A Rapid Analytical Method Using Flow Injection Preconcentration of Zinc on Dithizone Impregnated on Amberlite XAD-2 and its Determination in Water Samples by FAAS

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Abstract

An environment friendly and low cost flow injection-solid phase extraction technique was developed for on-line preconcentration and determination of Zinc at ppb levels in water sample. Dithizone functionalized Amberlite XAD-2 packed in a minicolumn was used as the sorbent material. This novel chelating resin is an example of recyclable material as it can be used for ~300 cycles of sorption-desorption without any significant change in its activity. This method affords quick and accurate results with good reproducibility. The sample acidity was adjusted over a pH of 8.0 for effective retention of Zn (II) ions on the resin. The enrichment factor was 139 for preconcentration time of 180 s and the detection limit was 0.1 µg L^{-1}. This resin offers better precision and the corresponding relative standard deviation (R.S.D.) values for seven successive determinations were 2.2 and 1.8 % for 40 and 80 µg L^{-1} respectively. The sample throughput was 30 h^{-1} for 5 mL of sample. The effect of common interfering ions present in industrial water samples on the selectivity of the resin towards Zn (II) ions was also studied and tolerance limit for them is reported. To test the accuracy of the developed on-line FI–FAAS procedure, Standard Reference Material (SRM 1643e, Trace elements in water) supplied by National Institute of Standard and Technology (NIST) Gaithersburg, MD, USA, was analysed. Spiked recovery studies in water samples were performed using a NIST certified Zinc nitrate solution to confirm the accuracy of the proposed preconcentration procedure.

1. Introduction

Zinc is an essential trace metal ion which 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, gene expression, cell division and for nucleic acid recognition in protein folds. It is of major importance in various commercial fields such as waste water control, metallurgy, alloy manufacturing, agriculture (fertilizers and soil analysis) and pharmaceuticals. The permissible limit for zinc in drinking water as recommended by WHO is 5 mg L^{-1} (WHO, 2011). Zinc deficiency is closely associated with neurological diseases such as Alzheimer's, Parkinson's disease, Epilepsy and also impairs the immune system. On the other hand, if present in excess, it accelerates oxidative damage in the human body which leads to premature ageing (Flinn et al, 2005). Therefore, development of a selective, sensitive and swift method to monitor zinc ion concentration in water samples is required.

There is a critical need for selective separation, preconcentration and determination of zinc ions at trace level from complex matrices. Flame atomic absorption spectrometry (FAAS) is one of the most extensively used techniques, for various element determinations with significant precision and accuracy. Various techniques have been used for preconcentration of Zn (II) ions such as co-precipitation, liquid-liquid extraction, cloud point extraction and solid phase extraction (Baga et al, 2006). Preconcentration using solid phase extraction prior to the final measurement is usually required in order to bring the analyte concentration into the dynamic range of the detector. It is required to overcome the lack of sensitivity or selectivity of analytical methods. In the present work, Amberlite XAD-2 functionalized with Dithizone in on-line flow injection column preconcentration system was used for the determination of Zinc.

2. Experimental

2.1 Instrumentation

A PerkinElmer (Shelton, CT, USA) Model AAnalyst™ 400 flame atomic absorption spectrometer, coupled with the FIAS™ 400 flow injection system, was used for the automatic processing of the method and operated in the preconcentration mode. The whole system was controlled by a personal computer and Winlab32™ (Version 6.5.0.0266) application software. FIAS 400 preconcentration system comprises of two peristaltic pumps, two positional valves, and a preconcentration column. Two Tygon® R3607 tubes (i.d.1.14 mm) were applied for both pumps in most of the experiments. An IR spectrum was recorded on a PerkinElmer Model Spectrum RX-1. CHNS was

carried out on a Model Varo EL-III Elementor. Thermal analysis (TGA) was performed with a PerkinElmer Model Diamond DSC.

