

SHORT COMMUNICATION

DETERMINATION OF TRACE AMOUNTS OF ZINC BY FLAME ATOMIC ABSORPTION SPECTROMETRY AFTER SEPARATION AND PRECONCENTRATION ONTO MODIFIED NATURAL ANALCIME ZEOLITE LOADED 2,3,5,6-TETRA(2-PYRIDYL)PYRAZINE

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ABSTRACT. Zinc ions were separated by solid phase extraction onto modified natural analcime zeolite loaded with 2,3,5,6-tetra(2-pyridyl)pyrazine (TPPZ). Extraction efficiency and the influence of sample matrix, flow rate, pH, and type and minimum amount of stripping eluent were investigated. Solutions of zinc ions were passed through a glass column packed with 1.0 g of the sorbent at pH range of 3.8-4.4. The adsorbed zinc ions were eluted with 5.0 mL of 2.0 M HNO₃ at a flow rate of 1.0 mL min⁻¹. The calibration curve using the preconcentration system was linear from 0.05 to 2.0 µg mL⁻¹ in final solution with a correlation coefficient of 0.9991. The relative standard deviation (RSD) for eight replicate determinations at 0.5 µg mL⁻¹ zinc was ± 0.92%. Detection limit was 2.9 ng mL⁻¹ in final solution and preconcentration factor was 170. The proposed method was successfully applied to the determination of zinc in various standard and water samples.

KEY WORDS: Zinc determination, Solid-phase extraction, Analcime zeolite, Preconcentration, 2,3,5,6-Tetra(2-pyridyl)pyrazine

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]. Zinc concentration in unpolluted water samples is very low. Therefore, very sensitive analytical techniques such as electrothermal atomic absorption spectrometry (ETAAS) [5] or inductively coupled plasma-mass spectrometry (ICP-MS) [6] are required for its determination. However, inductively coupled plasma-atomic emission spectrometry (ICP-AES) [7] and flame atomic absorption spectrometry (FAAS) [8] 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.

Many methods, on-line or batch systems have been developed for the preconcentration of trace metals from various samples, including co-precipitation, liquid-liquid extraction, liquid-solid extraction, solid phase extraction, cloud point extraction and the use of filter paper impregnated with a complexing agent [9, 10].

Solid phase extraction (SPE) is one of the most important methods for separation and preconcentration of trace elements in samples [11-16]. The high enrichment factors possible in SPE systems in particular, allow the analytical determination of zinc at very low level.

Since the introduction of the concept of solid phase extraction technique about 30 years ago, there has been sustained interest in the application of this method to various contaminants in

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complex matrix environmental samples. This preconcentration technique has the advantage of high recovery, short analysis time, high enrichment factor, low cost and consumption of organic and inorganic solvents [17].

Up to now, several kinds of sorbents, such as thiol cotton [18], activated carbon [19], adsorption resins [20], cellulose [21], polythioether [22], microcrystalline naphthalene [23], Amberlite XAD-2 resin [24], Amberlite XAD-1180 [25], natural and synthetic zeolites [26] and silica gel organofunctionalized compound have been used [27-30] in SPE. Zeolites are highly crystalline aluminosilicates with $[\text{SiO}_4]^{4-}$ tetrahedral and $[\text{AlO}_4]^{5-}$ octahedral units as frameworks. An oxygen bridge joins Si and Al atoms. Counter ions such as Na^+ , K^+ and Ca^{2+} are required for neutralization of overall negative surface charge. Due to the changed nature of the framework and its ability to form Bronsted acid sites, zeolites are useful catalyst for many applications [31]. Zeolites have been used in purification processes like gas sweetening and air decontamination as well as in separation processes [32] and it is believed that the attitude is attributed to the adsorption of cationic surfactants onto zeolite surface [33]. The potential of synthetic zeolites for the enrichment of metallic traces has been investigated [34]. Also Taher *et al.* [35] and Afzali *et al.* [36] assessed the potential of natural analcime zeolite as sorbent for the preconcentration of some metallic ions.

In the present work, we have developed a simple, selective, sensitive and cheap method for determination of zinc ions. In this method zinc ions were adsorbed onto modified natural analcime zeolite loaded TPPZ and then, the adsorbed ions were recovered with 5.0 mL of 2 M nitric acid solution for subsequent measurement with flame atomic absorption spectrometry (FAAS).

