ECLÉTICA
Química
www.scielo.br/eq
www.ecletica.iq.unesp.br
Volume 33, número 2, 2008

Solid phase extraction of zinc with octadecyl silica membrane disks modified by N,N'-disalicylidene-1,2-phenylendiamine and determination by flame atomic absorption spectrometry

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Abstract: A procedure for separation and preconcentration of trace amounts of Zn(II) from aqueous media is proposed. The procedure is based on the adsorption of Zn^{2+} on octadecyl bonded silica membrane disk modified with N,N'-disalicylidene-1,2-phenylendiamine at pH 7. The retained zinc ions were then stripped from the disk with a minimal amount of 1.5 mol L^{-1} hydrochloric acid solution as eluent, and determined by flame atomic absorption spectrometry. Maximum capacity of the membrane disk modified with 5 mg of the ligand was found to be 226 µg Zn^{2+}. The relative standard deviation of zinc for ten replicate extraction of 10 µg zinc from 1000 mL samples was 1.2%. The limit of detection of the proposed method was 14 ng of Zn^{2+} per 1000 mL. The method was successfully applied to the determination of zinc in natural water samples and accuracy was examined by recovery experiments and independent analysis by graphite furnace atomic absorption spectrometry (GFAAS).

Keywords: zinc; solid phase extraction; octadecyl silica membrane disk; flame atomic absorption spectrometry.

Introduction

Zinc has been known to be an essential trace element for humans, plants and animals. It is a cofactor for more than 300 enzymes, particularly for RNA and DNA polymerases, and for enzymes involved in protein synthesis and cell growth [1, 2]. Zinc deficiency resulting from poor diet, alcoholism and malabsorption, causes dwarfism, hypogonadism and dermatitis; while toxicity of zinc, due to excessive intake, may lead to electrolyte imbalance nausea and lethargy [3, 4].

Metallic zinc has many commercial uses; it has been used as coating to prevent rust, in dry cell batteries and also it has been mixed with other metals to make alloys like brass and bronze. Zinc compounds are widely used in industry to make white paints, ceramics, rubber, wood preservatives, dyes and fertilizers. Thus, the widespread use of zinc and its compounds has led to an increase in zinc levels monitored in environment to safeguard human life [5, 6].

Zinc concentration in unpolluted water samples is very low. Therefore, very sensitive analytical techniques such as electrothermal atomic absorption spectrometry (ETAAS) [7, 8] or inductively coupled plasma-mass spectrometry (ICP-MS) [9, 10] are required for its determination. However, inductively coupled plasma-atomic emission spectrometry (ICP-AES) [11] and flame atomic absorption spectrometry (FAAS) [12] do not have sufficient sensitivity for direct trace determinations of zinc. Thus, for lowering the detection limits of zinc analysis by these techniques a separation/preconcentration step is required. Various procedure for the separation and preconcentration of trace amounts of zinc have been developed, including liquid-liquid extraction [13], cloud point extraction [14, 15], precipitation [16] membrane-based extraction [17] and solid phase extraction [18]. The high enrichment factors possible in SPE systems in particular, allow the analytical determination of zinc at very low level.

Over the last 15 years, solid phase extraction (SPE) using alkyl-bonded silica and other surface modified silica gel has been used as an alternative to liquid-liquid extraction in the analysis of various samples [19]. Octadecyl-bonded silica membrane disks have been widely applied in the environmental analysis of pesticides, polyaromatic hydrocarbons, substances of biochemical origin and other organic compounds [20-23]. Moreover, this sorbent has also been used for the separation and sensitive determination of metal ions. The base of metal separation by C_{18}-bonded silica membrane disk is addition of a complexing reagent to the sample solution, followed by the retention of metal complexes on the disk [24, 25]. Membrane disk has also been modified by chelating agents for selective extraction and determination of metal ions [26-30]. Schiff base compounds derived from salicylaldehyde (salens and salophens) as polydentate ligands are able to form stable complexes with several transition metal ions [31-33]. These ligands have been applied as ionophore in construction of membrane electrodes [34], optical sensors [35], and as modifiers in solid phase extraction [36-38].

