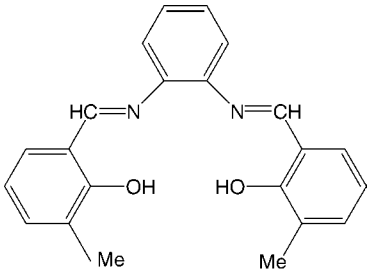

Fig. 1. Structure of *N*,*N*′-bis (3-methylsalicylidene) ortho phenylene diamine (MSOPD).

centrations in samples. This technique reduces consumption of and exposure to solvent, disposal costs, and extraction time [6,7]. Octadecyl-bonded silica (ODBS) membrane disks have been utilized for the extraction and analysis of many different organic and environmental matrices [8,9]. Moreover, these membrane disks modified by suitable ligands are successfully used for the separation and sensitive determination of metal ions [10,11].

The Schiff's bases derived from salicylaldehyde (salens) as polydentate ligands are known to form very stable complexes with transition metal ions [12,13]. According to our knowledge there is no method in the literature based on the SPE of nickel ions on the modified ODBS membrane disks with Schiff's bases. The aim of this work was the development of a highly sensitive and efficient method for the selective extraction and concentration of trace amounts of Ni^{2+} ions from aqueous media using ODBS membrane disks modified with a newly synthesized Schiff's base *N*,*N*′-bis (3-methylsalicylidene) ortho phenylene diamine (MSOPD), with the structure that is shown in Fig. 1, and its determination by flame atomic absorption spectrometry.

2. Experimental

2.1. Reagents

2.1.1. Synthesis of MSOPD

2-Hydroxy-3-methyl-benzaldehyde(1.36 g, 10 mmol) was dissolved in methanol (15 ml) and then ortho-phenylenediamine (0.54 g, 5 mmol) was added to this solution. The resulting mixture was refluxed and stirred for 30 min. The reaction mixture was cooled to room temperature and washed with cold methanol. The product was recrystallized from methanol to give Schiff base MSOPD in 95% yield as yellow crystaline solid, m.p. 113 °C, IR(KBr, Cm^{-1}) 740(m), 1290(s), 1520(s), 1640(s, C=N), 2890–2970(m), 3300–3500(m, br); ^{1}H NMR($CDCl_3$) δ(ppm), 1.9(s, 6 H), 6.2–7.4(m, 10 H), 8.3(s, 2H), 12.1–13(s, br, 2H).

2-Hydroxy-3-methyl-benzaldehyde as starting material for synthesis of Schiff's base MSOPD was prepared through procedure that was recently reported [14].

2.1.2. Standard nickel solution

Dissolve 0.2000 g of high purity nickel in 10 ml concentrated nitric acid, dilute with doubly distilled water to volume in a 1000 ml calibration flask and mix well. Working solutions were prepared by appropriate dilution of the stock solution in doubly distilled water.

2.1.3. Phosphate buffer solution (pH = 7)

Dissolve 0.375 g of potassium dihydrogen phosphate and 0.556 g of disodium hydrogen phsphate in doubly distilled water and dilute to 100 ml in a calibrated flask.

All other reagents were of analytical grade reagents.

2.2. Apparatus

The nickel determination was carried out on a Shimadzu AA-680 flame atomic absorption spectrometer with a hollow cathode lamp at a wavelength of 232.0 nm using an air–acetylene flame and a deuterium background corrector. The operating parameters were set as recommended by the manufacturer. The AAS determination of all other cations was performed under the recommended conditions for each metal. The pH was determined with a model 691 Metrohm pH meter with a combined glass–calomel electrode.

2.3. Filter preparation

Extractions were performed with Empore membrane disks (47 mm diameter and 0.5 mm thick) containing ODBS (8 μm particles, 6 nm pore size) from xx. The typical composition of the disks was 90% w/w ODBS and 10% w/w PTFE fibers. The disks were used in conjunction with a standard S&S 47 mm filtration apparatus connected to a vacuum. In order to remove potential interferences and to ensure optimal extraction of the analyte of interest, the disk cleaning and conditioning should be done before its use. Thus, after placing the membrane disk in the filtration apparatus, 10 ml methanol was poured onto the disk and immediately drawn through the disk by applying a slight vacuum to remove all contaminants arising from the manufacturing process and the environment. After all of the solvent has passed through the disk, passing air through it for a few minutes dried it. This procedure is especially important for the disks, which are used for the first time. After drying the disk, a solution of 3 mg MSOPD in 3 ml chloroform was introduced onto the disk and allowed to penetrate inside the solid phase completely. Then, the solvent was evaporated at 60 °C. Then the modified disk was washed and preconditioned by passing a 10 ml portion of buffer solution (pH = 7) to prewet the surface of the disk prior to the extraction of Ni^{2+} 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 contact the surface of the disk.

