Flow Injection On-line Preconcentration of Trace Zinc(II) Ions in Water Samples Using a Synthesized 8-Hydroxyquinoline Functionalized Amberlite XAD-2 Resin and Determination by Flame Atomic Absorption Spectrometry

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ABSTRACT

An on-line flow injection preconcentration method for trace amounts of zinc at ppb (parts per billion) levels in real water samples was developed using flow injection flame atomic absorption spectrometry (FI-FAAS). A new chelating resin of 8-hydroxyquinoline functionalized Amberlite XAD-2 was synthesized, characterized, and used for complexation of zinc. Optimization of the flow injection variables was done for the determination and quantitative preconcentration of zinc. The sample acidity was adjusted to pH 8.0 for the effective retention of zinc ions on the resin. The chelating resin can be reused for 90-100 cycles of sorption-desorption without any significant change in its activity. The adsorbed zinc ions were eluted with 0.3 mol L⁻¹ HNO₃. The calibration graph obtained

was found to be linear over the concentration range of 0 to 80 µg L⁻¹. An enhancement factor of 137-fold for a sample volume of 15 mL was obtained by using the time-based technique. The detection limit for the preconcentration method was found to be 0.33 µg L⁻¹. The precision (RSD %) for 10 replicate determinations at 40 and 80 µg L⁻¹ concentration was 2.5 and 2.1%, respectively. The sample throughput was 30 h⁻¹ for a 5-mL sample. The effect of common interfering ions present in water samples on the selectivity of the resin towards zinc was also studied and the tolerance limit for them is reported. To test the accuracy of the developed on-line FI-FAAS procedure, standard reference material (SRM) NIST 1643e Trace Elements in Water was analyzed. Further-more, the developed procedure was successfully tested for spiked water samples.

other hand, if present in excess, it accelerates oxidative damage in the human body which leads to premature ageing (6). Therefore, the development of a selective, sensitive, and swift method to monitor zinc ion concentrations in water samples is required.

Many methods have been employed for zinc determination such as spectrophotometry (7,8), flame atomic absorption spectrometry (FAAS) (9,10), electrothermal atomic absorption spectrometry (ETAAS) (11), graphite furnace atomic absorption spectrometry (12), inductively coupled plasma mass spectrometry (ICP-MS) (13,14), and X-ray fluorescence spectrometry (15). The methods mentioned above are highly sensitive and accurate. However, certain disadvantages such as high cost, loss of analyte, use of toxic reagents, and prolonged operational time limits their use. For this, on-line solid phase extraction (SPE) (16) has shown great promise and become one of the most active research fields in automated solution analysis in recent years because of its advantages, such as high preconcentration factor, high recovery, low cost, low consumption of organic solvents, and the ability to couple with different detection techniques. On-line column preconcentration is based on the incorporation of minicolumns packed with various sorbent materials (17). The selection of a sorbent is an important step in SPE as it controls analytical parameters such as selectivity, affinity, and capacity (18). The materials which have been used as sorbents for on-

INTRODUCTION

Zinc is an essential trace metal ion for humans and plays a crucial role in various metabolic and environmental processes. It is an essential part of more than 200 enzymes involved in biochemical activities as diverse as digestion, metabolism, reproduction, cell replication, protein synthesis and gene expression. Furthermore, the biological functions of zinc, which are versatile and observed in many tissues, are

most often associated with proteins (1). It is also used for galvanization of steel and iron and in dry batteries, photoengraving, and lithography (2). It is of major importance in various commercial fields such as wastewater control, metallurgy, alloy manufacturing, agriculture (fertilizers and soil analysis), and pharmaceuticals (3). The permissible limit for zinc in drinking water as recommended by WHO is 5 mg L⁻¹ (4). Zinc deficiency is closely associated with neurological diseases such as Alzheimer's and Parkinson's disease, Epilepsy, and also impairs the immune system (5). On the