To the best of our knowledge, there is no previous report on the use of modified silica membrane disks for the preconcentration and separation of zinc. The aim of this study was to develop a rapid and efficient preconcentration method using an octadecyl silica membrane disk modified by N,N'-disalicylidene-1,2-phenylendiamine (Fig. 1), for preconcentration and determination of zinc in various media by flame atomic absorption spectrometry.

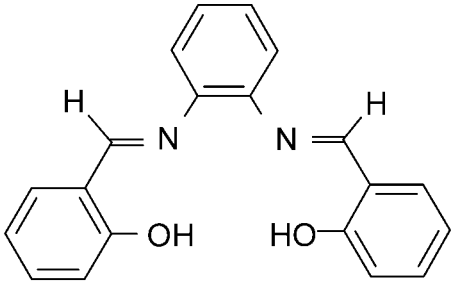

Figure 1. Structure of the N,N'-disalicylidene-1,2-phenylendiamine.

Experimental Details

Doubly distilled deionized water and analytical reagent grade chemicals were used throughout the experiments. All organic solvents used were of HPLC reagent grade and was purchased from Merck Company.

The stock solution of zinc (1000 µg mL^{-1}) was prepared by dissolving an appropriate amount of $Zn(NO_3)_2.6H_2O$ (Merck) in water and diluting to the mark in a 100 mL volumetric flask. Working solutions were prepared daily from the stock solution by appropriate dilution with water.

A buffer solution (pH 7.0) was prepared by mixing 0.1 mol L^{-1} potassium dihydrogen phosphate and 0.1 mol L^{-1} disodium hydrogen phosphate solutions in an appropriate ratio.

N,N'-disalicylidene-1,2-phenylendiamine (salophen) was prepared according to the literature by condensation of 1,2-phenylendiamine with salicylaldehyde (1:2 mol stoichiometric ratio) in methanol at room temperature and was purified by crystallization from hot ethyl acetate.[39]

A Buck Scientific atomic absorption spectrometer (model 210 VGP, USA), furnished with a zinc hollow cathode lamp and air acetylene flame was used for all measurements. The analytical wavelength and spectral bandwidth were 213.9 nm and 0.7 nm, respectively. A Metrohm pH meter model 691 was employed for pH measurements. Solid phase extractions were performed with 47 mm diameter x 0.5 mm thickness 3M Empore membrane disks containing octadecyl-bonded silica (8 µm particles, 60 Å pore size). The formulation of the disks was 90% w/w octadecyl-bonded silica and 10% w/w polytetrafluoroethylene

(PTFE). The disk was used in conjunction with standard Millipore 47 mm filtration apparatus.

Preparation of Modified Membrane Disk

The membrane disk was placed in filtration apparatus and it was washed with 10 mL methanol and 10 mL acetonitrile to remove all contaminants. The disk was dried by passing air through it for several minutes. Then, a solution of 5 mg salophen in 3 mL of dioxane was introduced to the reservoir of the apparatus and was drawn slightly through the disk by applying a slight vacuum. After complete penetration of salophen, the solvent was evaporated in an oven at 50 °C for about 15 min. Then, the modified disk was washed with 20 mL of distilled water and dried by passing air through it. The membrane disk is modified with salophen and can be used for extraction and preconcentration of zinc ions.

Analytical Procedure

The pH of the sample solution (not more than 3 L) was adjusted to 7 by addition of phosphate buffer solution (for each 100 mL of sample solution, 2 mL of buffer is enough) and was passed through the modified membrane disk at a flow rate of 40 mL min^{-1} with the aid of a suction pump. After passage of the sample, the disk was eluted with 10 mL of 1.5 mol L^{-1} hydrochloric acid at a flow rate of 3 mL min^{-1}. The zinc concentration was then determined by flame atomic absorption spectrometry using an appropriate calibration graph.