2.4. Extraction, elution and determination

The general procedure for the extraction of Ni^{2+} ions on a membrane disk was as follows: 100 ml of the sample solution containing 2 ml of pH 7 phosphate buffer and 10 μg Ni^{2+} was passed through the modified membrane, at 20 ml min^{-1} flow rate. The disk was dried completely by passing air through it. After the extraction, a 25 × 200 mm test tube was then placed under the extraction funnel. The nickel ions was stripped from the modified disk using 2 × 5 ml of 0.5 M solution of nitric acid at 5 ml min^{-1} flow rate. The nickel concentration was then determined at 232.0 nm by flame atomic absorption spectrometry against a reagent blank (external linear calibration range 0.2–2 μg ml^{-1}, $r = 0.9998$).

2.5. Analytical procedure for Ni^{2+} in water samples

A 1000 ml aliquot of the water sample was first passed through a **xx** filter paper to remove particles. Then the filtrate was passed through an ODBS membrane disk without MSOPD to remove organic compounds that may be present in the water and then complete the determination as recommended procedure.

3. Results and discussion

N,*N*′-bis (3-methylsalicylidene) ortho phenylene diamine with two oxygen, two nitrogen donating Schiff's base is insoluble in water at pH = 7. In order to confirm the stochiometry of the complex additional spectrophotometric measurements were performed by using continuos variations or Job's method in methanol solvent, and a 1:1 stochiometry of the complex was found. Thus, we decided to examine the capability of MSOPD as a suitable reagent for the preconcentration and separation of Ni^{2+} ions via solid-phase extraction by ODBS membrane disks. Some preliminary experiments were carried out in order to investigate the quantitative retention of Ni^{2+} ions by an ODBS membrane disk in the absence and presence of MSOPD. It was found that the bare membrane disk itself did not show any tendency for the retention of Ni^{2+} ions, while the modified disks with MSOPD are capable to retain Ni^{2+} ions in the sample solution (100 ml buffered solution at pH 7, containing 10 μg Ni^{2+}).

3.1. Choice of eluent

In order to choose a proper eluent for the retained Ni^{2+} ions after extraction of 10 μg of nickel in a 100 ml buffered solution by the modified disks, the nickel ions were stripped with 2 × 5 ml of different concentrations of various mineral acids, and the results are listed in Table 1. Results showed that all acids could afford the quantitative elution of Ni^{2+} from the modified disk. Subsequent quantitative elution of the complex was carried out with 0.5 M HNO_3 solution. The reason for choice of nitric acid as eluent was that nitrate ion is reported to be a more acceptable matrix for both flame and electrothermal AAS experiments than chloride and sulfate ions [15].

Table 1
Percent recovery of Ni^{2+} from modified membrane disks using 2 × 5 ml of different stripping acid solutions[a]

Acid	Concentration (M)		
	1.0	0.5	0.2
HNO_3	101.5	100.0	97.5
HCl	100.1	100.2	93.0
H_2SO_4	102.0	99.6	98.3

[a] Initial samples contained 10 μg Ni^{2+} ion in 100 ml of water (pH = 7).

3.2. Effect of pH on the adsorption of Ni^{2+}

The influence of the pH of aqueous sample on the recovery of 10 μg of Ni^{2+} from 100 ml solution was studied in the pH range 2–7.5. The pH was adjusted by using 0.01 M of either nitric acid or sodium hydroxide solutions. The results obtained are shown in Fig. 2. Maximum and constant retention of Ni^{2+} ion by the modified membrane disk was obtained in the pH range 6–7.5. Therefore, a pH 7 was chosen for the determination. Higher pH values (>7.5) were not tested because of the possibility of the hydrolysis of ODBS in the disks. Addition of 1–3 ml phosphate buffer was sufficient for pH adjustment. Hence, an addition of 2 ml was chosen.