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line preconcentration of metal ions are silica gel modified with niobium(V) oxide (19), divinylbenzene functionalized with 1-(2-pyridylazo) 2-naphthol (PSDVB-PAN) (20), o-amino benzoic acid functionalized with Amberlite XAD-4 (21), chitosan resin functionalized with 2-amino-5-hydroxy benzoic acid and 8-hydroxyquinoline (22,23), 3,4-dihydroxybenzoic acid functionalized with Amberlite® XAD-4 (24), Xylenol orange functionalized with Amberlite XAD-2 (25,26), and salicylic acid functionalized with Amberlite XAD-2 (27). Chelating ions have a triple function: ion exchange, chelate formation, and physical adsorption which makes them a better choice for the preconcentration of metal ions over solvent extraction and ion exchange (28). The functional groups responsible for chelation usually include oxygen, nitrogen, and sulfur atoms. The selectivity and sorption capacity of a chelating resin can be affected by factors such as chemical activity of the chelating group, nature of the metal ions, pH of the solution, ionic strength, and nature of the sorbent material (29).

In the present work, the chelating resin 8-hydroxyquinoline (oxine) loaded onto Amberlite XAD-2 was synthesized and used for the first time in an on-line flow injection column preconcentration system for the determination of zinc. All analytical parameters such as pH, concentration of eluent, sample and eluent flow rates, and also the effect of matrix components and interfering ions were studied and are described.

EXPERIMENTAL

Instrumentation

A PerkinElmer® (Shelton, CT, USA) AAnalyst™ 400 flame atomic absorption spectrometer, coupled with the FIAS™ 400 flow injection system (Figure 1), was used for the automatic processing of the

method and operated in the preconcentration mode. The instrumental parameters are listed in Table I. The whole system was controlled by a personal computer and WinLab32™ (Version 6.5.0.0266) application software. The FIAS 400 preconcentration system is equipped with two peristaltic pumps, two positional valves, and a preconcentration column. Tygon® R3607 tubes (i.d. 1.14 mm) were used for both pumps in most of the experiments. The pH measurements were made with a Model LI614 pH meter (Elico Ltd., India). An IR spectrum was recorded on a PerkinElmer Spectrum RX-1. CHNS was carried out on a Model Vario EL-III Elementor (Elementar

Analysensysteme GmbH, Germany). Thermal analysis was performed with a PerkinElmer Diamond DSC. Scanning electron microscopy (SEM) was carried out using the Scanning Electron Microscope FEI Quanta 200F (ICON, The Netherlands).

Standard Solutions and Reagents

A 1000 mg L⁻¹ stock solution of zinc was prepared from analytical reagent grade Zn(II) nitrate in doubly distilled water obtained from a double distillation unit (Double Distillation Water Unit, WDU-2000, Quartz H, Mohindra Glass Industries, New Delhi, Delhi) and stan-

Fig. 1. Flow injection preconcentration system using the PerkinElmer FIAS 400.

TABLE I
AAnalyst Flame AAS 400 Instrumental Operating Parameters

Recommended Conditions	Zinc
Wavelength	213.86 nm
Slit Width	2.7/1.8 mm
Lamp Current	25 mA
Relative Noise	1
Characteristic Conc.	0.006 mg/L
Sensitivity Check	0.3 mg/L
Linearity	0.75 mg/L
Oxidant	Air
Oxidant Flow	10.0 L/min
Acetylene Flow Rate	2.5 L/min
WinLab32™ Software	Version 6.5.0.0266

standardized titrimetrically with ethylenediaminetetraacetic acid (EDTA) before use. Standard solutions were prepared by dilution of the stock solutions with doubly distilled water. The pH adjustments were made with 0.1M HCl, 0.1M NaOH. All laboratory glassware was kept overnight in a 10% (v/v) nitric acid solution and washed before use with doubly distilled water. Amberlite XAD-2 resin (Sigma Aldrich, USA) has a surface area of approximately 300 m²/g, a moisture holding capacity of 54–60%, particle size of 20–60 mesh, pore diameter of 90 Å (mean pore size), and a pore volume of 0.65 mL/g. The 8-hydroxyquinoline (E. Merck) used was of analytical reagent grade. All analytical reagents were procured from either E. Merck (Darmstadt, Germany) or Thomas Baker (India). Certified Zn(II) nitrate solution, traceable to NIST, was procured from E. Merck. The standard reference material (SRM) NIST 1643e Trace Elements in Water was obtained from the National Institute of Standards and Technology, Gaithersburg, MD, USA.

