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# Flame atomic absorption determination of ultra-trace zinc in environmental samples after pre-concentration by solid phase extraction

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ABSTRACT

A simple, reliable and rapid method for pre-concentration and determination of ultra-trace zinc using octadecyl silica membrane disk modified by a new Schiff base ligand, and flame atomic absorption spectrometry is presented. Various parameters including, pH of aqueous solution, flow rates, the amount of ligand and type of stripping solvents were optimized. The breakthrough volume is greater than 1000 mL with an enrichment factor of more than 200 and 120 ng/L detection limit. The capacity of the membrane disks modified by 8 mg of the ligand was found to be 260 µg of zinc. The effects of various cationic interferences on percent recovery of zinc ion were studied. The method was successfully applied for the determination of zinc ion in different samples, especially determination of ultra-trace amount of zinc in waters and plants.

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## 1. Introduction

Zinc is a biologically essential micronutrient. Physical and chemical properties of zinc ion allow it to poorly coordinate with macromolecules as a cofactor to confer catalytic function of structural integrity. Such metalloproteins have been implicated in diverse functions ranging from protein, nucleic acid, carbohydrate, and lipid metabolism, to gene transcription [1]. Maintaining cellular zinc homeostasis is important for proper biological function, yet the mechanisms of zinc uptake and metabolism are largely undefined. Zinc deficiency, although rare in humans, can be propagated by either genetic disorders or inadequate dietary intake or adsorption. Zinc deficiency has been linked to such symptoms as severe dermatitis and growth retardation in humans [1]. These conditions, although problematic have proven non-lethal. Regulation of gene transcription by zinc is of particular interest.

Zinc is frequently present at trace level in other transition metals and their compounds. However, the spectrophotometric determination of this element in these matrices is troublesome because many of the chromogenic reagents proposed also react with base transition metals. Numerous methods have been published for such determination; however, they are not simple and usually require extensive and laborious steps for separation of zinc from other metallic and counter ions using procedures which involve: liquid-liquid extraction [2-5], ion exchange [6], and precipitation [7,8].

The determination of toxic metal ions is becoming increasingly important because of the increased interest in environmental samples including water, soil, plant, etc. Although flame atomic absorption spectrometry is widely used because of its low cost, its sensitivity is usually insufficient for the low concentrations found in environmental samples. Matrix interferences are another problem in atomic absorption spectrometric determinations of trace elements. Solving these problems requires a pre-concentration and a matrix elimination step [9]. The most widely used pre-concentration methods are co-precipitation [10], ion exchange [11], solvent extraction [12], and solid phase extraction [13-18]. Solid phase extraction is an attractive technique based on the use of a sorbent that retains the analytes. The analytes are eluted from the sorbent using a suitable solvent. Solid phase extraction (SPE) is an attractive technique that reduces consumption of and exposure to solvent, disposal costs and extraction time. Recently, SPE cartridges and disks were successfully utilized for the pre-concentration and separation of trace metal ions from different matrices [19-21].

There is growing evidence that the operationally defined fractionation protocol based on use of SPE, except for water samples, might be used to determine the distribution of metals


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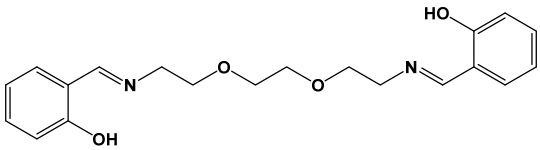


**Figure 1.** *N,N´-Bis*(salicylidene)1,8-diamino-3,6-dioxaoctan Schiff base ligand (L).

among the chemical species in dietary food and beverages, yielding useful knowledge on nutritional value, safety or authenticity of analyzed products. Previously, different anion and cation exchange resins as well as chelating and absorbing media were applied to fractionation of metal ions in that sort of samples, e.g. Ca, Mg, Fe and Zn in milk [22] and metals in water [23], Al, Ba, Ca, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Sr and Zn in tea and coffee infusions [24-26], Cu, Fe, and Zn in wines and beers [27,28], or Cd, Co, Cu, Fe, Mn, Ni, and Zn in beers [29], honeys and juices [30], providing valuable information on change of metal species or their distribution.

