RSC Advances

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

Flow injection online solid phase extraction system using Amberlite XAD-16 functionalized with 8-Hydroxyquinoline for copper and zinc determination by flame atomic absorption spectrometry

Reena Saxena* and Prem Lata Meena

Department of Chemistry, Kirori Mal College, University of Delhi, Delhi -110007, India.

***reenasax@hotmail.com**

Abstract

A newly functionalized resin has been applied in an on-line preconcentration system for copper and zinc determination. Amberlite XAD-16 functionalized with 8-hydroxyquinoline packed in a minicolumn was used as sorbent material.The retained metals can be quickly eluted from sorbent material, with the eluent stream consisting of nitric acid solution, directly to the nebulizer burner system of the FAAS. The sample acidity was adjusted over a pH 4.0 and 8.0 for effective retention of copper and zinc ions on the resin.The linearity was maintained between 0-180 and 0-90 µg L^{-1} for copper and zinc respectively. The sample throughputs of analytes were 30 h^{-1} for 5 mL of sample. The enrichment factors obtained were 80 for copper and 147 for zinc, while the limits of detection were estimated as 0.16 and 0.2 µg L^{-1} for copper and zinc respectively using a preconcentration time of 180 s.The precision (RSD %) obtained were 1.2 % (50 µg L^{-1}) and 2.2 % (40 µg L^{-1}) for copper and zinc respectively. The effects of foreign ions on the adsorption of these metal ions were 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 analyzed. Spike recovery studies in water samples were performed using a NIST certified copper and zinc nitrate solution to confirm the accuracy of the proposed preconcentration procedure.

Keywords: Flow-injection, Solid-phase extraction, 8-Hydroxyquinoline, Amberlite XAD-16, copper, zinc and flame atomic absorption spectrometry.

INTRODUCTION

The increased use of metals and chemicals in many industries has resulted in the generation of large amounts of polluted aqueous effluents which contain high concentration of heavy metals and pose environmental disposal problems for plants, animals and human beings. Copper is an essential trace element for humans, plants and other animals but also causes contamination in water. Thus, even low copper levels in the human body may cause diarrhea, stomach aches, vomiting and dizziness. Long-term exposure to high levels of copper may cause kidney or liver damages and mental disorders, such as Alzheimer's disease and is also responsible for causing gastroenteritis and Wilson's disease (a genetic disorder). Thus, high concentration levels of Cu (II) ions in industrial waste waters must be reduced to acceptable levels before discharging them into the environment [1, 2]. Zinc is an essential trace element of great importance for humans, plants, and animals. It is of prime importance in diverse fields, such as environmental, waste water control, metallurgy, agriculture, alloy manufacturing, pharmaceutical and clinical fields [3]. Zinc is a co-factor in many enzymes and it is necessary for production of insulin in humans. However, excessive consumption of zinc can lead to inhibition of Cu (II) absorption, altered iron function, reduced immune function, and reduced levels of high-density lipoproteins. The permissible limits for copper and zinc in drinking water as given by World Health Organization (WHO) are 0.05 mg L^{-1} and 5 mg L^{-1} respectively [4]. In this manner, the determination of trace amounts of copper and zinc in several matrices is very important to identify the contamination in environment, water or human body.

The direct determination of trace amount of copper and zinc is generally associated with insufficient sensitivity or matrix interference. Thus, sensitive reproducible and accurate analytical methods for determination of copper and zinc in contaminated water samples are required. Flame Atomic Absorption Spectrometry (FAAS) [5, 6] is a well-established technique for this purpose due to its low cost and good analytical performance. The determination of these metal ions in contaminated water samples is influenced by several factors, such as low concentration of metal in the sample and the loss of analyte during the sampling step. Therefore, preliminary preconcentration and separation techniques such as co-precipitation[7], liquid–liquid extraction[8], cloud-point extraction[9] and solid phase extraction (SPE) [10, 11] for metal ions have been used. Solid phase extraction has been extensively used for the preconcentration of trace metals and the elimination of matrix interferences prior to AAS determination. This is because it offers advantages such as improved accuracy, high enrichment factor and low consumption of organic solvents. Besides, all these advantages, the batch-mode of SPE can be time-consuming, require large sample or reagent volumes and has the potential for contamination and analyte loss[12].There has been sustained interest in the application of on-line flow injection preconcentration procedures using solid phase extraction for determination of various trace elements in water samples. This combination has the advantages of short analysis time, high enrichment factor, high precision, easy automation, low cost and low consumption of reagents. Recently, various sorbents as solid phase extractor have been used for on-line preconcentration and determination of copper and zinc, such as activated carbon [13,14], activated alumina [15], silica [16], polyurethane foam [17] and different polymeric supports [18,19]. The most widely used polymeric sorbents are styrene-divinyl benzene copolymers, such as commercially available resins of Amberlite XAD series [20-22] which have a high hydrophobic character. Amberlite XAD-16, which is a polystyrene-divinylbenzene copolymer on ligand immobilization, gives chelating resins of better sorption capacities than those of other Amberlite XAD based chelators. The improvement in the sorption capacity may result due to higher surface area of Amberlite XAD-16. It adsorbs and releases ionic species through hydrophobic and polar interactions, usually used under isocratic conditions.

This work aims to synthesize 8-hydroxyquinoline functionalized with Amberlite XAD-16 resin to be used as a solid phase extractor (SPE) and to develop an on-line Flow injection preconcentration method for Cu (II) and Zn (II) determination in water samples using Flame Atomic Absorption Spectrometry (FAAS) as a detection method.

Experimental

Instrumentation

A Perkin-Elmer AAnalyst 400 flame atomic absorption spectrometer equipped with deuterium lamp background correction and an air- acetylene burner for metal determination was used throughout the study. The wavelength for the resonance line of copper and zinc hollow cathode lamp were set at 324.8 and 213.86 nm respectively. A Perkin Elmer (Shelton, CT, USA) FIAS 400 flow injection system was coupled with flame atomic absorption spectrometer. This complete online system was controlled by a personal computer and Winlab32 TM (version 6.5.0.0266) application software. The online preconcentration system was built with two peristaltic pumps P1, P2, a 5-port 2-positional injection valve and a preconcentration column. All connections of flow system were made using fittings and unions made up of plastic and Polyether ether ketone (PEEK) materials. For measuring pH, a pH meter Model LI614 (Elico Ltd., India) was used. Thermal analysis was done using a Perkin Elmer Diamond DSC. An IR spectrum was recorded on a Perkin Elmer Model Spectrum RX-1(resolution 4 cm^{-1}, number of scan 16 and range 400-4000 cm^{-1}). CHNS elemental analysis was carried out on an Elementor Model Vario EL-III. SEM was carried out using Scanning Electron Microscope model FEI Quanta 200F, Icon, Netherland.

Reagents and solutions

All chemicals used were of analytical reagent grade and double distilled water from a WDU-2000 Double Water Distillation Unit was used throughout the study. Amberlite XAD-16 (Sigma-Aldrich) has a surface area of approximately 800 m^2/g, moisture holding capacity of 62-72%. The 8-hydroxyquinoline used was of analytical reagent grade. All analytical reagents were obtained either from E. Merck or Thomas Baker. Certified Cu (II) and Zn (II) nitrate solution traceable to National Institute of Standards and Technology (NIST) was procured from E. Merck.

A stock solution of 1000 mg L^{-1} Cu (II) and Zn (II) was prepared by dissolving analytical reagent grade Cu (II) and Zn (II) nitrate in doubly distilled water and the metal ion solutions were standardized by complexometric titration with EDTA before use. All standard solutions were prepared from this stock solution. The pH adjustments were made with 0.1 mol L^{-1} HCl and 0.1 mol L^{-1} NaOH. All the glassware which were used for the laboratory purpose were kept overnight in a 10% (v/v) nitric acid solution and double distilled water was used to wash the glassware.