Real Water Samples

The water samples were collected from three different places: Noida (U.P), Narayana, and Mayapuri, Delhi, India. These places were near industries where galvanization of steel is taking place. The samples were stored in polyethylene bottles and after pretreatment with nitric acid, they were immediately placed in the refrigerator until analysis.

Synthesis of Amberlite XAD-2 Functionalized with 8-Hydroxyquinoline (AXAD2-HQ) Chelating Resin

Amberlite® XAD-2 (styrene-divinylbenzene copolymer) was modified according to the procedure reported in the literature (19). Synthesis involves nitration of

5.0 g of Amberlite XAD-2 with a nitrating mixture of 10 mL of concentrated HNO₃ and 25 mL of concentrated H₂SO₄ placed in a round bottom flask. This solution was then put on a hot plate at 60 °C for 30 minutes and mixed with a magnetic stirrer. The nitrated resin was filtered, repeatedly washed with doubly distilled water until free from acid, then reduced to form an aromatic amine by using 40 g of SnCl₂, 45 mL of concentrated HCl, 50 mL of ethanol, and refluxing for 10 hours at 90 °C. This amine facilitates the formation of a stable diazonium salt. The diazotized resin was filtered, washed with cold doubly distilled water, and reacted with hydroxyquinoline at 0–3 °C for 24 hours. The resulting brown-colored beads were filtered, washed with doubly distilled water, and air-dried. The structure of AXAD2-HQ resin is shown in Figure 2.

Fabrication of Mini-column

The newly synthesized AXAD2-HQ resin (~150 mg) was packed in a fabricated mini-glass column (3.0 cm length and 3.0 mm i.d.). The mini-column was treated with 2.0 mol L⁻¹ HNO₃ and washed with doubly distilled water until the

Fig. 2. Proposed structure of Amberlite XAD-2 functionalized with 8-hydroxyquinoline resin.

resin was free from acid. The two ends of the column were sealed with cotton. A suitable volume of the solution containing zinc (5 mL) in the concentration range of 0–80 µg L⁻¹ was passed through this column after adjusting its pH to an optimum value. The column continually performed during all experiments and there was no need for any regeneration or repacking.

Precocentration Procedure Using the FIAS 400 Flow Injection System

The flow injection (FI) FAAS analysis program was controlled by a computer program (Table II) which includes the pre-filling, filling, loading and elution steps (21). The preconcentration and determination of zinc was carried out using two peristaltic pumps fitted with Tygon® tubes, a three-way rotary valve, and a mini-column packed with AXAD2-HQ resin coupled to the FAAS. The flow system was operated in a time-based mode. A 5-mL sample solution containing 50 µg L⁻¹ of zinc(II) ions was buffered at pH 8.0, pumped at 5.0 mL min⁻¹, and then passed through a mini-column that retains the Zn(II) ions. The elution was carried out using HNO₃ at an optimum flow rate of 5.0 mL min⁻¹. The signals were recorded as absorbance using the instrument software. The sampling rate achieved was 30 samples per hour for a preconcentration time of 60 seconds and an elution time of 30 seconds.

TABLE II
Online Flow Injection Program for the
Preconcentration of Trace Metal Ions

Step	Time(s)	Pump 1	Pump 2	Loading	Elution	Reading
Pre-fill	1	+	+	+	-	-
1	10	+	-	+	-	-
2	20	-	+	-	+	-
3	50	+	-	+	-	-
4	10	+	+	+	-	-
5	30	-	+	-	+	+

RESULTS AND DISCUSSION

Characterization of Amberlite XAD-2 Functionalized With 8-Hydroxyquinoline (AXAD2-HQ) Chelating Resin

FT-IR Spectrum

The chelating resin shows bands (Figure 3) of Amberlite XAD-2 and the chelating agent 8-hydroxyquinoline is loaded onto the resin. The AXAD2-HQ resin has bands at 3421 cm^{-1} (O-H stretching), 2924 cm^{-1} (C-H stretching), 1615 cm^{-1} (C=N), 1346 cm^{-1} (C-N), 1109 cm^{-1} (C-O), and 1515 cm^{-1} (N=N), which did not appear in the IR spectrum of the Amberlite XAD-2 except the C-H stretching. This supports the fact that the 8-hydroxyquinoline is loaded onto Amberlite XAD2 by diazotized (N=N) coupling.

