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On-line Determination of Zinc in Water and Biological Samples after Its Preconcentration onto Zincon Anchored Polyurethane Foam

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A fast and sensitive on-line procedure for the determination of zinc in water and biological samples was developed. Zinc was preconcentrated in a mini-column packed with polyurethane foam (PUF) chemically modified with zincon *via* -N=N- bonding. The optimal conditions for preconcentration were pH 8.5 and sample flow rate of 4.0 mL min^{-1}. Quantitative desorption of Zn(II) was obtained by 0.1 mol L^{-1} hydrochloric acid and subsequent spectrophotmetric determination using 4-(2-pyridylazo)-resorcinol at 498 nm. The obtained detection limit was found to be 3.0 ng mL^{-1}, precision (RSD) was 4.8 and 6.7% at 20 and 110 ng mL^{-1}, respectively, for 60 s preconcentration time and enrichment factor was 31. The linearity range was from 10 to 120 ng mL^{-1} and maximum sample throughput was 20 h^{-1}. Finally, the method was successfully applied to the determination of zinc in tap water, Nile River water and human urine samples with RSD in the range of 1.1 - 8.3%.

Keywords Zincon, polyurethane foam, preconcentration, spectrophotometry

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Introduction

Industrial and household waste discharge can leak into sewage systems and reach water sources, resulting in pollution of surface and underground water.[1] Investigation of toxic heavy metals such as zinc is of great importance in environmental chemistry. Thus, there is a great need to develop new analytical techniques that allow for the separation of zinc prior to its measurement.

There are several methods for the determination of zinc such as anodic stripping voltammetry,[1] spectrophotometry,[2] AAS,[3] FAAS,[4] GFAAS,[5] and ICP-MS.[6] These methods are of high sensitivity and accuracy. But some are expensive, time-consuming, troublesome, and others are toxic. Thus, there are increasing calls for more automated, safe, and simple techniques.

Preconcentration techniques can improve the detection limit as well as the selectivity of the method. On-line preconcentration methods can improve analytical features of the procedure such as by increasing analytical throughput, precision, and accuracy while decreasing the volume of reagent and sample consumption.[7]

On-line solid-phase preconcentration/separation of zinc has been performed by using mini-columns packed with several solids, such as ethylvinylacetate,[8] styrene-divinylbenzene,[9] alumina,[10] silica gel,[11] and polyurethane foam.[12,13] On-line preconcentration procedures are advantageous compared with the off-line batch systems, because they feature low volume sample/reagent consumption, high enrichment factors and high throughputs.[14]

Polyurethane foam (PUF) is a pragmatic material for preconcentration and separation of a wide variety of inorganic and organic compounds in different media due to its low cost, high available surface area and cellular structure and stability in acidic or basic media. PUF has been used unloaded or associated to physically immobilized chelating reagents in preconcentration and sampling procedure.[15] The high retention capacity of polyether-type PUF due to its large available surface area, the resilient property, the resistances in many acids, bases and organic solvents, and also the low cost have established PUF as a perfect sorbent material for on-line column preconcentration/separation techniques.[16]

Since Jesus *et al.*[12] and Casella *et al.*[17] employed unloaded PUF for on-line zinc preconcentration and determination, similar procedures have been reported using PUF modified with 2-[2′-(6-methyl-benzothiazolylazo)]-4-bromophenol[13] and 4-(2-pyridylazo)-resorcinol.[18]

Zincon (2-carboxy-2′-hydroxy-5′-sulfoformazylbenzene) has long been known as an excellent colorimetric reagent for the detection of zinc and copper ions in aqueous solutions. This formazan dye has been shown to serve as an excellent chromophore for the quantification of both elements in aqueous solutions of particular relevance in biological systems such as metalloproteins.[19] Although zincon could be used as a spectrophotometric reagent for zinc and copper, at a pH above 8 it reacts only with zinc.[1]

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In this work, a new method is proposed for on-line preconcentration and spectrophotometric determination of Zn using chemically modified PUF with zincon. The new sorbent is employed for on-line preconcentration and determination of zinc ions in tap water and river water as well as human urine.

Experimental

Apparatus

Absorbance measurements were recorded on a UV-Vis double beam spectrophotometer Model 1601 Shimadzu (Kyoto, Japan) working under kinetic mode. The spectrophotometer was equipped with a Hellma quartz flow cell type 174.010-QS with dead volume of 1.5 mL and 10 mm path length. A Metrohm pH meter (Herisau, Switzerland) Model 780 combined with glass electrode was used for pH adjustments using diluted solutions from sodium hydroxide and hydrochloric acid.

A Homemade ismatec fixed-speed peristaltic pump with four-channels furnished by Tygon tubes with internal diameter 1.54 mm was used to propel the solutions. A three-way Teflon PTFE valve connected to Teflon tubes of 0.56 mm i.d, *via* two Teflon connectors was used to select a specified solution. Each Teflon tube was dipped into a sample, carrier water or eluent solution.

A single tube leaving the pump was connected to a mini-column made from polyethylene tube (3.0 cm long, 3.0 mm i.d.). The emerging terminal from the mini-column was connected to a mixing coil to meet a stream of PAR reagent propelled by separate tubing route. Infrared spectra (4000 – 700 cm^{-1}) were recorded on a Mattson Satellite FTIR spectrometer (Madison, USA) Model 2000 using the KBr technique.