2.2 Reagents

A 1000 mg L^{-1} stock solution of zinc was prepared from analytical reagent grade zinc nitrate in doubly distilled water and standardized titrimetically with EDTA before use. The standard solutions were prepared by dilution of the stock solutions with doubly distilled water. The pH adjustments were made with 0.1M HCl and 0.1 M NaOH. Amberlite XAD-2 resin (Sigma–Aldrich) has a surface area of approximately 300 m^2/g, 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. Dithizone used was of analytical grade. All analytical reagents were procured form either E. Merck (Darmstadt, Germany) or Thomas Baker (India). Certified Zinc nitrate solution, traceable to NIST, was procured from E. Merck. The standard reference material SRM-1643e Trace Elements in Water was obtained from National Institute of Standards and Technology, Gaithersburg, MD, USA (NIST).

2.2 1 Synthesis and Characterization of Amberlite XAD-2 functionalized with Dithizone (AXAD2-DZ)

Amberlite XAD-2 functionalized with Dithizone resin was synthesized according to the procedure given in literature (Dongmei et al, 2006). The IR spectra of chelating resin AXAD2-DZ shows bands of Amberlite XAD-2 and dithizone which shows that chelating agent has been loaded on resin. The presence of (-N=N-) peak suggest that the loading of dithizone onto Amberlite XAD-2 is through diazotized (N=N) coupling. The TGA of the resin supported the presence of only one water molecule per repeat unit of chelating resin). The elemental analysis (CHNS) provides a mean for the rapid determination of carbon, hydrogen, nitrogen and sulphur in organic matrices. The C, H, N and S % in AXAD2-DZ resin, resin was found to be C: 63.58%, H: 5.02%, N: 16.1% and S: 7.8% while calculated for $C_{21}H_{19}N_4S.1H_2O$ was C: 65.45%, H: 4.9%, N: 16.6% and S: 8.3 %.

2.3 Fabrication of Mini-column

The synthesized AXAD2-DZ resin (~150 mg) was packed in a mini glass column (3.0 cm length and 3.0 mm internal diameter), and both ends of the column were sealed with cotton. The minicolumn was treated with 2.0 mol L^{-1} HNO_3 and washed with doubly distilled water until the resin was free from acid. A suitable volume of the solution containing zinc in the concentration range of 0–95μg L^{-1} was passed through this column after adjusting its pH to an optimum value. The column had a constant performance during all experiments and there was no need for any regeneration or repacking.

2.4 Online Fiow Injection –Flame Atomic Absorption Spectrometry (FI-FAAS) Determination of Zinc

FI-FAAS system used involves two simple preconcentration and elution steps as shown in Fig 1. Flow Injection analysis program was controlled by a computer program which includes: pre-filling, filling, and loading and elution steps (Saxena and Singh, 2013). In the preconcentration step, the injection valve is in the 'load' position and the sample was typically pumped by Pump1 through the AXAD2-DZ minicolumn. During the elution step, the above valve is in the 'injection' position, and the elution solution, nitric acid is propelled by Pump 2 through the column in order to elute the sorbed complex and transport directly into the nebulizer of the spectrometer. Signals were recorded as absorbance using the instrument software. The sampling rate achieved was 30 samples h^{-1} for a preconcentration time of 60 s and an elution time of 30 s.
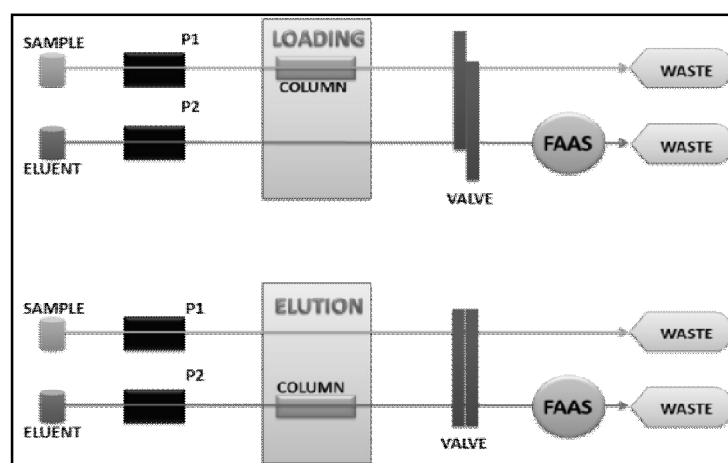