Thermogravimetric Analysis (TGA)

The thermogravimetric analysis (TGA) curve of freshly prepared AXAD2-HQ resin showed a very slow but steady weight loss up to 600°C . The observed weight loss was 6.9% up to 120°C . This is due

to physisorbed water on the resin, which showed the presence of only one water molecule per repeat unit of chelating resin. It can be assumed that with each ring one dye molecule is covalently bonded to an azo group and occupies a para position to the $-\text{CH}-\text{CH}_2-$ group.

CHN Elemental Analysis

The CHN elemental analysis provides a mean for the rapid determination of carbon, hydrogen, and nitrogen in organic matrices. The C, H, and N % in AXAD2-HQ resin was found to be C=70.42%, H=4.86%, N=15.02%, while calculated for $\text{C}_{17}\text{H}_{14}\text{N}_3\text{O}\cdot 1\text{ H}_2\text{O}$ it was C=69.38%, H=4.76%, N=14.28%. It further confirmed that one water molecule per repeat unit of chelating resin was formed.

SEM

A scanning electron microscope (SEM) is a type of electron microscope that produces images of a sample by scanning it with a focused beam of electrons (30). The electrons interact with electrons in the sample, producing

various signals that can be detected and that contain information about the sample's surface topography and composition. The micrographs (Figures 4 a and 4 b) show that the pure resin has a smooth and flat surface, while the modified chelating resin shows dense microstructures and granular grains. This shows that the ligand loads onto the support. The substrate surface was changed after functionalization with 8-hydroxyquinoline. The newly synthesized AXAD2-HQ resins are agglomerated polymeric materials with irregular shapes and sizes and vary from 30 to $500\text{ }\mu\text{m}$.

Optimization of Flow Injection Variables

In order to improve the performance characteristics of the method, both chemical and flow variables were thoroughly studied for Zn(II). A standard solution of $50.0\text{ }\mu\text{g L}^{-1}$ Zn(II) with a 60-second preconcentration time for all major variables such as sample pH, eluent, sample, and eluent flow rate was analyzed using FI-FAAS.

The effect of pH (ranging from 2.0–10.0) on samples containing Zn(II) ions was examined. The results show that the Zn(II) ions were quantitatively adsorbed at pH 8.0 (Figure 5). The low absorbance of Zn(II) at high acidity was due to the low complex formation rather than the low retention efficiency of the packing material. In order to obtain the best conditions for the determination after preconcentration, the pH 8.0 was chosen.

Elution studies were performed in order to obtain maximum recovery with minimal concentration and volume of elution solution. For desorbing metal ions already adsorbed on the adsorbent, different concentrations of the eluent ranging from $0.01\text{--}2.0\text{ mol L}^{-1}$ HNO_3 were examined. The results show that with an increase in the HNO_3 concentration

Fig. 3. Infrared spectra of Amberlite XAD-2 functionalized with 8-hydroxyquinoline resin: (a) AXAD2-HQ resin, (b) 8-hydroxyquinoline, (c) Amberlite XAD-2.

up to 0.3 mol L^{-1} , the absorbance increases, then decreases at higher concentrations (see Figure 6). Thus, $0.3 \text{ mol L}^{-1} \text{ HNO}_3$ was selected for the quantitative recovery of the Zn(II).

The influence of eluent flow rate in the elution step was studied within the range of $2.0 - 7.0 \text{ mL min}^{-1}$ because it establishes the velocity of the acid solution through the mini-column. The results obtained showed that the analytical signal is maximum at an eluent flow rate of 5.0 mL min^{-1} (Figure 7). Moreover, higher flow rates increase back pressure which could cause leakage from the column. The elution time

was fixed at 30 seconds in order to ensure the complete elution of adsorbed Zn(II) ions even at high concentrations.