Synthesis of Amberlite XAD-16 functionalized with 8-Hydroxyquinoline (AXAD16-8HQ)

The synthesis process of AXAD16-8HQ (styrene-divinylbenzene copolymer) was modified according to the procedure reported in the literature [20]. The first step of the procedure involves nitration of styrene-divinylbenzene copolymer, followed by reduction to form an aromatic amine. This amine was then diazotized to form a stable diazonium salt. The diazotized polymer formed was filtered, washed with cold water and then reacted at 0-5°C for 24 h with 2 g of 8-hydroxyquinoline, dissolved in 400 mL of water and 200 mL of glacial acetic acid. The reddish brown beads obtained were filtered, washed with double distilled water and stored in desiccator until use. The AXAD16-8HQ resin was synthesized by the reactions as shown in Figure 1.

Fig.1 Synthesis of Amberlite XAD-16 functionalized with 8-hydroxyquinoline and its proposed structure.

Packing of minicolumn

The functionalized AXAD16-8HQ resin minicolumn was prepared by packing 150 mg of the sorbent in a mini glass column (3.0 cm length and 3.0 mm internal diameter). The slurry of the resin in beads form was injected into the minicolumn with a syringe. The ends of the column were sealed with cotton to retain the resin. The column was washed with 2.0 mol L^{-1} HNO_3 and after that with deionized water. The column had a constant performance during all experiments and there was no need for any regeneration or repacking.

On-line Preconcentration Procedure for copper and zinc determination

The schematic diagram of the online preconcentration flow system (FI-FAAS) is shown in Fig.2. The manifold was operated in a time based mode and the operational steps of the optimized procedure for copper and zinc determination are given in Table1. FI-FAAS set is controlled by a computer program which includes: pre-filling, filling, loading and elution step. Each preconcentration cycle starts with a short loading and elution step performed to filled the tubes. Loading time is 60 s and elution includes 30 s reading time. During the sample loading step, 10 s before the valve is moved to the elution position so that signal readings are stabilized with the eluent solution. The flow rate is set in the elution step to ensure recovery of maximum metal. Absorbance peak is recorded and its height is the analytical signal. The sample solution was adjusted with definite pH and pumped at the flow rate of 5 mL min^{-1} during the preconcentration mode. The resin AXAD16-8HQ loaded with Cu (II) and Zn (II) ion were eluted with HNO_3 and then subjected to on-line FAAS determination. Similar procedure was followed for the unknown water sample solution for metal ions preconcentration and determination. Three replicates of measurements were carried for every standard and sample solution. Each measurement was followed by a blank check.

Fig. 2 Flow injection preconcentration system using FIAS 400.

Table 1 Online Flow Injection Program for 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 the Amberlite XAD-16 functionalized with 8-Hydroxyquinoline (AXAD16-8HQ) chelating resin

FT-IR spectrum

The FT-IR spectrum of chelating resin AXAD16-8HQ shows bands of Amberlite XAD-16 and 8-hydroxyquinoline which shows that chelating agent has been loaded on resin. AXAD16-8HQ resin has bands at 3448 cm^{-1} (O-H stretching), 2930 cm^{-1} (C-H stretching), 1637cm^{-1}(C=N), 1337 cm^{-1} (C-N), 1127 (C-O) and 1525 cm^{-1} (-N=N-). This supports the loading of 8-hydroxyquinoline resin onto Amberlite XAD-16 through diazotized (N=N) coupling as shown in Fig.3a.

Comparative analysis of the FT-IR spectra as shown in Fig. 3b and 3c of AXAD16-8HQ resin before and after Cu (II) and Zn (II) sorption showed that O-H and C-N of AXAD16-8HQ resin at 3440, 1347 cm^{-1} and 3438,1344 cm^{-1} vibrations were shifted by 5-10 cm^{-1}. Conclusive evidence of the bonding is also shown by the observation that new bands in the FT-IR spectra of the Cu (II) metal complexes at 479 and 440 cm^{-1} assigned to (Cu-O) and (Cu-N) while for Zn (II) metal complexes at 562 and 440 cm^{-1} assigned to (Zn-O) and (Zn-N) stretching vibrations respectively.

Fig. 3a Infrared spectra of Amberlite XAD-16 functionalized with 8-hydroxyquinoline resin.

Fig. 3b Infrared spectra of Amberlite XAD-16 functionalized with 8-hydroxyquinoline resin after sorption of copper

Fig. 3c Infrared spectra of Amberlite XAD-16 functionalized with 8-hydroxyquinoline resin after sorption of zinc

TGA The thermo gravimetric analysis (TGA) curve of freshly prepared AXAD16-8HQ resin showed a very slow but steady weight loss up to 598 ^{o}C. The observed weight loss was 16.1% up to 120 ^{o}C. This was due to physisorbed water on the resin, which supported the presence of three water molecules per repeat unit of chelating resin in AXAD-16.

CHN 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 AXAD16-8HQ resin was found to be 62.04% for C, 4.80% for H, 12.76% for N while calculated for $C_{17}H_{14}N_{3}0$. $3H_2O$ was 61.81% for C, 4.2% for H and 12.72% for N.

SEM 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. 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 (Fig. 4) show that the pure resin had a smooth and flat surface, while the modified chelating resin shows dense microstructures and granular grains. This signifies that the ligand loads onto the support. The substrate surface was changed after functionalization with 8-hydroxyquinoline. They are agglomerated polymeric materials with irregular shapes and sizes varies from 50 µm to 500 µm.

Fig. 4 Scanning electron micrograph (SEM) images of
(a)Amberlite XAD-16 (b) AXAD16-8HQ resin

Optimum conditions for recoveries of analytes

Effect of pH

The sample acidity plays a major role in the preconcentration studies; due to this the effect of pH was studied over the range (2-10) with 100 µg $L^{-1}$of Cu (II) and 50 µg L^{-1} of

Zn (II) solution for AXAD16-8HQ resin keeping other parameters constant. The result obtained is presented in Fig. 5 and it showed that Cu (II) and Zn (II) ions were completely adsorbed on the adsorbent over the pH of 4.0 and 8.0 respectively.

Therefore, to achieve high efficiency and better selectivity, all subsequent studies were carried out at pH 4.0 for Cu (II) and pH 8.0 for Zn (II) respectively.

Fig. 5 Effect of pH on the preconcentration of Cu (II) and Zn (II).

Effect of Eluent concentration

In order to achieve enough protons to protonate the chelating sites, two acids HNO_3 and HCl, have been examined as potential eluents for Cu (II) and Zn (II) desorption from AXAD16-8HQ resin. HNO_3 is considered to be more convenient for FAAS assays because of its improved and sharper signals in comparison to HCl. The effect of HNO_3 concentration was studied in the range of 0.01– 2.0 mol L^{-1}. The results show (Fig. 6) that with increase in the HNO_3 concentration up to 0.5 for Cu (II) and 0.3 mol L^{-1} for Zn (II), absorbance increases and then decreases at higher concentrations. Optimization of the elution conditions were performed in order to obtain the maximum recovery with the minimal concentration and volumes of the eluent. Therefore, 0.5 mol $L^{-1}$and 0.3 mol L^{-1} HNO_3 was chosen as eluent while the elution time was fixed at 30 s in order to ensure the complete elution of adsorbed Cu (II) and Zn (II) ions.

Fig. 6 Effect of eluent concentration on the preconcentration of Cu (II) and Zn (II).

Effect of Sample and Eluent Flow Rate

Online preconcentration system depends upon the flow rate of the sample solution as it regulates transfer of metal ions from liquid to solid phase. Therefore, the effect of flow rate was examined under pH 4.0 and 8.0 for Cu (II) and Zn (II) solution respectively through the mini column with flow rate in the range of 2.0-7.0 mL min^{-1}. At higher flow rates, backpressure is produced in the minicolumn. Besides, the analytical signal decreased owing to short residence time of ions, which resulted in an incomplete retention. While low flow rates decreases sample throughput resulting in a long time of analysis. In order to improve analytical efficiency, 5.0 mL min^{-1} was chosen as the loading rate for both Cu (II) and Zn (II) ions for AXAD16-8HQ resin as shown in Fig.7. Higher preconcentration times could be beneficial for the determination of the samples with lower Cu (II) and Zn (II) concentrations. However, long periods are not interesting for flow injection preconcentration system as sample throughput is low. So, a preconcentration time of 60 s was used for the determination of Cu (II) and Zn (II) ions in water samples.