EXPERIMENTAL

Apparatus. A Varian model SpectrAA 220 atomic absorption spectrometer (Mulgrave, Victoria, Australia) was used for measuring Zn(II) in an air-acetylene flame. The operating conditions were as follows: wavelength, 213.9 nm; lamp current, 5.0 mA; slit width, 1.0 nm; acetylene flow, 1.5 L min⁻¹; air flow 4.5 L min⁻¹. The pH measurements were made by a Metrohm model 713 pH meter equipped with a combined electrode. The preconcentration system consisted of glass column (50 mm × 10 mm) packed with sorbent.

Reagents. High purity reagents from Sigma (St. Louis, MO, USA) and Merck (Darmstadt, Germany) were used for preparation of all standard and sample solutions. Zinc nitrate was dissolved in double distilled water and diluted to 1000.0 mL in a volumetric flask and standardized by known methods [37]. A buffer solution (pH 4.0) was prepared by mixing of 0.1 M sodium acetate and 0.1 M acetic acid solutions in appropriate ratios. A 0.1% solution of quaternary amine, benzyltrimethyltetradecyl ammonium chloride-dihydrate ($\text{C}_{23}\text{H}_{42}\text{ClN}\cdot 2\text{H}_2\text{O}$), 98% purity, was prepared by dissolving in water. Natural analcime zeolite was collected from Torfeh in the Shahr Babak area of Kerman province in Iran. A 0.1% solution of 2,3,5,6-tetra(2-pyridyl)pyrazine was prepared by dissolving in a mixture containing of methanol and ethanol. Alkali metal salts and various metal salts were used to study the interference of anions and cations, purchased from Merck, Sigma and Aldrich. Laboratory glassware was kept overnight in a 10% v/v HNO_3 solution and then rinsed with distilled water.

Preparation of analcime zeolite TPPZ loaded. Prior to all experiments, the analcime zeolite was milled and sieved to fraction of grain size less than 125 μm . After purification of zeolite, 10 g of analcime zeolite was mixed with 100 mL of 0.5 M ammonium nitrate and was shaken for three days. After separation of zeolite from NH_4NO_3 at the end of third day, it was dried at 100 °C in oven. Ammonium ion has high affinity to analcime zeolite that it cannot be replaced by another cation. For preparation of H-zeolite and removing NH_3 from analcime zeolite, it was put in

furnace at 350 °C for 2 h. A benzyldimethyltetradecyl ammonium chloride-dihydrate solution ($C_{23}H_{42}ClN \cdot 2H_2O$) was used for modifying surface of zeolite in batch mode. The modification of zeolite was performed as follows: 50 mL of benzyldimethyltetradecyl ammonium chloride solution (0.1%) was added to analcime zeolite and was shaken for 24 h. Then TPPZ solution was added to modified zeolite for 24 h while the mixture was shaken for preparation modified analcime zeolite TPPZ loaded sorbent. The sorbent in this form was dried at 50-60 °C in the oven and was kept in desiccators.

Procedure for sorption of zinc ions. A 1.0 g portion of the sorbent was added to a glass column equipped with Teflon tap and 2.5 mL of buffer adjusted to pH 4.0 passed through it. An aliquot of the solution containing 0.25-10.0 µg of zinc ions was taken in a 100 mL beaker and 5 mL of buffer (pH 4.0) added to it, then diluted to ~50 mL with distilled water. This solution was passed through the column at a flow rate of 1 mL min⁻¹. The column content was then eluted with 5.0 mL of 2.0 M nitric acid solution at a flow rate of 1 mL min⁻¹. All fractions obtained during the elution stage were gathered separately and analysed by FAAS. The sorption capacity of the modified natural analcime zeolite TPPZ loaded was obtained to be 0.475 mg of zinc per gram of modified analcime zeolite. The column was regenerated with passing of distilled water and buffer solution. This column could be used ten times after regenerating.

Sample preparation. The proposed method was applied to the determination of zinc in some standard reference materials such as NKK CRM No. 1021, NKK No. 920 Aluminum and NKK CRM No. 916 Aluminum Alloys. A 0.10 g sample of these standard alloys was completely dissolved in 10 mL of hydrochloric acid and nitric acid solution (1:1) while heating on a water-bath and then 1 mL of 30% (v/v) hydrogen peroxide was added to it. The sample was heated on the water-bath to decompose the excess peroxide. Then the solution was cooled, filtered (if needed) and diluted to 100.0 mL with distilled water in a volumetric flask. An aliquot of the pretreated sample solution was taken and was analyzed by the general procedure.