Fig. 1: Flow injection preconcentration system using FIAS 400

3. Results and Discussion

3.1 Optimization of Experimental parameters for Online Preconcentration of Zinc

In order to improve the performance of the online preconcentration method for Zn (II) ions determination, all major chemical and flow variables were examined in detail using the FI-FAAS manifold with standard solution of 50 μg L^{-1} of Zn (II) ions. The effect of the sample pH on the Zn (II) ions retention and absorbance was investigated within the range of 2.0–12.0 after adjusting pH with appropriate buffer solutions. The pH of sample solutions for the online preconcentration was adjusted at 8.0 as it shows maximum absorbance. The elution of Zn (II) ions from the minicolumn was studied by using HCl and HNO_3 solutions at different concentrations (0.01–2.0 mol L^{-1}). HNO_3 was considered to be more convenient for FAAS assays because of its improved and sharper signals in comparison to HCl. The maximum elution was obtained at 0.5 mol L^{-1} HNO_3. So, 0.5 mol L^{-1} HNO_3 was selected as eluent for further studies. To study

the effect of sample flow rate 5.0 mL of solution containing 50 µg L^{-1} Zn (II) was pumped into the system at flow rates from 2.0– 7.0 mL min^{-1}. Moreover, high flow rates increases back-pressure and this could cause leakage. Thus, a sample flow rate of 5.0 mL min^{-1} was chosen for further experiments. The flow rate of the eluent in the elution stage was investigated in the range 2.0–7.0 mL min^{-1}. The analytical signals slowly decreased as flow rate increased. The results obtained showed that the analytical signal was maximum at eluent flow rate of 6.0 mL min^{-1}.

3.2 Analytical Fig. s of merit

The analytical characteristics of the proposed method under the optimum conditions for Zn (II) ions determination are listed in Table 1. The enhancement factor was calculated as the ratio of the slope of the calibration curve obtained with the online preconcentration to the slope without preconcentration. The detection limit based on the 3s criterion was found to be 0.1 µg L^{-1}.

Table 1: Analytical Features of the online Zn (II) preconcentration system using AXAD2-Dithizone.

Parameters	Optimum	Conditions	
Preconcentration time (s)	60	120	180
Sample consumption (mL)	5	10	15
Sample throughput (h^{-1})	30	20	15
Enhancement factor	34	84	139
Linear range (µg L^{-1})	0-95	0-40	0-22
Limit of detection (µg L^{-1})	0.65	0.22	0.1
Correlation coefficient	0.992514	0.995285	0.994362
Regression equation 6 standards, n=3; Zn(II)/ µg L^{-1} (with preconcentration)	$A_{60} = 0.05184 + 0.01072$ [Zn(II)] $A_{120} = -0.01167 + 0.02626$ [Zn(II)] $A_{180} = 0.02157 + 0.04352$ [Zn(II)]		
Regression equation 6 standards, n=3;Zn(II)/ µg L^{-1} (without preconcentration)	$A = 0.02056 + 0.00031252$ [Zn(II)]		
Precision (R.S.D %) n=5	2.2, [Zn(II)] = 40 µg L^{-1} 1.8, [Zn(II)] = 80 µg L^{-1}		

3.3 Effect of Electrolytes

The application of the preconcentration method for the determination of Zn (II) ions in samples with complicated matrix, the influences of some alkali, alkaline earth and transition metal ions on the recoveries of the Zn (II) ions were also investigated. The effect of these ions on the sorption efficiency of AXAD2-DZ resin for 50 µg L^{-1} Zn (II) ions was studied using the recommended flow-injection column method under the optimum conditions. The tolerance limits of these ions in the preconcentration of Zn

(II) ions are given in Table 2. A species is considered to interfere when it lowers the recovery of metal ions by more than ± 5%.