Results and Discussions

N,N’-disalilicydene-1,2-phenylendiamine (salophen) is a 2N-2O donating Schiff base, which is insoluble in water at neutral pH. In the preliminary study it was found that the salophen is capable of forming a complex with zinc ions. Furthermore, the stoichiometry of the complex of salophen with zinc was determined by measurement of its absorption in methanol at 431 nm using Job and mole ratio methods and was found to be 1:1. Therefore, the capability of salophen as a suitable compelexing agent for the separation and preconcentration of Zn^{2+} ions via solid phase extraction by octadecyl silica membrane disks was investigated.

The first groups of experiments were designed to investigate whether unmodified and salophen-modified membrane disks have any affinity to retain Zn^{2+} ions. It was found that while the unmodified disk did not show any tendency toward retention of Zn^{2+} ions, the modified disk with salophen was capable of retaining Zn^{2+} ions from solutions.

The optimal amount of salophen for proper modification of the octadecyl silica membrane disks for the quantitative extraction of 10 ?µg Zn^{2+} ions from 100 mL aqueous sample was investigated by varying the amounts of ligand from 1 to 7 mg at pH 7.5. The results indicated that the extraction of zinc is quantitative above 3 mg of salophen. Hence, for safety subsequent SPE experiments were carried out with 5 mg of the ligand.

The effect of pH on recovery of 10 µg Zn^{2+} from 100 mL of solution was studied in the pH rang of 2-8. The pH was adjusted by using 0.1 mol L^{-1} of either nitric acid or sodium hydroxide solutions. The results indicated that the Zn^{2+} ions can be retained quantitatively by the modified membrane disk in the pH rang of 6.5-8.0. The decrease in retention at low pH is due to protonation of donating groups. The pH above 8 was not examined due to the possibility of the hydrolysis of octadecyl silica in the disks and the precipitation of zinc as zinc hydroxide. Therefore, pH 7 was chosen for further studies. Addition of 2 mL phosphate buffer was sufficient for pH adjustment. Hence, an addition of 2 mL was chosen.

Desorption of retained Zn^{2+} ions from modified membrane disk, after the extraction of 10 µg zinc from 100 mL solution was examined with varying volumes of 1.5 mol L^{-1} of different acids. The results are summarized in Table 1. It is obvious that, among four different stripping agents investigated, hydrochloric acid was the most promising one. The elution of zinc from modified membrane disk was quantitative with 10 mL of 1.5 mol L^{-1} HCl. In other experiments it was found that with lower concentration of hydrochloric acid, the larger volume of acid solution is needed. Thus, 10 mL of 1.5 mol L^{-1} hydrochloric acid was used for all subsequent experiments.

Sample flow rate can affect the recovery of Zn^{2+} ions in the solid phase extraction. The effect of this parameter was also studied by processing 200 mL of the solution containing 10 µg of zinc

Table 1. Percent recovery of zinc from the modified membrane disk using different volumes of 1.5 mol L^{-1} solutions of different acids: zinc, 10 µg; sample volume, 100 mL; sample pH, 7; sample flow rate, 20 mL min^{-1}; eluent flow rate, 2 mL min^{-1}.

Stripping acid solution	Recovery (%)			
	2.5 mL	5.0 mL	7.5 mL	10.0 mL
CH_3COOH	40.1	52.3	61.6	72.0
H_2SO_4	55.0	75.2	92.3	97.2
HNO_3	58.1	71.0	88.5	93.1
HCl	71.5	93.4	98.3	100.0

through the modified disk at different flow rates. It was found that retention of Zn^{2+} by the disk was not affected by the sample flow rate in the range of 5-45 mL min^{-1}. On the other hand, quantitative recovery of Zn^{2+} from the salophen-modified disk with 10 mL of 1.5 mol L^{-1} hydrochloric acid was achieved at a flow rate of 1-4 mL min^{-1}. At higher flow rates, a larger volume of eluent was needed for quantitative recovery of zinc.