The flow rate of the sample solution through the column not only affects the recovery of the analyte but also controls the time of the analysis. The effect of sample flow rate on the preconcentration of $50 \mu\text{g L}^{-1} \text{ Zn(II)}$ for a 60-second loading time under pH 8.0 was studied in the range of $2.0 - 7.0 \text{ mL min}^{-1}$. Quantitative recovery of the Zn(II) ion was obtained with a flow rate of 5.0 mL min^{-1} . At higher flow rates, back pressure is produced by the mini-column. Low flow rates

decrease the sample throughput and results in a long analysis time. In order to improve the analytical efficiency, 5.0 mL min^{-1} was chosen as the loading rate for Zn(II) ions (Figure 8).

Analytical Performance of the On-line Preconcentration System for Zn(II) Determination

The characteristic data under the optimum chemical and flow conditions, including the regression equation before and after the preconcentration method for the on-line preconcentration system for Zn(II) with AXAD2-HQ resin, are listed in Table III. The enhance-

Fig. 4 (a and b). SEM images: (a) Amberlite XAD-2, (b) Amberlite XAD2-HQ resin.

Fig. 5. Effect of pH on the absorbance. Conditions: Preconcentration of 5 mL of $50 \mu\text{g L}^{-1} \text{ Zn(II)}$ with flow rate of 5 mL min^{-1} and elution with $0.3 \text{ mol L}^{-1} \text{ HNO}_3$ at flow rate of 5 mL min^{-1} .

Fig. 6. Effect of eluent concentration on the absorbance. Conditions: Preconcentration of 5 mL of $50 \mu\text{g L}^{-1} \text{ Zn(II)}$ buffered at pH 8.0 and elution with HNO_3 at flow rate of 5 mL min^{-1} .

ment factor (EF) was based on the ratio of the slopes of the calibration curves, obtained with and without preconcentration, using FAAS. It was observed that the detection limits and the enrichment factors will increase with a longer preconcentration time. The calibration graphs were linear at a preconcentration time of 60, 120, and 180 seconds. By using pH 8.0 and a sample flow rate of 5.0 mL min^{-1} , the enhancement factors obtained were 28, 68, and 137, respectively. The detection limits (DL) were found to be 1.38, 1.092, and $0.33 \text{ } \mu\text{g L}^{-1}$, respectively. The precision (RSD) of 2.5% and 2.1% was obtained at 40 and $80 \text{ } \mu\text{g L}^{-1}$ Zn(II), respectively. The sample throughput of 30 h^{-1} was obtained at a 60-second preconcentration time. A lower sample throughput of 20 and 15 h^{-1} was obtained by using longer preconcentration times of 120 and 180 seconds. Higher preconcentration times could be beneficial for the determination of samples with lower Zn(II) concentrations. However, long time periods are not suitable for flow injection preconcentration systems as sample throughput is low. Hence, a preconcentration time of 60 seconds was used for the determination of Zn(II) in water samples.

TABLE III
Analytical Features of the On-line Zn(II) Preconcentration System Using AXAD2- HQ Resin

Parameters	Optimum Conditions		
pH	8.0		
Sample Flow Rate	5.0 mL min^{-1}		
Eluent Flow Rate	5.0 mL min^{-1}		
Acid Conc. for Desorption	$0.3 \text{ mol L}^{-1} \text{ HNO}_3$		
Preconcentration Time	60 s	120 s	180 s
Linear Range ($\mu\text{g L}^{-1}$)	0–80	0–35	0–22
Limit of Detection ($\mu\text{g L}^{-1}$)	1.38	1.092	0.33
Sample Throughput (h^{-1})	30	20	15
Enhancement Factor	28	68	137
Regression Equation	$A_{60} = 0.00923 + 0.00841 [\text{Zn(II)}]$		
(6 Standards, Zn(II) / $\mu\text{g L}^{-1}$) (with preconcentration)	$A_{120} = -0.01018 + 0.02112 [\text{Zn(II)}]$ $A_{180} = 0.00264 + 0.04283 [\text{Zn(II)}]$		
Regression Equation	$A = 0.02056 + 0.00031252 [\text{Zn(II)}]$		
(6 Standards, Zn(II) / $\mu\text{g L}^{-1}$) (without preconcentration)			
Correlation Coefficient (r)	0.994262	0.999553	0.995232
Precision (%)	2.5, $[\text{Zn(II)}] = 40 \text{ } \mu\text{g L}^{-1}$ 2.1, $[\text{Zn(II)}] = 80 \text{ } \mu\text{g L}^{-1}$