Table 2: Effects of Matrix Ions on the recovery of Zn (II) ions

Interfering ion	Tolerance Limit (mg L^{-1})
Na^+	45,000
Cl^-	25,000
Br^-	15,000
Mg^{2+}	15,000
SO_4^{2-}	3,500
NO_3^-	4,500
Cd^{2+}	20
Pb^{2+}	25
Ca^{2+}	15
K^+	18
Al^{3+}	12
Cu^{2+}	12

3.4 Determination of Zinc in water Samples

The on-line preconcentration procedure was applied to the determination of Zn (II) ions in water samples. These water samples were collected from three different places Noida (U.P.), Nariana and Mayapuri, Delhi, India. All the water samples were filtered through 0.45 µm pore size membrane filter to remove suspended particulate matter. The method validation was made through spike recovery tests with the addition of 20 µg L^{-1} Zn (II) using certified zinc nitrate solution, traceable to NIST. The recoveries from the spiked samples were varied in the range 97-99%. The analytical results along with the recovery are summarized in Table 3.

Table 3: Analytical Results obtained for the Determination of
Zn (II) in Water Samples.

Sample	Conc. Determined (µg L^{-1})	Conc. Determined by 20 µg L^{-1} Spiked Zn (II) (µg L^{-1})	Recovery (%)
Noida, Industrial Area, U.P, India	40.25 ± 1.9	60.25 ± 1.5	98%
Nariana, Industrial Area, Delhi, India	42.65 ± 2.2	62.65 ± 2.0	99 %
Mayapuri, Industrial Area, Delhi, India	29.65 ± 1.6	49.65 ± 2.5	97 %

3.5 Accuracy of the method
In order to evaluate the accuracy of the developed on-line preconcentration procedure, it was tested by determining the Zn (II) content in certified standard reference material NIST SRM 1643e Trace elements in water. It was found that there is no significant difference between achieved results by proposed method and certified results. The recoveries occur in the range 97-99%.

3.6 Comparison of performance characteristics of newly designed chelating resin with other selected on-line SPE methods
In Table 4, the Fig. s of merit of the present and other selected on-line SPE preconcentration FAAS methods are summarized for comparative purposes. The proposed method showed good sensitivity (detection limit), better precision (RSD) and high sample throughput with very high enhancement factor over other on-line preconcentration methods.

Table 4: Comparison of performance Characteristics among Selected Online SPE

Support	Chelating Agent	Eluent	PT(s)	RSD (%)	DL ($\mu g\ L^{-1}$)	EF	Ref.
Activated carbon	-	HNO_3	-	0.82	1.9	10.9	Teixeira et al, 2005
Alumina	Alizarin Red S	HNO_3	300	3.0	0.2	144	Alves et al, 2011
Amberlite XAD-4	3,4-dihydroxybenzoic acid	HCl	60	2.1	2.3	54	Shabani et al, 2009
Amberlite XAD-4	2,6-dihydroxyphenyl-diazoaminoazobenzene	HCl	60	2.7	0.2	31	Liu et al,2007
Micelle	N,N$^{/}$-bis(2-hydroxy-5-bromobenzyl)1,2diaminopropane (HBDAP)	HNO_3	60	-	0.89	8.4	Kara,2009
PTFE turnings	Ammonium pyrrolidine dithiocarbamate	IBMK	30	3.2	0.3	65	Anthemidis et al,2010
Amberlite XAD-2	**Dithizone**	**HNO_3**	**180**	**1.8**	**0.1**	**139**	**This Work**

4. Conclusion

The use of Amberlite XAD-2 resin modified with Dithizone as an adsorbent for the determination of Zn (II) ions in aqueous samples in an on-line FI-FAAS system was very efficient, presenting an excellent sensitivity and analytical frequency. Zinc was quantitatively recovered from the mini-column with a high precision. The obtained enrichment factor (EF) was better than other online SPE methods described in the literature (Table 4). The proposed chelating resin and FI–FAAS System gave good results for the recovery test carried out on real samples and certified materials, low limit of detection and good precision which resulted in greater analytical throughputs. Such characteristics are very important and of practical interest for routine laboratories equipped just with FAAS for element analysis.

5. Acknowledgment

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