Analytical Performance

The capacity of the modified disk containing 5 mg of salophen was determined by processing 100 mL of sample solution containing 1000 µg zinc at pH of 7, followed by AAS determination of the retained metal ions. The maximum capacity of the disk was found to be 226 ± 4 µg of zinc.

The breakthrough volume of the disk was examined by processing 10 µg of zinc in different volumes of water (100-3500 mL) under optimal conditions according to the recommended procedure. The results showed that up to 3000 mL, the extraction was quantitative. Thus, the breakthrough volume for the method is 3000 mL. Consequently, a preconcentration factor of 300 was determined based on consideration of the final elution volume (10 mL) and the breakthrough volume (3000 mL).

The limit of detection (LOD) of the proposed method defined as three times the standard deviation of the blank signal (3s) was 14 ng per 1000 mL. The relative standard deviation for ten replicate recoveries of 10 µg Zn^{2+} from 1000 mL aqueous solutions was found to be 1.2%.

The extraction efficiency of the proposed method was investigated in the presence of various cations. A relative error of less than 5% was considered to be within the range of experimental error. The results are given in Table 2. From the results obtained, it can be deduced that the presence of major cations have not significant effect on zinc determination by given procedure.

Application

The proposed procedure was applied to determination of zinc in tap water, river water and sea water (taken from Persian Golf). The samples were filtered through a Millipore 0.45 µm pore-size membrane into previously cleaned polyethylene bottles and were treated according to the given procedure within 6 h of collection. Reliability was checked by spiking experiment and comparing the results with data obtained by graphite furnace atomic absorption spectrometry (GFAAS). The results of Table 3 show that the proposed method can be successfully applied to the determination of zinc in different water samples.

Table 2. Effect of diverse ions (in binary mixtures) on percent recovery of 5 µg Zn^{2+} from 100 mL of sample solution: sample pH, 7; eluent, 10 mL of 1.5 mol L^{-1} HCl; sample flow rate, 40 mL min^{-1}; eluent flow rate, 4 mL min^{-1}.

Diverse ion	Mole ratio [M^{n+}/Zn^{2+}]	Recovery (%)
Na^+	1000	99.8
K^+	1000	100.0
Ca^{2+}	1000	99.6
Mg^{2+}	1000	98.5
Sr^{2+}	1000	97.6
Ba^{2+}	1000	100.0
Pb^{2+}	800	99.2
Cd^{2+}	500	99.3
Fe^{2+}	400	99.1
Mn^{2+}	300	99.9
Ni^{2+}	250	97.4
Cu^{2+}	200	98.2
Ag^+	200	98.7
Co^{2+}	40	97.8

Table 3. Determination of zinc in water samples.

Sample	Added ($\mu g\ L^{-1}$)	Found[a] ($\mu g\ L^{-1}$)	Recovery (%)	Furnace AAS[a] ($\mu g\ L^{-1}$)
Tap water	0	23.81 ± 0.14		24.40 ± 0.75
	10	33.76 ± 0.25	99.5	
Sea water	0	18.62 ± 0.21		18.32 ± 0.53
	10	28.44 ± 0.38	98.2	
River water 1	0	13.50 ± 0.16		14.06 ± 0.62
	10	23.47 ± 0.41	99.7	
River water 2	0	10.21 ± 0.23		9.90 ± 0.28
	10	20.13 ± 0.40	99.2	

[a] Mean and standard deviation of three determinations.

Conclusions

The proposed solid phase extraction procedure based on octadecyl silica membrane disks modified with salophen is a convenient, accurate and precise technique for the determination of zinc by flame atomic absorption spectrometry. A high preconcentration factor of 300, achieved by this method, makes it a very sensitive procedure in comparison with the previously reported SPE methods.[40-45] The preparation of the modified disk is very simple. The modified disk is reusable and can be used at least 10 times without any significant change in the recovery. The method can be successfully applied to the preconcentration and determination of zinc in natural waters.

Acknowledgments

The authors wish to thank the graduate school of Yazd University for their support.

Received 04 January 2008
Accepted 02 June 2008

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