3.3. Effect of flow rates

The effect of flow rates of the sample and stripping solutions on the retention and recovery of Ni^{2+} ion was investigated. It was found that, in the range of 5–35 ml min^{-1}, the retention of nickel by the membrane disk was not considerably affected by the sample solution flow rate. Similar results for the extraction of organic [8,9] and inorganic [10,11] materials by ODBS disks have been reported in the literature. The flow rate of sample was maintained at 20 ml min^{-1}

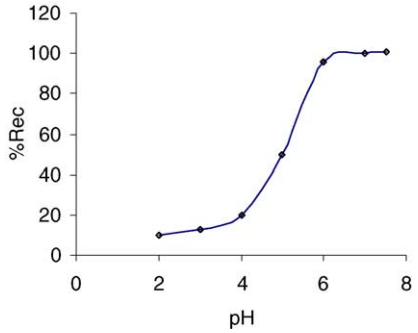

Fig. 2. Effect of pH on the extraction of Ni^{2+} by the modified membrane disk.

Table 2
Tolerance limits of diverse ions on the recovery of 10 μg of Ni^{2+} from 100 ml buffer solutions (pH = 7) by the modified membrane disks[a]

Ion	Found of foreign ion (%)	Tolerated ratio of foreign ion to nickel ion
Ca^{2+}	1.3 (1.9)	5000[b]
Mg^{2+}	1.4 (2.2)	5000[b]
Li^{+}	0.9 (1.7)	10000[b]
Na^{+}	1.5 (1.6)	10000[b]
K^{+}	0.3 (2.2)	10000[b]
Ba^{2+}	0.2 (1.5)	430
Co^{2+}	1.5 (3.1)	200
Cr^{3+}	3.1 (2.3)	530
Ag^{+}	0.6 (1.1)	300
Mn^{2+}	1.0 (1.2)	760
Cu^{2+}	4.5 (2.7)	230
Cd^{2+}	1.5 (2.5)	560
Fe^{3+}	5.0 (1.5)	300
Zn^{2+}	3.5 (1.3)	390

[a] Values in parenthesis are RSDs based on three replicate analysis.
[b] Above of which was not tested.

through the experiment. Quantitative stripping of nickel ions from the disk achieved in a flow rate range of 1–10 ml min^{-1}, using 2 × 5 ml of 0.5 M HNO_3 as a stripping solution. At higher flow rates, a large volume of eluent was necessary for the quantitative stripping of Ni^{2+} ions. Hence, subsequent experiments were carried out with a flow rate of 5 ml min^{-1}.

3.4. Effect of amount of MSOPD

In order o investigate the optimum amount of MSOPD on the quantitative extraction of nickel by the membrane disk, extraction of 10 μg of Ni^{2+} from 100 ml solution under the optimal conditions was conducted by varying the amounts of ligand from 1 to 6 mg. In all cases, the extraction of nickel was found to be quantitative. Hence, subsequent SPE experiments were carried out with 3 mg of the ligand.

3.5. 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 loss of analyte during elution of the sample. The breakthrough volume of the sample solution was tested by dissolving 10 μg nickel in 100, 300, 700, 1000, 1500, and 2500 ml of water 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 grater than 2500 ml. Consequently, by considering the final elution volume of 10 ml and the sample solution volume of 2500 ml, an enrichment factor of 250 was easily available.

The maximum capacity of the disk modified by 3 mg MSOPD was determined by passing 100 ml portions of an aqueous solution (pH = 7) containing 1000 μg Ni^{2+} through the disk, followed by determination of the retained Ni^{2+} ions using FAAS. The maximum capacity of the disk obtained from three replicate measurements was 146 ± 4 μg of nickel on the disk.

The limit of detection (LOD) of the proposed method for the determination of nickel was studied under the optimal experimental conditions. The LOD based on 3σ of the blank

Table 3
Recovery of nickel added to 1000 ml of different water samples (pH = 7.0)[a]

Sample	Ni^{2+} added (μg)	Ni^{2+} determined (μg l^{-1})	Recovery (%)
Tap water	0.0	1.5 (2.5)	–
	5.0	6.2 (1.9)	94.0
	10.0	11.4 (2.2)	99.0
River water	0.0	1.12 (3.0)	–
	5.0	6.09 (2.1)	99.4
	10.0	11.01 (2.0)	98.9
Mahmood-Abad shore	0.0	3.17 (0.5)	–
	5.0	8.2 2(1.2)	101.0
	10.0	13.06 (2.3)	98.9
Anzali shore	0.0	5.64 (1.7)	–
	5.0	10.57 (1.5)	98.6
	10.0	15.73 (3.1)	100.9
Synthetic sample 1 Na^{+}, Ag^{+}, Ca^{2+}, Zn^{2+}, Fe^{3+}, Cr^{3+}, Mn^{2+}, 2 mg of each cation	0.0	n.d.	–
	5.0	4.66 (1.3)	93.2
	10.0	9.39 (1.9)	93. 9
Synthetic sample 2 K^{+}, Li^{+}, Mg^{2+}, Ba^{2+}, Cd^{2+}, Co^{2+}, Cu^{2+}, 2 mg of each cation	0.0	n.d.	–
	5.0	4.80 (2.2)	96.0
	10.0	9.74 (1.9)	97.4

[a] Values in parenthesis are RSDs based on three replicate analysis; n.d.: not determined.

is 30 ng per 1000 ml. The reproducibility of the proposed method for the extraction and determination of 10 μg nickel from 100 ml water was also studied. The results obtained on 10 replicate measurements revealed a RSD of 2%.