Fig. 7. Effect of eluent flow rate on the absorbance. Conditions: Preconcentration of 5 mL of $50 \text{ } \mu\text{g L}^{-1}$ Zn (II) buffered at pH 8.0 with flow rate of 5 mL min^{-1} and elution with $0.3 \text{ mol L}^{-1} \text{ HNO}_3$.

Fig. 8. Effect of sample flow rate. Conditions: Preconcentration of 5 mL of $50 \text{ } \mu\text{g L}^{-1}$ Zn (II), buffered at pH 8.0, and elution with $0.3 \text{ mol L}^{-1} \text{ HNO}_3$ at flow rate of 5 mL min^{-1} .

Interference Studies

Application of the proposed pre-concentration method for the determination of Zn(II) ions in samples with a complicated matrix was also investigated such as the influences of some alkali, alkaline earth, and transition metal ions on the recovery of Zn(II). Chloride, nitrate, and sulfate ions commonly found in natural water samples have the capability to complex with many metal ions (31). Therefore, in their presence, the efficiency of the chelating resins to bind metal ions may be hampered resulting in the reduction of the overall enrichment. Thus, the effect of Na^+ , Cl^- , NO_3^- , SO_4^{2-} , Br^- , Mg^{2+} , Pb^{2+} , Cd^{2+} , Cu^{2+} , Ca^{2+} , Al^{3+} , and K^+ on the sorption efficiency of AXAD2-HQ resin for $50 \mu\text{g L}^{-1}$ Zn(II) was studied using the recommended flow injection column method under optimum conditions. The tolerance limits of several foreign substances in the preconcentration of Zn(II) are listed in Table IV. A species is considered to interfere when it lowers the recovery of the metal ions by more than $\pm 5\%$. The results in Table IV demonstrate that the presence of large amounts of these metal ions in the sample have no significant effect on the analytical signal of Zn(II).

TABLE IV
Effects of Matrix Ions on the Recovery of Zn(II)

Interfering Ion	Tolerance Limit (mg L^{-1})
Na^+	40,000
Cl^-	18,000
Br^-	15,000
Mg^{2+}	8,000
SO_4^{2-}	3,000
NO_3^-	2,500
Cd^{2+}	25
Pb^{2+}	18
Ca^{2+}	15
K^+	12
Al^{3+}	10
Cu^{2+}	10

Analytical Application for Water Samples

The proposed method was applied for the analysis of tap water samples and validated by spiking the samples with known amounts of certified Zn(II) nitrate solution, traceable to NIST. These water samples were collected from three different places: Noida (U.P.), Narayana, and Mayapuri, Delhi, India. These places are near industries where galvanization of steel takes place. For these samples, the only pre-treatment performed was acidification to pH 2.0 with nitric acid, which was done immediately after collection in order to prevent adsorption of the Zn(II) ions on the flask walls. The samples were stored in polyethylene bottles and immediately placed in a refrigerator until analysis. All water samples were filtered through a $0.45 \mu\text{m}$ pore size membrane filter to remove suspended particulate matter. The filtrate was adjusted to pH 8 by addition of a buffer solution and subjected to on-line

FI-FAAS determination using AXAD2-HQ resin as column material and following the procedure described above. The recoveries from the spiked samples ranged from 97–99%. The analytical results along with the recoveries are summarized in Table V.

Accuracy of On-line Preconcentration Method

In order to evaluate the accuracy of the developed on-line preconcentration procedure, it was verified by the analysis of NIST SRM 1643e Trace Elements in Water (National Institute of Standards and Technology, Gaithersburg, MD, USA). The certified value of 78.5 ± 2.2 for Zn(II) was used to verify the accuracy of the proposed methodology on total concentration determination. The concentration found was $76.8 \pm 2.6 \mu\text{g L}^{-1}$ which is in good agreement with the certified values listed in Table VI.