The influence of eluent flow rate in the elution step was also studied over the range 2.0-7.0 mL min^{-1} (Fig. 8), because it establishes the velocity of acid solution through the minicolumn. Results obtained showed that the analytical signal is maximum at eluent flow rate of 6.0 and 5.0 mL min^{-1} for Cu (II) and Zn (II) ions respectively.

Fig. 7 Effect of sample flow rate on the preconcentration of Cu (II) and Zn (II).

Fig. 8 Effect of eluent flow rate on the preconcentration of Cu (II) and Zn (II).

Interference studies

In order to evaluate the selectivity of the preconcentration system, the effect of interfering ions on the determination of Cu (II) and Zn (II) ions were investigated using the recommended online method under optimum conditions. The chloride, nitrate, sulfate and phosphate ions commonly found in natural water samples have the capability to form complex with many metal ions. Therefore, in their presence, the efficiency of the chelating resin to bind with metal ion may be hampered, resulting in the reduction of overall enrichment. Thus, the effect of Na^+, Cl^-, NO_3^-, SO_4^{2-}, Br^-, Mg^{2+}, Pb^{2+}, Cd^{2+}, Cu^{2+}, Zn^{2+}, Ca^{2+}, Al^{3+} and K^+ on the sorption efficiency of AXAD16-8HQ resin for 100 µg L^{-1} Cu (II) and 50 µg L^{-1} Zn (II) were studied. The tolerance limits of these ions in the preconcentration of Cu (II) and Zn (II) are given in Table 2. The effect of each species was considered interference when the signal in the presence of the species resulted in an absorbance deviation of more than ±5%.The results demonstrate that the presence of large amounts of these metal ions in the sample have no significant effect on the analytical signal of Cu (II) and Zn (II).

Table 2 Effects of Matrix Ions on the recovery of Cu (II) and Zn (II) ions of AXAD16-8HQ resin

Interfering ion	**Tolerance Limit (mg L^{-1})**	
	Cu (II)	**Zn (II)**
Na$^+$	45,000	40,000
Cl$^-$	25,000	30,000
Br$^-$	30,000	18,000
Mg^{2+}	25,000	20,000
SO$_4^{2-}$	18,000	4,000
NO$_3^-$	20,000	4,000
Cd^{2+}	30	25
Pb^{2+}	30	30
Ca^{2+}	25	20
K$^+$	20	18
Al^{3+}	15	10
Cu^{2+}	-	12
Zn^{2+}	18	-

Column Stability and Reusability

The repeated cycles of loading and elution of copper and zinc with AXAD16-8HQ beads were studied under optimum experimental conditions. The sorption capacity was found to vary < 5.0% than that of untreated resin. The reproducibility of the recovery data of Cu (II) and Zn (II) were almost same even after ~300 cycles of sorption-desorption. This shows that repeated use of the resin is possible. The present resin can withstand acid concentrations up to 5.0 mol L^{-1}.The leaching of the reagent i.e., 8-hydroxyquinoline was not observed as it is chemically immobilized on Amberlite XAD-16. The low volume and concentration of acid used under optimized conditions shows that resin is stable and column has a long lifetime.

Analytical Performance

The analytical performance of the FI–SPE–FAAS method for Cu (II) and Zn (II) ions with AXAD16-8HQ resin under the optimum experimental conditions is summarized in Table 3. Enrichment factor was calculated as the ratio of the slopes of the calibration curves with and without preconcentration. As the preconcentration time increases from 60 to 180 s, the enrichment factor increases. The enrichment factor obtained for Cu (II) with 60,120 and 180 s is 24, 51 and 80 and for Zn (II) is 36, 96 and 147. The detection limit based on 3σ criteria, defined as concentration that gives a response equivalent to three times the standard deviation of the blank and found to be 0.5, 0.3 and 0.16 µg L^{-1} for Cu (II) while 0.4, 0.3 and 0.2 µg L^{-1} for Zn (II) solution respectively. The precision (% RSD) was found to be 1.2 and 1.5% for 50 and 100 µg L^{-1}Cu (II) and 2.2 and 1.7% for 40 and 80 µg L^{-1} Zn (II) solutions respectively.

Table 3 Analytical Performance of Flow Injection On-line Method for Cu (II) and Zn (II) determination using AXAD16-8HQ resin

Parameters	**Cu (II)**			**Zn (II)**		
Preconcentration time (s)	60	120	180	60	120	180
Sample consumption (mL)	5	10	15	5	10	15
Sample throughput (h^{-1})	30	20	15	30	20	15
Enhancement factor	24	51	80	36	97	147
Linear range (μg L^{-1})	0-180	0-130	0-90	0-90	0-35	0-22
Limit of detection (μg L^{-1})	0.5	0.3	0.16	0.4	0.3	0.2
Correlation coefficient	0.998304	0.992763	0.997139	0.992506	0.993088	0.993386
Regression equation 6 standards, n=3; Cu(II)/Zn(II)/ μg L^{-1} (with preconcentration)	A_{60}= 0.01058 + 0.00366 [Cu(II)] A_{120}= 0.05960 + 0.00768 [Cu(II)] A_{180} = 0.00929 + 0.01217 [Cu(II)]			A_{60}= 0.06809 + 0.01112 [Zn(II)] A_{120}= 0.02718 + 0.03015[Zn(II)] A_{180}= 0.05837 + 0.04575[Zn(II)]		
Regression equation 6 standards, n=3; Cu(II)/Zn(II)/ μg L^{-1} (without preconcentration)	A= 0.00086 + 0.00015204 [Cu(II)]			A=0.02056+ 0.00031252 [Zn(II)]		
Precision (R.S.D %) n=5	1.2, [Cu (II)] =50 (μg L^{-1}) 1.5, [Cu (II)] =100 (μg L^{-1})			2.2, [Zn (II)] = 40 (μg L^{-1}) 1.7, [Zn (II)] = 80 (μg L^{-1})		

Analytical applications

In order to assess the accuracy and applicability of AXAD16-8HQ resin for Cu (II) and Zn (II) ions determinations, the water samples were collected from three different places, Mayapuri, Narayana and Noida industrial area. The samples were filtered through a 0.45 μm pore size filter to remove any suspended particulate matter prior to its preconcentration. Then 5 mL of each sample was preconcentrated (sample flow rate 5 mL min^{-1} and sample loading time 60 s) and analyzed by the proposed method. As analyte concentration of water sample was too low for direct method, therefore water samples were spiked using certified Cu (II) and Zn (II) nitrate solution traceable to NIST. The accuracy of the preconcentration procedure was performed by the recovery experiments for spiked sample. The results are given in Table 4. It has been found that the addition of Cu (II) and Zn (II) ions gives very good recovery.

Table 4 Analytical Results Obtained for the Determination of Cu (II) and Zn (II) in Water Samples

Sample	Copper amount*			Zinc amount*		
	Conc. Determined (µg L^{-1})	**Conc. Determined By 20 µg L^{-1} Spiked Cu (II) µg L^{-1}**	**Recovery (%)**	**Conc. Determined (µg L^{-1})**	**Conc. Determined By 20 µg L^{-1} Spiked Zn (II) µg L^{-1}**	**Recovery (%)**
Nariana, IndustrialArea, Delhi, India	36.09 ± 1.2	54.98 ± 2.2	98.0%	59.39 ±2.0	78.39 ±2.3	98.7%
Noida, IndustrialArea, U.P, India	25.79 ± 1.5	44.52 ± 1.9	97.0%	56.83 ±1.2	75.80 ±2.1	98.6%
Mayapuri, IndustrialArea, Delhi, India	19.68 ± 0.6	39.07 ± 1.8	98.0%	58.02 ±1.6	**77.**02 ±2.2	98.7%

***Confidence interval: 95%**

Accuracy of the Online Preconcentration method

The accuracy of the proposed method was tested by determining the Cu (II) and Zn (II) concentration of a certified reference material NIST SRM 1643e (National Institute of Standard and Technology, Trace elements in water). The results are described in Table 5 at confidence intervals of 95%. It was found that there is no significant difference between achieved results by proposed method and certified results.