In the present study, a simple separation-pre-concentration method for atomic absorption spectrometric determination of $Zn^{2+}$ ion in water samples and two agricultural plants samples after extraction of *N,N´-bis*(salicylidene)1,8-diamino-3,6-dioxaoctan Schiff base ligand (L) (Figure 1) complexes of $Zn^{2+}$ ion on an octadecyl silica disk has been established. The effect of different parameters such as sample matrix, amount of ligand, type of eluent for elution of $Zn^{2+}$ ion from disk, flow rates of sample solution and eluent and breakthrough volume were evaluated. The method has also been extended to the extraction of $Zn^{2+}$ ion in the presence of a large amount of other elements and from a number of water samples.

## 2. Experimental

### *2.1. Instrumentation*

The $Zn^{2+}$ ion determination were performed on a Philips Pye Unicam 9100X atomic absorption spectrometer with Hollow Chatod Lamp (HCL) and equipped with a deuterium background corrector. The absorbance wavelength was set at 213.9 nm, 0.2 nm spectral bandwidth and 5 mA lamp current. The determination of all other ions was carried out with same atomic absorption spectrometer under the recommended conditions for each metal ion. A model 3510 digital Jenway pH meter equipped with a combined glass-calomel electrode was used for the pH adjustments.

### *2.2. Chemicals and reagents*

Methanol, acetonitrile, and other organic solvents used were of spectroscopic grade, and all acids and water used were of Pro Analysis from Merck. Analytical grade zinc nitrate, sodium hydroxide, and nitrate or chloride salts of copper, magnesium, manganese, cobalt, lead, nickel, barium, sodium, potassium, calcium, iron, and chromium (all from Merck) were of the highest purity available and used without any further purification except for vacuum drying over $P_2O_5$. The new synthesized *N,N´-bis*(salicylidene)1,8-diamino-3,6-dioxaoctan Schiff base (L) (Figure 1) with highest purity was used as the chelating ligand. The standard stock solution of zinc was prepared by dissolving 1.0000 g of zinc metal (from Merck) in 30 mL 5.0 M hydrochloric acid and dilute to 1 liter in a volumetric flask with pro analysis water from Merck. Working standards were prepared by appropriate dilution of the stock solution with pro analysis water.

Acetate buffer solutions used for the pH range of 4.0 to 5.5 of were prepared as follows. Concentrated glacial acetic acid (5.8 mL) (99.5%, $d$ = 1.05 g/mL) was transferred to a 1000 mL beaker, then 200 mL pro analysis water was added and the pH of solution was controlled by pH meter, the stirring solution was titrated to desired pH with 0.1 M NaOH solution. Then the solution transferred to a 1000 mL volumetric flask and diluted to mark with pro analysis water.

Phosphate buffer solutions used for pH ranges 6.0-7.5 were prepared as follows. 7.80 g $NaH_2PO_4.2H_2O$ was weighted and transferred to a 1000 mL beaker, and it was dissolved in 500 mL pro analysis water. In the presence of a glass electrode and magnetic stirrer, enough 0.1 M NaOH solutions were added until desirable pH was achieved. Then the solution transferred to a 1000 mL volumetric flask and diluted to the mark with pro analysis water.

### *2.3. Sample extraction*

Extraction were performed with 47 mm diameter × 0.5 mm thickness, Empore high performance extraction membrane disk containing octadecyl-bonded silica (8 µm particles, 6 nm pore size) from 3M company. The disks were used in conjunction with a standard Schott Duran 47 mm filtration apparatus.