TABLE V
Analytical Results Obtained With FIAS-400 Flow Injection System for the Determination of Zn (II) in Real Water Samples

Sample	Conc. Determined ($\mu\text{g L}^{-1}$)	Conc. Determined by $20 \mu\text{g L}^{-1}$ Spiked Zn (II) ($\mu\text{g L}^{-1}$)	Recovery (%)
Noida, Industrial Area, U.P., India	40.44 ± 2.2	59.39 ± 2.1	98.2%
Naryana, Industrial Area, Delhi, India	46.59 ± 2.5	65.72 ± 2.3	98.6%
Mayapuri, Industrial Area, Delhi, India	42.56 ± 2.6	60.70 ± 2.7	97.0%

TABLE VI
Zn(II) Determination in SRM NIST Trace Elements in Water

Sample	Zn(II) Amount ($\mu\text{g L}^{-1}$)		
	Certified Value	Proposed Method	Recovery (%)
SRM1643e, Trace Elements in Water	78.5 ± 2.2	76.8 ± 2.6	98.61

Comparison of Performance Characteristics of Newly Developed Chelating Resin With Other On-line SPE Methods

In Table VII, the figures of merit of the present and other selected on-line SPE preconcentration FAAS methods are summarized for comparative purposes. The proposed method shows good sensitivity (detection limit 0.33), better precision (2.1% RSD), and high sample throughput (30) with a very high enhancement factor (137-fold) over other on-line preconcentration methods.

CONCLUSION

The use of Amberlite XAD-2 modified with 8-hydroxyquinoline as an adsorbent for the determination of Zn(II) in aqueous samples in an on-line FI-FAAS system was very efficient, resulting in excellent sensitivity and analytical frequency. The parameters including pH of the sample, sample volume, type and volume of eluents, and effect of foreign ions were studied. The principle interest in using this chelating resin for trace metal analysis is based on the simplicity of the method for the separation and preconcentration of the Zn(II) ions. Other advantages include low detection limit (0.33 $\mu\text{g L}^{-1}$), high preconcentration factor (137-fold), short analysis time, and high selectivity. This proposed online system has high tolerance to interferences from matrix ions and thus allows the determination of Zn in a large range of samples. The sorbed ions can readily be desorbed with common mineral acids, resulting in a recovery of ~98% in real water samples and the certified material.

TABLE VII
Comparison of Performance Characteristics
Among Selected On-line SPE Methods and the Developed Method
for the Zn(II) Determination with FAAS

Support	Chelating Agent	Eluent	PT (s)	RSD (%)	DL ($\mu\text{g L}^{-1}$)	EF	Ref.
Activated carbon	-	HNO_3	-	0.82	1.9	10.9	(32)
Alumina	Alizarin Red S	HNO_3	300	3.0	0.2	144	(33)
Amberlite XAD-4	3,4-dihydroxybenzoic acid	HCl	60	2.1	2.3	54	(10)
Amberlite XAD-4	2,6-dihydroxyphenyl-diazoaminoazobenzene	HCl	60	2.7	0.2	31	(34)
Amberlite XAD-16	3-((2,6-dichlorophenyl)(1H-indol-3-yl)methyl)-1H-indole (DCPIMI)	HNO_3	-	2.3	1.5	225	(35)
-	(2-pyridylazo)resorcinol (PAR)	oxalic acid	300	3.55	0.42	-	(36)
Micelle	HBDAP(N,N-bis(2-hydroxy-5-bromobenzyl)1,2-diaminopropane)	HNO_3	60	-	0.89	8.4	(37)
PTFE turnings	Ammonium pyrrolidine dithiocarbamate	IBMK	30	3.2	0.3	65	(38)
Styrene-Divinylbenzene	2-[hydroxy-bis(4vinylphenyl)methyl]pyrrolidine-1-carboxylic acid ethyl ester	HCl	2400	6.5	0.98	-	(39)
Amberlite XAD-2	8-hydroxyquinoline	HNO_3	180	2.1	0.33	137	This Work

PT: Preconcentration time; RSD: precision (relative standard deviation); DL: detection limit; EF: enhancement factor.

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