Table 5 Cu (II) and Zn (II) determination in Standard reference material, Trace elements in water

Sample	Cu (II) amount (µg L^{-1})*			Zn (II) amount (µg L^{-1})*		
	Certified value	**Proposed methodology**	**Recovery (%)**	**Certified value**	**Proposed methodology**	**Recovery (%)**
SRM 1643e, Trace elements in water	22.76± 0.31	22.08 ± 0.45	97.01 %	78.5 ± 2.2	76.9 ± 0.2	97.90 %

***Confidence interval: 95%**

Comparison of performance characteristics of newly designed chelating resin with other selected on-line SPE methods

For comparative purposes, the performance characteristics of the proposed method and other selected on-line SPE preconcentration FAAS methods reported in the literature are given below in Table 6 and 7. The proposed method shows ***good sensitivity (detection limit), better precision (RSD) and high sample throughput with very high enhancement factor*** over other on-line preconcentration methods.

Table 6 Comparison of performance Characteristics among Selected Online SPE Methods and the Developed Method for the Cu (II) Determination with FAAS.

Support	Chelating Agent	Eluent	PT(sec)	RSD (%)	DL	EF	Ref.
Amberlite XAD-2	Pyrocatechol	HNO_3	180	3.8	0.3	36	23
Amberlite XAD-2	3,4-dihydroxybenzoic acid	HCl	120	1.1	0.2	33	24
Amberlite XAD-2	2-aminothiophenol	HNO_3	180	-	0.5	35	25
Amberlite XAD-4	3,4-dihydroxy benzoic acid	HCl	60	2.1	2.3	22	26
Amberlite XAD-4	β-nitroso-α-napthol	HNO_3	180	2.8	0.4	58	27
Amberlite XAD-4	2,6-dihydroxyphenyl-Diazominoazobenzene	HNO_3	60	2.7	0.3	28	28
Amberlite XAD-4	Schiff Bases	HNO_3	60	-	1.2	13.3	29
Chitosan bipolymer	5-Sulphonic acid-8-hydroxyquinoline	HNO_3	90	0.7	0.3	19.1	30
Chloromethylated polystyrene	1-phenyl-1,2-propanedione-2-oxime thiosemicarbazone (PPDOT)	HNO_3	240	2.0	0.5	41	31
Micelle	N,N, -bis(2-hydroxy-5-bromo-benzyl)-1,2-diaminopropane (HBDAP)	HNO_3	30	-	3.2	-	32
Polyurethane foam	2-(6-methyl-2-benzothiazolylazo)chr	HCl	90	2.9	1.2	14.1	33

	omotropic acid (Me-BTANC)						
styrene-divinylbenzene	(*S*)-2-[hydroxy-bis-(4-vinyl-phenyl)-methyl]-pyrrolidine-1-carboxylic acid ethyl ester	HCl	120	1	1.1	42	34
styrene–divinylbenzene	salen-OMe complex	-	60	2.8	1.0	12	35
Amberlite XAD-16	***8-Hydroxyquinoline***	***HNO_3***	***180***	***1.2***	***0.16***	***80***	***This Work***

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

Table 7 Comparison of performance Characteristics among Selected Online SPE Methods and the Developed Method for the Zn (II) Determination with FAAS

Support	**Chelating Agent**	**Eluent**	**PT(s)**	**RSD (%)**	**DL ($\mu g\ L^{-1}$)**	**EF**	**Ref.**
Activated carbon	-	HNO_3	-	0.82	1.9	10.9	14
Alumina	Alizarin Red S	HNO_3	300	3.0	0.2	144	36
Amberlite XAD-4	3,4-dihydroxybenzoic acid	HC l	60	2.1	2.3	54	26
Amberlite XAD-4	2,6-dihydroxyphenyl-diazoaminoazobenzene	HCl	60	2.7	0.2	31	28
Amberlite XAD-16	3-((2,6-dichlorophenyl)(1H-indol-3-yl)methyl)-1H-indole (DCPIMI)	HNO_3	-	2.3	1.5	225	37
-	(2-pyridylazo)resorcinol (PAR)	oxalic acid	300	3.55	0.42	-	38
Micelle	HBDAP(N,N$^{/}$-bis(2-hydroxy-5-bromo-benzyl)1,2-diaminopropane)	HNO_3	60	-	0.89	8.4	32

PTFE turnings	Ammonium pyrrolidinedithiocarbamate	IBMK	30	3.2	0.3	65	39
Styrene-Divinylbenzene	2-[hydroxy-bis(4vinylphenyl)methyl] pyrrolidine-1-carboxylic acid ethyl esther	HCl	240	6.5	0.98	-	40
Amberlite XAD-16	***8-hydroxyquinoline***	***HNO_3***	***180***	***2.2***	***0.2***	***147***	***This Work***

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

CONCLUSION

A ***fast, sensitive and selective method*** for extraction, preconcentration, and determination of copper and zinc ions were introduced. The method is based on solid phase extraction of copper and zinc with AXAD16-8HQ resin as a new selective SPE sorbent. The resin was prepared by reaction of the diazotized copolymer with 8-hydroxyquinoline and was successfully applied to on-line preconcentration and determination of copper and zinc by FAAS. The synthesis resulted in a promising and ***very stable support*** that does not present problems of leaching. These features allow a ***long lifetime*** of the minicolumn packed with the resin, with its use for many cycles being possible. The on-line preconcentration procedure is simple, ***rapid, low-cost and sensitive***. The retained copper and zinc were eluted with a preconcentration factor of 80 and 147. Finally, the method was used for extraction and determination of Cu (II) and Zn (II) in industrial water samples with satisfactory results. Figures of merit for the proposed method and some recently reported on-line solid-phase extraction preconcentration FAAS methods are reported in Tables 6 and 7. By comparing the data in this table, it is clear that detection limit for the proposed method for copper and zinc determination is better than those obtained with other sorbent materials.

Acknowledgement

The authors are thankful to the Department of Science and Technology, Government of India, New Delhi, India, for financial assistance.

References

1 H.H. Dieter, T.A. Bayer and G. Multhaup, *Acta Hydroch Hydrob*., 2005, **33**, 72-78.

2 D. Strausak, J.F.B.Mercer, H.H. Dieter, W. Stremmel and G.Multhaup, *Brain Res. Bull.,* 2001, **55**, 175-185.

3 J. S. Carletto, K. C.Di P. Roux, H. Franc¸ M. E. Martendal, E. Carasek, *J. of Hazard. Mater*., 2008, **157**, 88–93.

4 Guidelines for Drinking-water Quality, Fourth Edition; *World Health Organisation*, 2011.

5 M. Ghaedi, M.R. Fathi, F. Marahel and F. Ahmadi, *Environ. Bull*., 2005, **14**, 158–1163.

6 M.C. Yebra, N. Carro and A. Moreno-Cid, *Spectrochimica Acta*, 2002, **Part B 57**, 85-93.

7 A. Efendioglu, M. Yagan and B.Bat, *J.Hazard. Mater*., 2007, **149,**160–165.

8 M.R. Jamali, Y. Assadi, R.R. Kozani and F. Shemirani, *E-J. Of Chem*., 2009, **6(4)** ,1077-1084.

9 M. Ghaedi, K. Niknam, E. Niknam and M. Soylak, *J. of theChineseChemical Society*, 2009, **56**,981-986.

10 A.N. Anthemidis and K.I.G. Ioannou, *Anal. Chim. Acta*, 2006, **575**,126-132.

11 M. Tuzen, M. Soylak and L. Elc, *Anal. Chim. Acta*, 2005, **548**,101–108.

12 D. Kara, *Anal. Letters*, 2011, **44**, 457-482.

13 E.A. Takara, S.D. Pasini-Cabello, S. Cerutti, J.A. Gasquez and L.D. Martinez, *J. Pharmaceut. Biomed*. 2005, **39,** 735–739.