The mentioned method was applied to the determination of zinc in water samples. A 150.0 mL sample of these waters was adjusted to pH = 1.0 with nitric acid and was filtered to remove suspended materials. Then 10 mL buffer with pH = 4.0 was added and diluted to 200.0 mL in volumetric flask. The solution was passed through the column and analyzed by the general procedure.

RESULTS AND DISCUSSION

Reaction conditions. In order to determine the optimum conditions for the quantitative separation of zinc on modified analcime zeolite, several parameters were tested. The effect of pH on recovery of zinc was investigated by calculating the percentage of recovery for zinc ions on the sorbent in the pH range of 2 to 12. The results have shown that zinc was adsorbed quantitatively between 3.8-4.4 pH range (Figure 1). The flow rate of sample solution was varied from 0.5 to 3 mL min⁻¹ and did not affect the adsorption. The recoveries of zinc were obtained with flow rate of 1 mL min⁻¹. The volume of the aqueous phase was varied in the range of 50-1000 mL under optimum conditions. It was observed that the recovery of zinc ions was almost constant up to 850 mL aqueous phase. However, for convenience, all the experiments were carried out with the 50 mL of aqueous phase.

Several solutions involving HNO₃, HCl and HClO₄ in concentrations varying from 0.5 to 3 M were used as an eluent. Consequently, HNO₃ was evaluated in this work at five different concentrations from 0.5 to 3 M and quantities recoveries of zinc ions were obtained with 2 M HNO₃. After this stage, different flow rates of eluent (0.5 to 3 mL min⁻¹) were investigated and a flow rate of 1 mL min⁻¹ was recommended in all experiments.

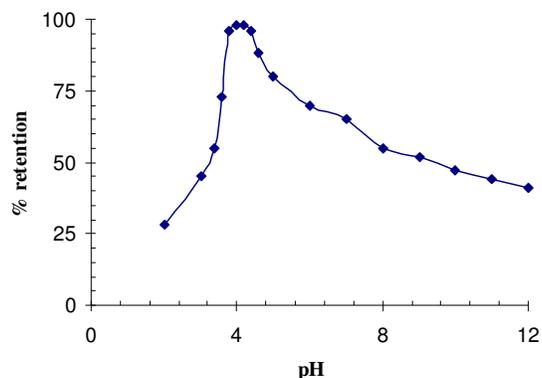


Figure 1. Effect of pH on adsorption of Zinc. Conditions: Zn, 2.5 μg ; flow rate of sample, 1.0 mL min^{-1} and eluent solution, 5.0 mL of 2.0 M HNO_3 at flow rate of 1.0 mL min^{-1} .

Sorption capacity. The capacity of modified analcime zeolite for zinc ions was evaluated considering the zinc in the aqueous phase volume which passed through the column and the amount of the zinc that is retained in this process. In this case, the column containing 1.0 g of modified analcime zeolite was used and different volumes of zinc solution ($50.0 \mu\text{g mL}^{-1}$) were passed through the column until zinc was detected in solution after passing. Modified analcime zeolite had capacity of 0.475 mg of zinc per gram of modified zeolite.

Calibration and sensitivity. Calibration curve was linear in the range of $0.05\text{--}2.0 \mu\text{g mL}^{-1}$ in the final solution with correlation coefficient of 0.9991. Eight replicate determinations of $0.5 \mu\text{g}$ of zinc in the final solution gave a mean absorbance of 0.1727 with a relative standard deviation of 0.92%. Detection limit was 2.9 ng mL^{-1} in the final solution and preconcentration factor was 170.

Effect of diverse ions. Various ions were added individually to a solution containing $2.5 \mu\text{g}$ of zinc and the general procedure was applied. The tolerance limit was set as the diverse ion required to cause a $\pm 4\%$ error in the determination of zinc. The obtained results are given in Table 1. Among the ions studied, most did not interfere at the milligram level. The interference ratio of Mn/Zn was $1.5 \text{ mg}/2.5 \mu\text{g}$ or 600 times and the interference ratio for Fe/Zn was $2 \text{ mg}/2.5 \mu\text{g}$ or 800 times. Therefore, in some of well water that has the ratio of Mn/Zn higher than 600 and/or the ratio of Fe/Zn higher than 800, the Mn and/or Fe might be interfere with determination of zinc. In this case the masking agent should be used for solving this problem.