After placing the membrane in the filtration apparatus it was washed with 10 mL methanol and then with 10 mL acetonitrile to remove all contaminations arising from the manufacturing process and the environment. After drying the disk by passing air through it for several minutes, a solution of 10 mg of the ligand (L) dissolved in 5 mL methanol was introduced to the reservoir of the apparatus and was drawn slowly through the disk by applying a slight vacuum. Then 2 mL water was added to the test tube and the resulting solution was again introduced to the reservoir and pass through the disk slowly. The filtration step was repeated until the passed solution was completely clear. Finally, the disk was washed with 25 mL water and dried by passing the air through it. The membrane disk modified by the Schiff base ligand (L) is now ready for sample extraction.

The modified disk was first washed with 2 mL methanol followed by 25 mL water. This step rewets the surface of the disk prior to the extraction of $Zn^{2+}$ ions from water. It is important to note that the surface of the disk was not left to become dry from the time the methanol was added until the extraction of $Zn^{2+}$ ions from water was completed. Then 500 mL of the sample solution containing 20 µg $Zn^{2+}$ was passed through the membrane (Flow rate = 20 mL/min). After the extraction, the disk was dried completely by passing air through it for a few minutes. The extracted zinc was stripped from the membrane disk using appropriate amounts of suitable eluent (the best eluent was 2 M hydrochloric acid). This step was done with 5 mL eluent solution and the $Zn^{2+}$ was determined with atomic absorption spectrometer.

## 3. Results and discussion

### *3.1. Choice of effluent*

In order to choose the most effective eluent for quantitative stripping of the retained ions from the modified disk after extraction of 20 µg $Zn^{2+}$ from 500 mL sample (in the presence of 10 mg ligand), the $Zn^{2+}$ ions were stripped with 5 and 10 mL of different inorganic solution, and the resulting data are listed in Table 1.

**Table 1**. Percent recovery of $Zn^{2+}$ ion from the modified membrane disk using different stripping acid solutions.

| Stripping acid | Solution (M) | % Recovery | |
|---|---|---|---|
| | | 5 mL | 10 mL |
| $HNO_3$ | 0.01 | 24 | 55 |
| | 0.10 | 65 | 85 |
| | 0.50 | 100 | 100 |
| $H_2SO_4$ | 0.01 | 27 | 59 |
| | 0.10 | 68 | 90 |
| | 0.50 | 100 | 100 |
| HCl | 0.01 | 25 | 55 |
| | 0.10 | 52 | 80 |
| | 0.50 | 100 | 100 |
| $CH_3COOH$ | 0.10 | 5 | 18 |
| | 0.50 | 48 | 78 |
| $H_2O$ | pH = 6.0 | 0 | 0 |

From the data given in Table 1, it is immediately obvious that 0.5 M solutions of nitric acid, sulfuric acid and hydrochloric acid can afford the quantitative stripping of the retained $Zn^{2+}$ ion from the modified disks. Since the nitrate ion is reported to be a more acceptable matrix for both flame and electrothermal AAS experiments than chloride and anions of other acids used [31], 5 mL of 0.5 M nitric acid was used as eluent for further studies.

It is interesting to note that the stripping step of the modified membrane disks accomplished with intense change in the color of the disk. The modified disks were yellow and after stripping changed to colorless.

### *3.2. Effect of ligand amount*

The amount of ligand plays an important role in obtaining quantitative recoveries of metal ions, because in its absence, the disk does not retain the metal ions. Therefore, the influence of the amount of ligand on recovery of the zinc ion was examined in the range of 1-12 mg using 250 mL solution containing 20 µg $Zn^{2+}$ ions. The recoveries of $Zn^{2+}$ ion increased when increasing the amount of ligand and reached to 100% with at least 8 mg of ligand (Figure 2). On this basis, in all studies were carried out with 8 mg of L ligand.