14 V.N. Alves, S.S.O. Borges, and N.M.M. Coelho, *Inter. J. of Anal. Chem*., 2011, 1.

15 S. Dadfarnia, A.M.H. Shabani, E.Tamaddon and M. Rezaei, *Anal.Chim.Acta*, 2005,**539**, 69–75.

16 E.L. Silva, A.O. Martins, A. Valentini, V.T. Favere and E. Carasek, *Talanta*, 2004, **64,**181–189.

17 V.A. Lemos, W.N.L.Santos, J.S. Santos and M.B. Carvalho, *Anal Chim Acta*, 2003, **481**, 283-290.

18 R.J. Cassella, O.I. B. Magalhaes, M.T. Couto, E.L.S. Lima, M.A.F.S.Neves and F.M.B. Coutinho,*Talanta*, 2005,**67**,121–128.

19 A. N. Anthemidis, G.A. Zachariadis and J.A. Stratis, *Intern. J. Environ. Anal. Chem*., 2010, **90**, 127-136.

20 R. Saxena and S.Saxena, *Indian J. of Chem*., 2012, **51A,** 1567-1573.

21 R. Saxena and S. Saxena, *At. Spect*., 2012,**33(3)**,83-91.

22 R. Saxena and S. Singh, *At. Spect*. 2013, **34(5)**, 155-163.

23 V. A. Lemos, D. G.da Silva, A. L. de Carvalho, D. de A.Santana, G. dos S. Novaes and A.S. dos Passos,*Microchem. J*., 2006, **84,** 14–21.

24 V.A.Lemos, P. X.Baliza, R.T.Yamaki, M. E. Rocha and A.P. O. Alves, *Talanta*, 2003,**61**, 675-682.

25 V.A. Lemos and P. X. Baliza, *Talanta*, 2005, **67**, 564–570.

26 L. S. G. Teixeira, M. de A. Bezerra, V. A. Lemos, H.C. dos Santos, D.S. de Jesus and A.C.S. Costa, *Sep.Sci. and Tech*., 2005,**40**, 2555–2565.

27 V.A. Lemos, E.S.Santos and E.M. Gama, *Sep. and Purifi. Tech*., 2007, **56**, 212–219.

28 Y.Liu1,Y.Guo, S. Meng, and X. Chang, *Microchim. Acta*., 2007, **158**, 239–245.

29 D. Karaa, A.Fisherb and S.J. Hill, *J. of Hazard. Mater*., 2009,**165**,1165–1169.

30 A.O. Martins, E. L. da Silva, E.Carasek, M.C.M. Laranjeira and V.T. de Favere, *Talanta*, 2004, **63**, 397–403.

31 M.A. Chamjangali, G. Bagherian, A. Mokhlesian and B. Bahramian, *J.of Hazard. Mater*., 2011,**192**,1641–1649.

32 D. Kara, *Talanta*, 2009, **79**, 429–435.

33 V.A. Lemos, A.A. de Jesus, E.M.Gama, G.T.David, and R.T.Yamaki, *Anal. Letters*, 2005, **38,** 683–696.

34 R.J. Cassella, O.I.B. Magalhaes, M. T. C., E.L.S. Limac, M.A.F.S. Neves and F.M.B. Coutinho, *Talanta*, 2005,**67,**121–128.

35 A. Tobiasz, S.Walas, B.Trzewik, P.Grzybek, M.M. Zaitz, M. Gawin and H. Mrowiec, *Microchem. J*., 2009, **93**, 87–92.

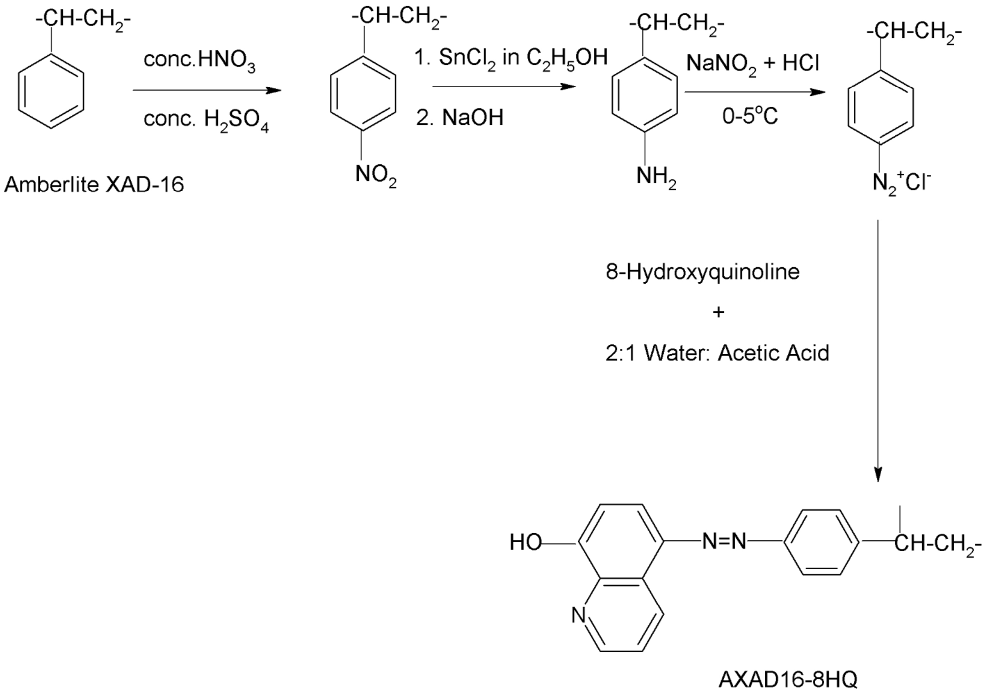
36 A.M. Haji Shabani, S. Dadfarnia and T. Moosavinejad, *Quim. Nova*, 2009, **32**, 1202-1205.

37 M. Ghaedi, K.Niknam, K. Taheri, H.Hossainian and M. Soylak, *Food Chem Toxicol.,* 2010, **48(3)**, 891-897.

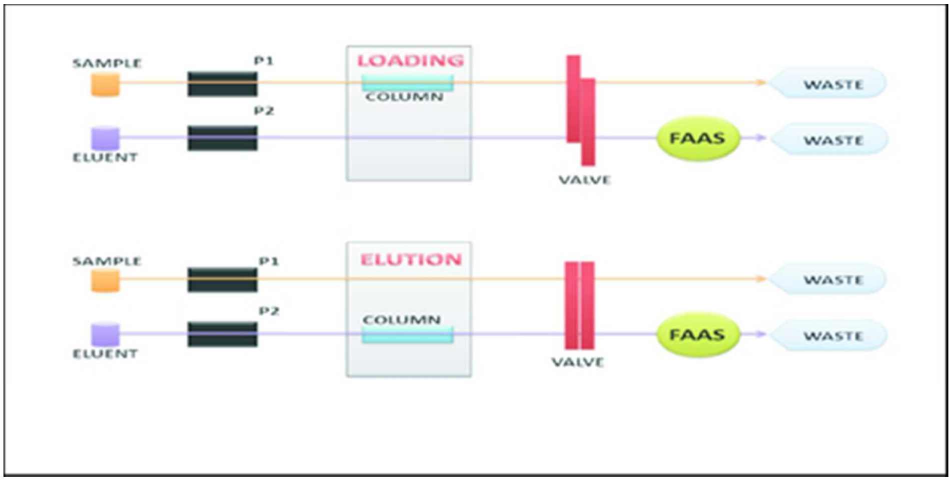
38 L. Wei, X.Zhang, Y.Dai, J.Huang, Y.H. Xie, and K. Xiao, *J.of Automated Methods and Management in Chem*., 2008, 5.