Table 1. Effect of diverse ions on the determination of zinc by the proposed method.

Ion	Tolerance limit (mg)	Ion	Tolerance limit (mg)
CH_3COO^-	250	Ti^{3+}	5
S^{2-}	175	Ni^{2+}	4.5
SO_3^{2-}	150	Cr^{3+}	3
HCO_3^-	25	Cu^{2+}	2.5
Ti^+	10	$\text{Mg}^{2+}, \text{Fe}^{3+}$	2
Ca^{2+}	40	$\text{Mn}^{2+}, \text{Sn}^{2+}$	1.5
Al^{3+}	45	Au^{3+}	0.1
Na^+	105		

The sample contained $2.5 \mu\text{g}$ of zinc.

Accuracy of the method. The accuracy of the proposed method was checked by applying to the determination of Zn(II) ion in NKK CRM No. 1021, NKK No. 920 Aluminum and NKK CRM No. 916 Aluminum Alloys. The results are given in Table 2. It was found that there is no significant difference between results obtained by the proposed method and the certified results. These results indicate the applicability of the developed procedure for zinc determination.

Table 2. Analysis of zinc in standard aluminum alloys using the proposed method (mean \pm standard deviation; n = 5).

Sample	Composition, %	Concentration of Zn (%)	
		Certified	Found
NKK. No. 920 Aluminum alloy	Si, 0.78; Fe, 0.729; Mg, 0.46; Cr, 0.27; Ti, 0.15; Bi, 0.06; Ga, 0.05; Ca, 0.03; Co, 0.10; Ni, 0.29; V, 0.15; Cu, 0.71; Mn, 0.20, Zn, 0.80	0.80	0.796 \pm 0.006
NKK. CRM No. 916 Aluminum alloy	Si, 0.41; Fe, 0.54; Mg, 0.10; Cr, 0.05; Ti, 0.10; Sn, 0.05; P, 0.040; Sb, 0.01; B, 0.0006; Zr, 0.05; Bi, 0.03; Co, 0.03; Mn, 0.11; Ni, 0.06; V, 0.02; Cu, 0.27, Zn, 0.30	0.30	0.294 \pm 0.002
NKK CRM No. 1021 Al, Si, Cu, Zn, alloy	Si, 5.56; Fe, 0.99; Mg, 0.29; Cr, 0.03; Ti, 0.04; Sn, 0.10; Pb, 0.18; Sb, 0.01; Zr, 0.01; Bi, 0.01; V, 0.007; Ca, 0.004; Mn, 0.11; Ni, 0.14; Cu, 2.72, Zn, 1.76	1.76	1.755 \pm 0.06

Analysis of water samples. The proposed procedure has been applied to the determination of zinc in different water samples. Also, graphite furnace atomic absorption spectroscopy was employed for the accuracy check, due to its better sensitivity. The results were shown in Table 3. These results demonstrate the applicability of the proposed procedure for zinc determination in water samples.

Table 3. Concentrations of Zn (mean \pm standard deviation; n = 5) in water samples determined by graphite furnace atomic absorption spectrometry (GF-AAS).

Water Sample	Concentration of zinc (ng mL ⁻¹)	
	Present method	GF-AAS
Well water ^a	22.75 \pm 0.32	22.77 \pm 0.15
Tap water ^b	11.50 \pm 0.24	11.76 \pm 0.39
Wastewater ^a	81.32 \pm 0.42	81.45 \pm 0.15
Filtered wastewater ^a	11.72 \pm 0.03	11.74 \pm 0.11

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CONCLUSIONS

The main advantages of this procedure are: (i) natural analcime zeolite is cheap; (ii) the preparation of extractor system is simple and fast; (iii) the eluent solution (nitric acid) is cheap; (iv) good preconcentration factor can be achieved; and (v) the TPPZ is selective for zinc. Furthermore, the proposed methodology is simple, accurate and low cost mainly if more sophisticated techniques such as GFAAS or ICP-OES are not available. The proposed procedure has been successfully applied for zinc determination in water samples.

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