3.6. Effect of foreign ions

The effect of other cations on the determination of nickel with MSOPD was studied by adding a known quantity of the desired ion to 100 ml aliquot of aqueous solution containing 10 μg nickel and 2 ml of pH 7 phosphate buffer, and the recommended procedure was followed. The tolerated ratios of foreign ions to nickel ion and the amounts of adsorbed foreign ions are listed in Table 2. The tolerance limit of foreign ions was taken as that value which caused an error of not more than ±5% in the absorbance. Most of the cations examined did not interfere with the extraction and determination of Ni^{2+}. Meanwhile, the retention of other cations by the disk was very low, and they could be separated from the Ni^{2+} ion.

3.7. Analysis of water samples

To test the applicability of the procedure developed, it was applied to the extraction and determination of nickel content from different water samples. Tap water (Tehran, taken after 10 min operation of tap), river water (Chalous road river, 10 January, 2003), two sea water samples (taken from Caspian sea near the Mahmood-Abad and Anzali shores, 23 December 2002), and two synthetic samples were analysed (Table 3). As can be seen from Table 3, the added nickel ions can be quantitatively recovered from the seawater samples by the aforementioned procedure, being thus a guarantee of the accuracy of the SPE and FAAS determination of nickel ion in sea water.

4. Conclusion

Results presented in this work well demonstrate the tremendous possibilities offered by the solid-phase extraction of trace amounts of Ni^{2+} in water samples using octadecyl-bonded silica membrane disks modified by a newly synthesized Schiff's base, *N*,*N*′-bis (3-methylsalicylidene) ortho phenylene diamine and its determination by flame atomic absorption spectrometry. The method developed is a precise and accurate alternative to conventional procedures for determining nickel in water samples. In conclusion, the developed SPE method has been successfully used on a routine basis and allows the quantitation in water samples.

It opens exciting possibilities for the determination of nickel in other samples and by other techniques, which some studies on this direction are now in progress in our laboratory.

References

[1] E. Merian (Ed.), Metals and their Compounds in the Environment, vol. 22 (part II), VCH, New York, 1991, pp. 1101.
[2] H.A. Mckenzie, L.E. Smythe, Quantitative Trace Analysis of Biological Materials, Elsevier, Amsterdam, 1988.
[3] H.L. Bohn, B.L. Mc Neal, G.A. O'Connor, Soil Chemistry, second ed., Wiley Interscience, Chichester, 1985.
[4] T. Kempf, M. Sonneborn, Mikrochim. Acta II 5–6 (1983) 445.
[5] J.L. Fernandez-Turiel, J.F. Llorens, F. Lopez-Vera, C. Gomez-Artola, I. Morell, D. Gimeno, J. Fresenius, Anal. Chem. 368 (2000) 601.
[6] R.E. Majors, LC–GC 4 (1989) 972.
[7] D.F. Hagen, C.G. Markell, G.A. Schmitt, D.D. Blevins, Anal. Chim. Acta 236 (1990) 157.
[8] Y. Yamini, A. Khorasani, J. High Resolut. Chromatogr. 17 (1994) 634.
[9] D.C. Messer, L.T. Taylor, J. Chromatogr. Sci. 33 (1995) 290.
[10] M. Shamsipur, A.R. Ghiasvand, Y. Yamini, Anal. Chem. 71 (1999) 4892.
[11] Y. Yamini, M. Shamsipur, Talanta 43 (1996) 2117.
[12] M. Calligaris, R. Randaccio, in: G. Wilkinson, R.D. Gillard, Mc Cleverty (Eds.), Compertensive Coordination Chemistry, Vol. 2, Oxford, London, 1987 (Chapter 20).
[13] D.A. Alwood, Coord. Chem. Rev. 195 (1997) 267.
[14] M. Mazlum Ardekany, A.A. Ensafi, H. Naeimi, A. Dastanpour, A. Shamelli, Russ. J. Electrochem. 39 (2003) 269.
[15] B. Welz, Atomic Absorption Spectrometry, VCH, Amesterdam, 1985.