39 A. N. Anthemidis, G.A. Zachariadis and J.A. Stratis, *Intern. J. Environ. Anal. Chem*., 2010, **90**, 127-136.

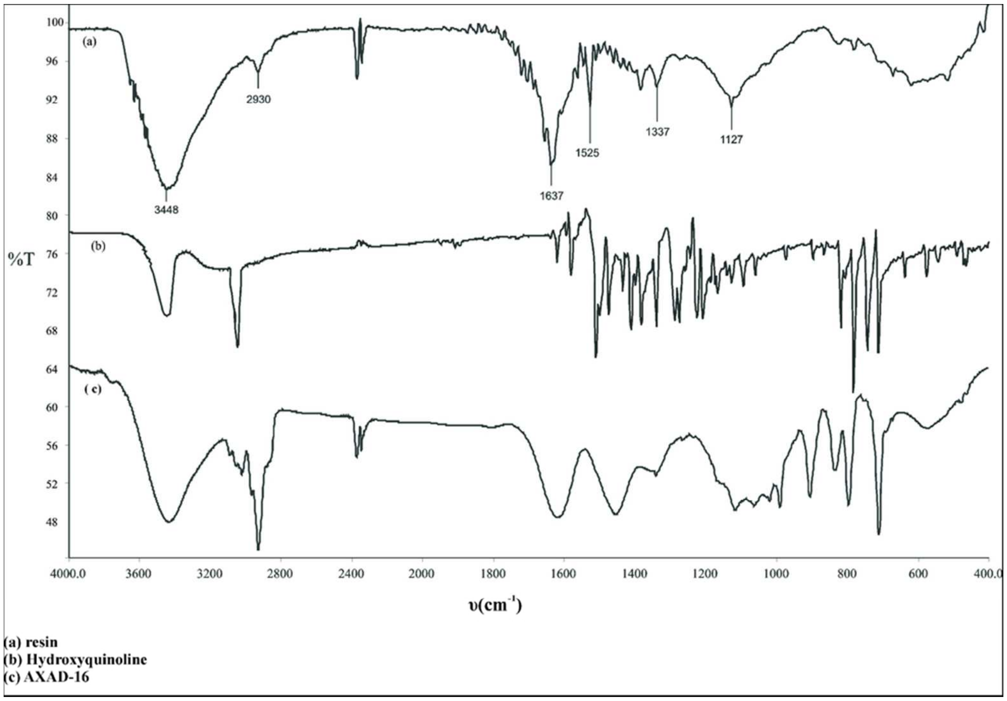
40 R.J. Cassella, O.I. Magalhaes, M.T.Couto, E. Lima, M.A. Neves and F.M. Coutinho*, Anal Sci.*, 2005, **8**, 939-944.



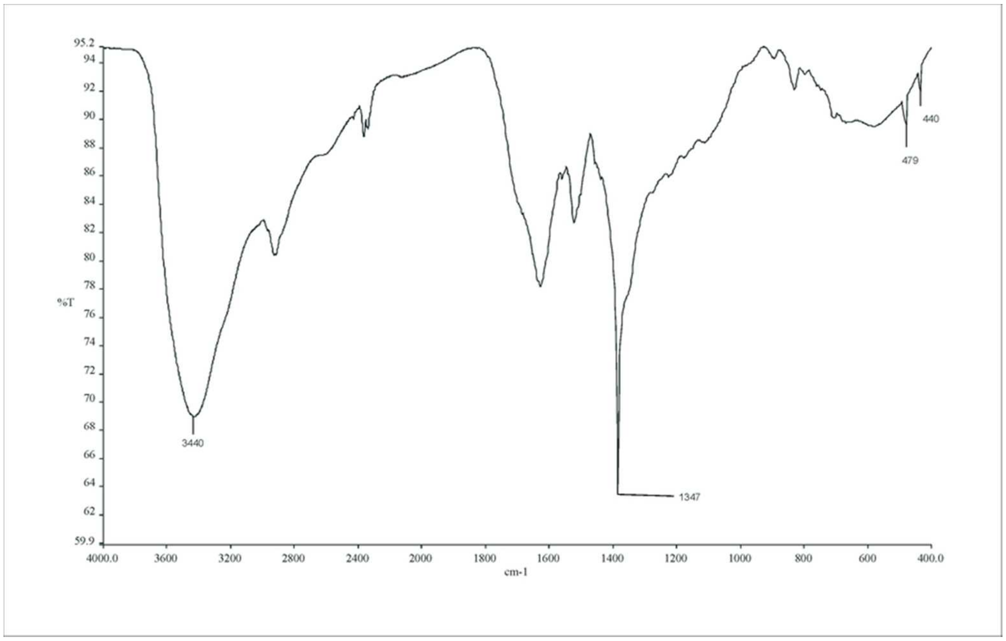
188x136mm (300 x 300 DPI)



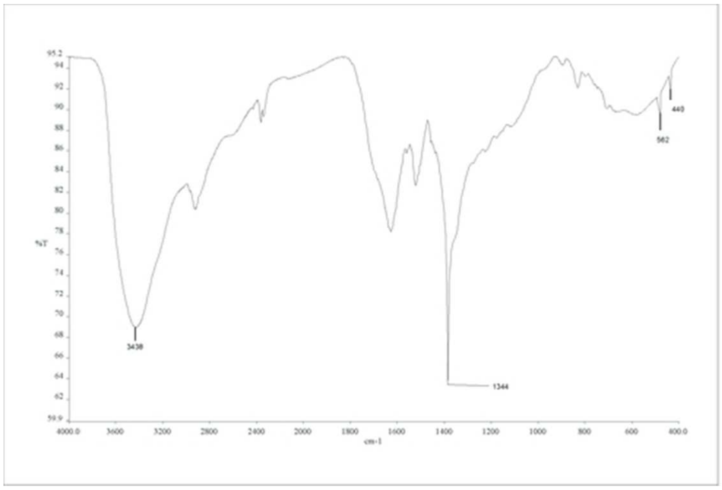
39x19mm (300 x 300 DPI)



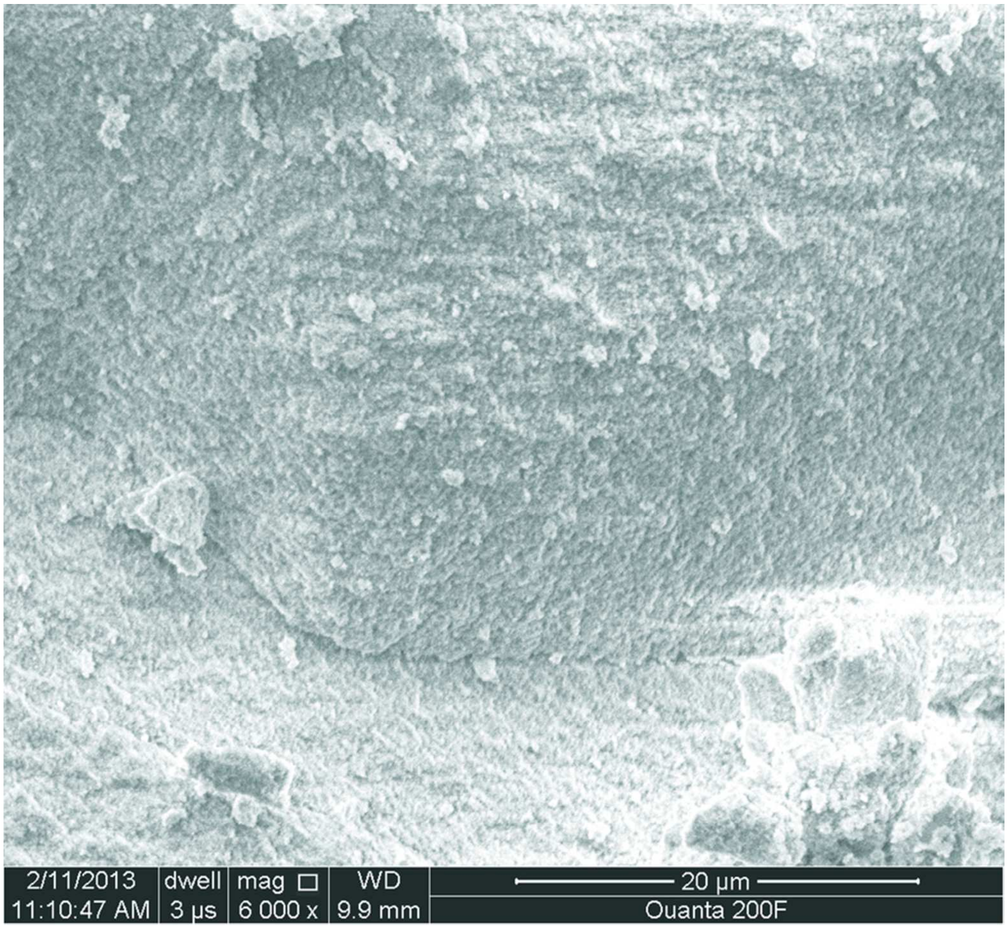
83x57mm (300 x 300 DPI)