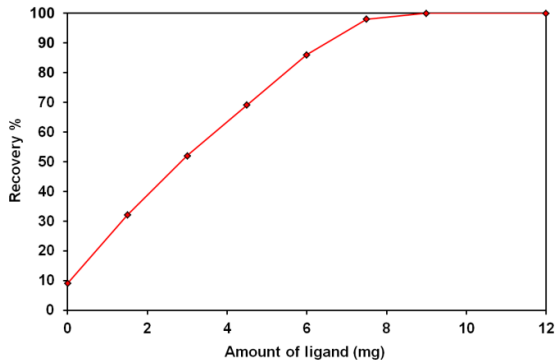


**Figure 2.** Effect of ligand amount on extraction efficiency of $Zn^{2+}$ ion.

### *3.3. Effect of flow rate and pH*

The effect of flow rates of the sample and stripping solutions from the modified membrane disk on the retention and recovery of $Zn^{2+}$ ion was investigated. It was found that, in the range of 5-30 mL/min, the retention of $Zn^{2+}$ ion by the membrane disk is not affected by the sample solution flow rate considerably. On the other hand, quantitative stripping of $Zn^{2+}$ ion from the disk was achieved in a flow rate of 1.0-8.0 mL/min, using 5 mL of 0.5 M nitric acid. At higher flow rates (up to 20 mL/min), quantitative stripping of $Zn^{2+}$ ion needed larger volumes of 0.5 M nitric acid.

Most chelating ligands (such as Schiff bases) 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 the metal complexes on the surface of the sorbent. Due to the presence of two hydroxyl group on the L ligand structure, it is expected that the extent of its complexation is sensitive to pH.

In order to investigate the effect of pH on the SPE of $Zn^{2+}$ ion, the membrane disk was modified with 8 mg of **L** and the pH of aqueous samples containing 20 µg $Zn^{2+}$ ion was varied from 3.0 to 7.0, using appropriate buffer solutions. The resulting percent recovery versus pH plot is shown in Figure 3. As seen, the percent recovery of $Zn^{2+}$ ion increases with increasing pH of solution until a pH of about 7.0 is reached. Quantitative extraction of zinc ion occurs at pH range of 6.5-7.5. pH values (>7) were not tested because of the possibility of the hydrolysis of octadecyl silica in the disks [32]. Thus, a buffer solution of pH = 7.0 was adopted for further studies.

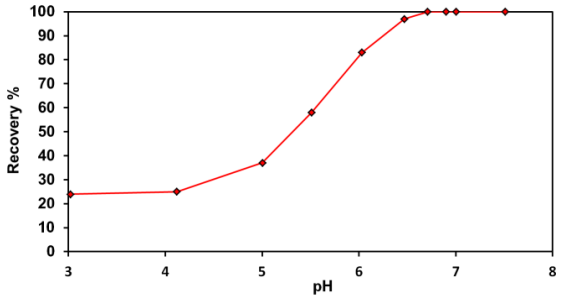


**Figure 3.** Effect of pH of test solution on the recovery of 20 µg $Zn^{2+}$ ion from 500 mL water sample.

### *3.4. Analytical performance*

#### *3.4.1. Sorption capacity*

The maximum capacity of the disk was determined by passing 500 mL portions of an aqueous solution containing 2000 µg $Zn^{2+}$ ion, through the modified disk with **L** ligand, followed by determination of the retained ions using atomic absorption spectrometry. The maximum capacity of the disk was found to be 260 µg zinc ion per 8 mg of ligand.

#### *3.4.2. Breakthrough volume*

The breakthrough volume of sample solutions was tested by dissolving 20 µg $Zn^{2+}$ ion in 250, 500, and 1000 mL water, and the solutions was passed through the modified disk. In all cases, the extraction by membrane disk was found to be quantitative (recovery 100 %). Thus, the breakthrough volume for the method should be greater than 1000 mL.