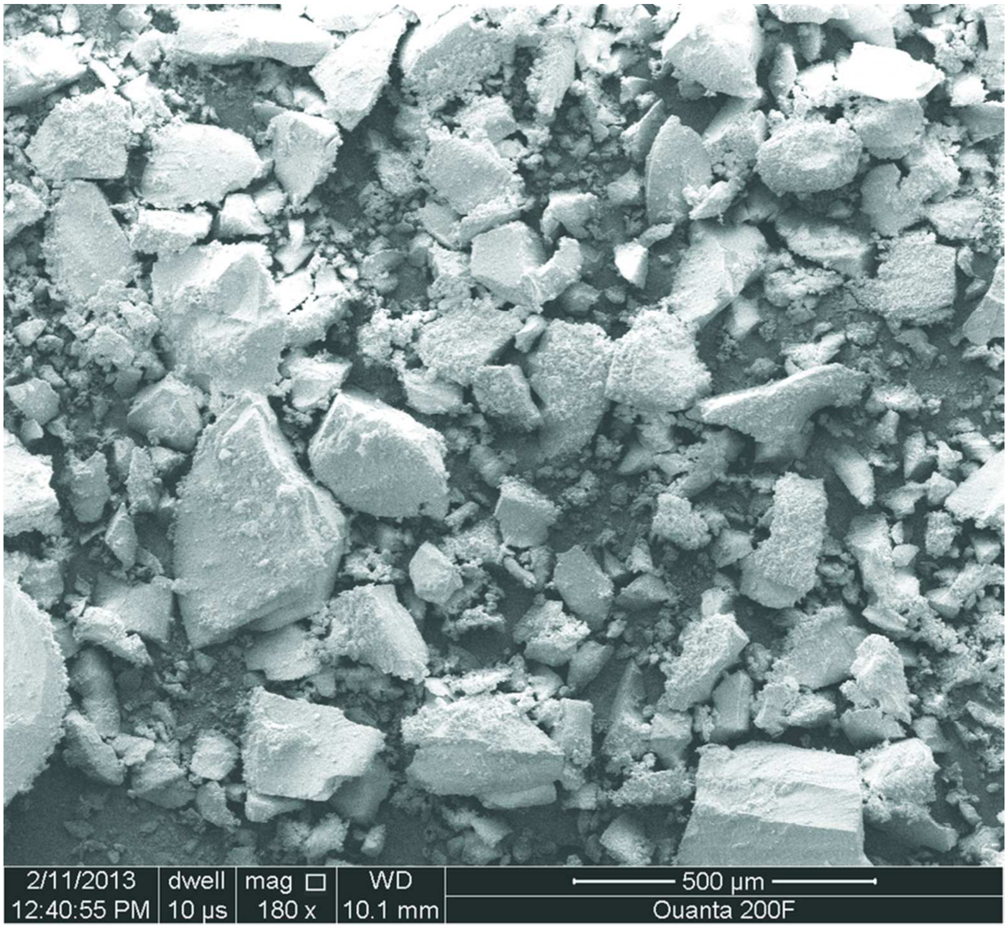
76x48mm (300 x 300 DPI)



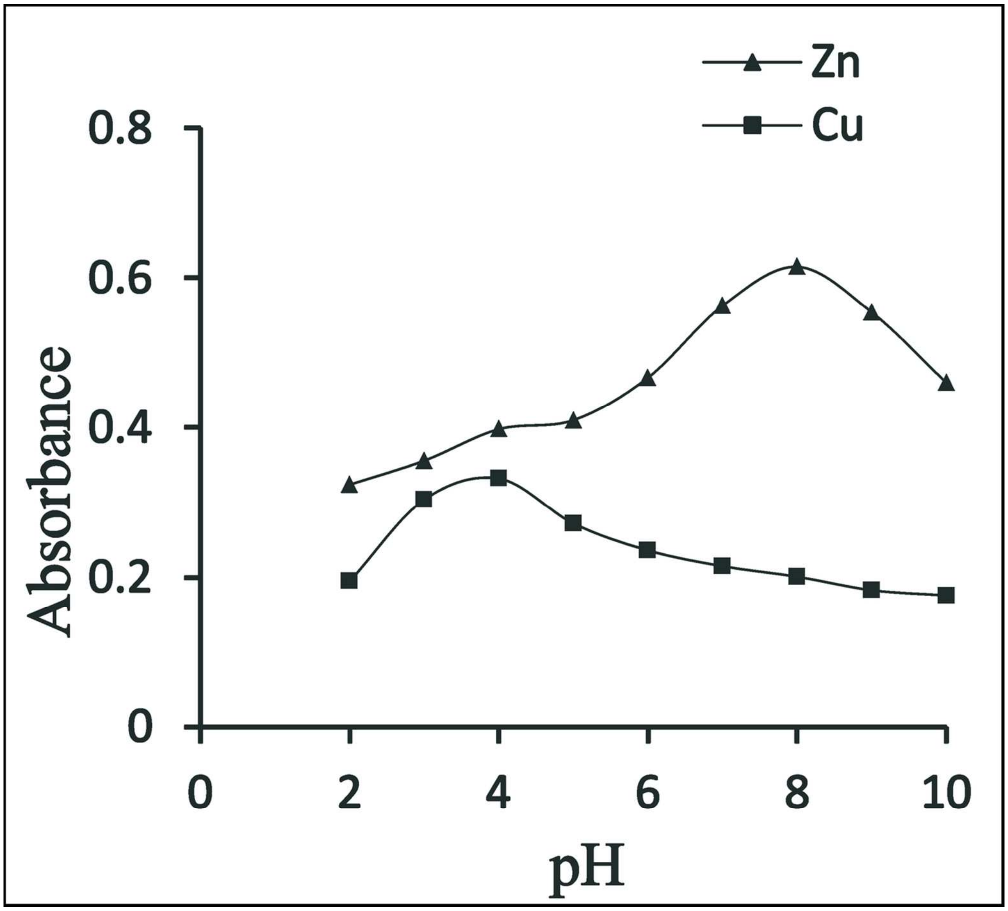
57x28mm (300 x 300 DPI)