**Table 2.** Recovery of 20 µg $Zn^{2+}$ from binary mixtures *.

| Diverse ion | Amount taken (mg) | % Recovery of $Zn^{2+}$ ion |
|---|---|---|
| $Li^{+}$ | 25 | 100.0 (1.0)** |
| $Na^{+}$ | 1000 | 99.5 (0.7) |
| $K^{+}$ | 200 | 98.6 (1.6) |
| $Ca^{2+}$ | 200 | 99.8 (0.8) |
| $Mg^{2+}$ | 500 | 100.0 (1.2) |
| $Ba^{2+}$ | 25 | 98.6 (1.1) |
| $Sr^{2+}$ | 25 | 98.5 (0.9) |
| $Mn^{2+}$ | 5 | 100.0 (1.0) |
| $Co^{2+}$ | 1 | 99.5 (1.5) |
| $Ni^{2+}$ | 1 | 99.5 (1.03) |
| $Cu^{2+}$ | 1 | 97.6 (1.5) |
| $Cd^{2+}$ | 1 | 100.0 (1.1) |
| $Pb^{2+}$ | 1 | 100.0 (1.0) |
| $Fe^{3+}$ | 1 | 98.9 (0.9) |

* Initial samples contained 20 µg $Zn^{2+}$ ion and different amount of diverse ions in 500 mL water samples.
** Values in parentheses are relative standard deviations (RSDs) based on three replicate analyses.

**Table 3.** Zinc determination of different samples.

| Samples | Zinc Concentration | |
|---|---|---|
| | SPE | ICP |
| Synthetic sample 1 ($Na^{+}$ 1000, $K^{+}$ 200 mg, $Mg^{2+}$, $Ca^{2+}$, 100 mg) | 19.80±0.12 µg/500 mL | 20.00±0.05 µg/500 mL |
| Synthetic sample 2 ($Na^{+}$ 1000, $K^{+}$ 200, $Ca^{2+}$ 100, $Mg^{2+}$ 100 mg, $Co^{2+}$, $Ni^{2+}$, $Cd^{2+}$, $Fe^{2+}$, 5 mg, $Pb^{2+}$, $Cu^{2+}$, 2 mg) | 19.56±0.15 µg/500 mL | 19.97±0.03 µg/500 mL |
| Spearmint sample | 38.9±2 µg/g | 40.0±4 µg/g |
| Alfalfa sample | 32.3±2 µg/g | 34.1±2 µg/g |

Consequently, and with respect to final elution volume of 5 ml and the sample solution volume of 1000 mL, an enrichment factor of 200 was easily achievable.

### *3.4.3. Limit of detection*

Calibration curve for $Zn^{2+}$ ion determination by FAAS method is shown in Figure 3. The limit of detection (LOD), of the proposed method for the determination of $Zn^{2+}$ ion was studied under the optimal experimental conditions. The LOD obtained from $C_{LOD} = K_b S_b m^{-1}$ [33] for a numerical factor $K_b = 3$ is 120 ng/L.

### *3.4.4. Effect of diverse ions on sorption of silver*

In order to investigate the selective separation and determination of $Zn^{2+}$ ion from its binary mixtures with diverse metal ions, a 500 mL aliquot solution containing 20 µg $Zn^{2+}$ and mg amounts of other cations was taken and the recommended procedure was followed. The results are summarized in Table 2. The results show that the $Zn^{2+}$ ion in the binary mixtures are retained almost completely by the modified membrane disk, even in the presence of up to about 100 mg of the diverse ions. It is interesting to note that retention of other cations by the disk is negligible and they can be separated completely from the $Zn^{2+}$ ion.

### *3.4.5. Analysis of artificial and real samples*

In order to assess the applicability of the method to real samples with different matrices containing varying amounts of variety ions, it was applied to the separation and recovery of 20 µg $Zn^{2+}$ ions from two 500 mL different synthetic samples and the results are summarized in Table 3. For determination of zinc in biological samples, two dry vegetable samples that were taken from agricultural region of Zanjan State (around of lead and zinc mines in Dandy), are analyzed by wet ashing and dry ashing, respectively, and the results are summarized in Table 3, too. As seen, the results of all sample analysis show that, in all cases, the $Zn^{2+}$ ion recovery is quantitative. There is also a satisfactory agreement between the results obtained by the proposed method and those by the inductively coupled plasma (ICP) method.

## 4. Conclusion

A simple, precise and accurate method was developed for selective separation, pre-concentration and determination of zinc from various complex matrices. The method can be determined zinc ion in present of lead, thus it is useful for analysis of zinc in ecology of zinc and lead mines.

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