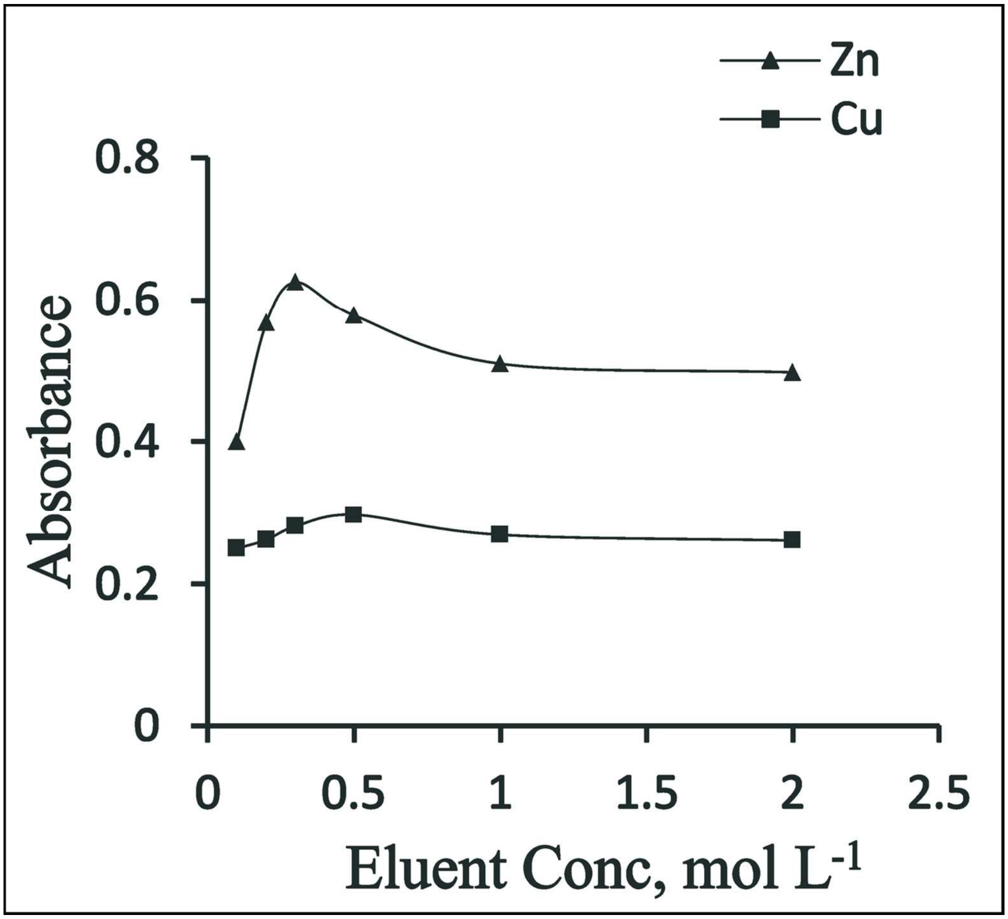
75x69mm (300 x 300 DPI)



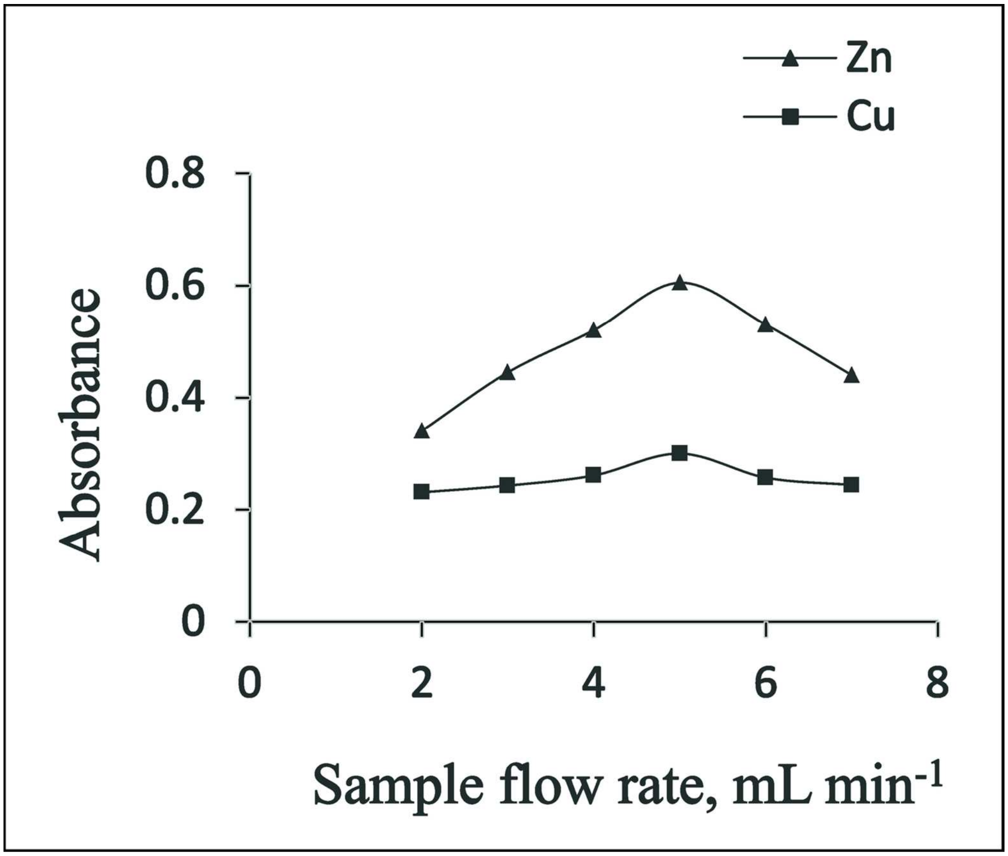
75x69mm (300 x 300 DPI)



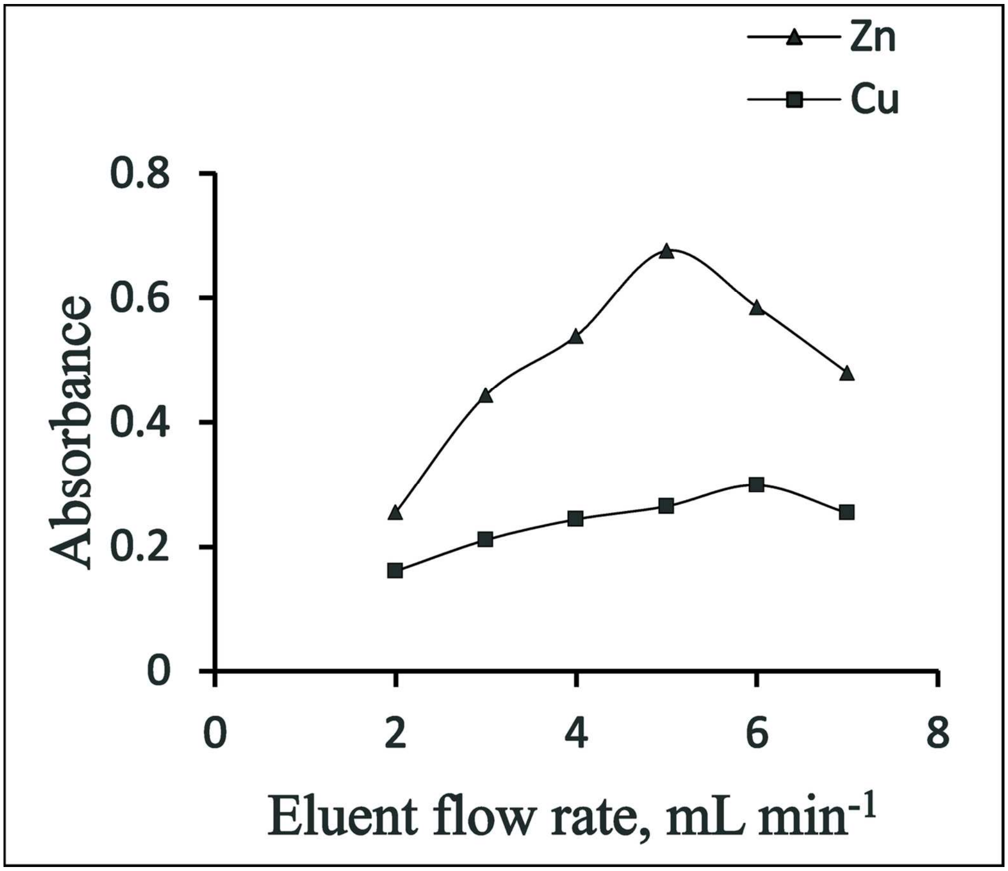
62x56mm (600 x 600 DPI)



62x56mm (600 x 600 DPI)



62x52mm (600 x 600 DPI)



63x54mm (600 x 600 DPI)