Reagents

Standard zinc solution containing 100 ng mL^{-1} was freshly prepared by appropriate dilution of 1000 mg L^{-1} atomic absorption stock solution maintained at pH 3.0 ± 0.2 obtained from Merck (Darmstadt, Germany). Buffer solutions with concentration of 0.5 mol L^{-1} from acetate (pH 3 – 5), phosphate (pH 6 – 7) or borate buffer (pH 8 – 9) were used to adjust the pH of the standard solution by adding appropriate volumes of buffer to the standard Zn solution to a final concentration of 0.05 mol L^{-1}.

Deionized water, supplied from Elix UV water purification system (Billerica, USA), was used in preparing all solutions. For the study, 4-(2-pyridylazo)-resorcinol (PAR) monosodium salt monohydrate was obtained from Fluka (Buchs, Switzerland). A 0.01% (w/v) solution was prepared by dissolving 0.1 g of PAR in 800 mL deionized water and adding 61.8 g of boric acid (Fluka) and 20.0 g of sodium hydroxide (Fluka). The resulting solution was adjusted to pH 10 and diluted with deionized water to 1000 mL. Any solid boric acid that appeared was removed by filtration then kept for at least two days before use. Zincon, 2-carboxy-2′-hydroxy-5′-sulphoformazylbenzene, was procured from Fluka (Switzerland). PUF open cell polyether-type, obtained from a commercial product (density 31 kg m^{-3}), was cut into cylindrical plugs with a hollow drill stainless steel cutter. To remove all contaminates from PUF plugs, they were washed thoroughly with 0.5 mol L^{-1} hydrochloric acid solution to remove inorganic impurity, then with deionized water until the washing was neutral, and finally with 30% (v/v) ethanol to remove any organic impurity, then dried in air.

Synthesis of zincon-PUF sorbent

Five grams from untreated PUF plugs were activated by soaking in 50% (v/v) hydrochloric acid solution for 6 h to assist hydrolysis of terminal isocyanate groups, thus leading to an increase in the number of free NH_2 in touidene moieties. After that, the plugs were washed successively by deionized water and squeezed between filter paper sheets to remove the acid. Azo coupling of zincon onto PUF was achieved according to the previously reported method by our group.[20] The plugs were suspended in an ice-water mixture and treated with 300 mL of 0.1 mol L^{-1} HCl and mechanically stirred. When the mixture cooled, sodium nitrite solution (1.0 mol L^{-1}) was added dropwisely from a burette until the foam attained a yellow color due to the formation of diazonium salt. A starch – iodide paper was used to confirm excess addition of nitrite by turning its color into blue. Then, the foam was left for one hour for cooling below 3°C. Next, the foam plugs were transferred into 200 mL of 1% (w/v) zincon solution (in 1.0 mol L^{-1} sodium hydroxide solution) and kept in a refrigerator for 12 h. Finally, the resulting orange plugs were washed repeatedly with deionized water, ethyl alcohol and dried in air.

A cylindrical polyethylene tube with 3.0 cm length and 3.0 mm i.d served as the mini-column. The tube was packed manually with approximately 300 mg of zincon-PUF plugs under suction by fixing the tube end into a suction port of the SPE manifold. The suctioning was continued after packing for 30 min to ensure effective packing and reduce channels inside the mini-column. Then, the two sides of the mini-column were end capped with two polyethylene joints of 1.2 mm i.d. and connected to the on-line system *via* Tygon tubes. Finally, the mini-column was preconditioned before use at the end of each preconcentration cycle by passing borate buffer with pH 8.5.

Manifold and procedure

A schematic diagram of the proposed on-line preconcentration system is depicted in Fig. 1. In the preconcentration step, a sample solution at concentration 100 ng mL^{-1} and adjusted to pH 8.5 was pumped at 4.0 mL min^{-1} and percolated through the zincon-PUF mini-column for 1.0 min. Then, the zinc ions were retained on the sorbent and the remaining effluent was directed to the waste route. Meanwhile, the deionized water as carrier solvent was mixed with the PAR reagent and passed through the flow cell of the spectrophotometer where baseline absorbance was adjusted. Switching the valve into the elution mode, a stream of eluent solution consisting of 0.1 mol L^{-1} hydrochloric acid flowing at 3 mL min^{-1} displaces the retained zinc. The stripped out zinc ions in the eluate merge in the mixing coil with the PAR solution to give a violet color from the Zn-PAR complex. The pH of this complex was adjusted to 9.0 by mixing a stream of 0.5 mol L^{-1} borate buffer passing at 0.5 mL min^{-1} and the analytical signal of the resultant solution was measured at 496 nm. The mixing coil acted to prevent backpressure inside the connection tubes since the PAR solution was flowing very slowly compared to the carrier or sample flow. Worth mentioning is that the peak height absorbance was recommended as an analytical signal to make all calculations because it is fast and reproducible. At the end of the elution step, the zincon-PUF mini-column was preconditioned for a new preconcentration cycle. The total elapsed time in each cycle was found to be 5 min consisting of 1 min for preconcentration, 3 min for elution time and 1 min for preconditioning.

Reaction of zinc in its salvation sphere $[Zn\ (H_2O)_n]^{2+}$ and monoprotonated PAR ($HPAR^-$) can take place at the working pH 9 and the formed complex $[Zn(H_2O)_{n-4}(HPAR)_2]$ is the spectrophotometric monitored species.[21] A plausible mechanism

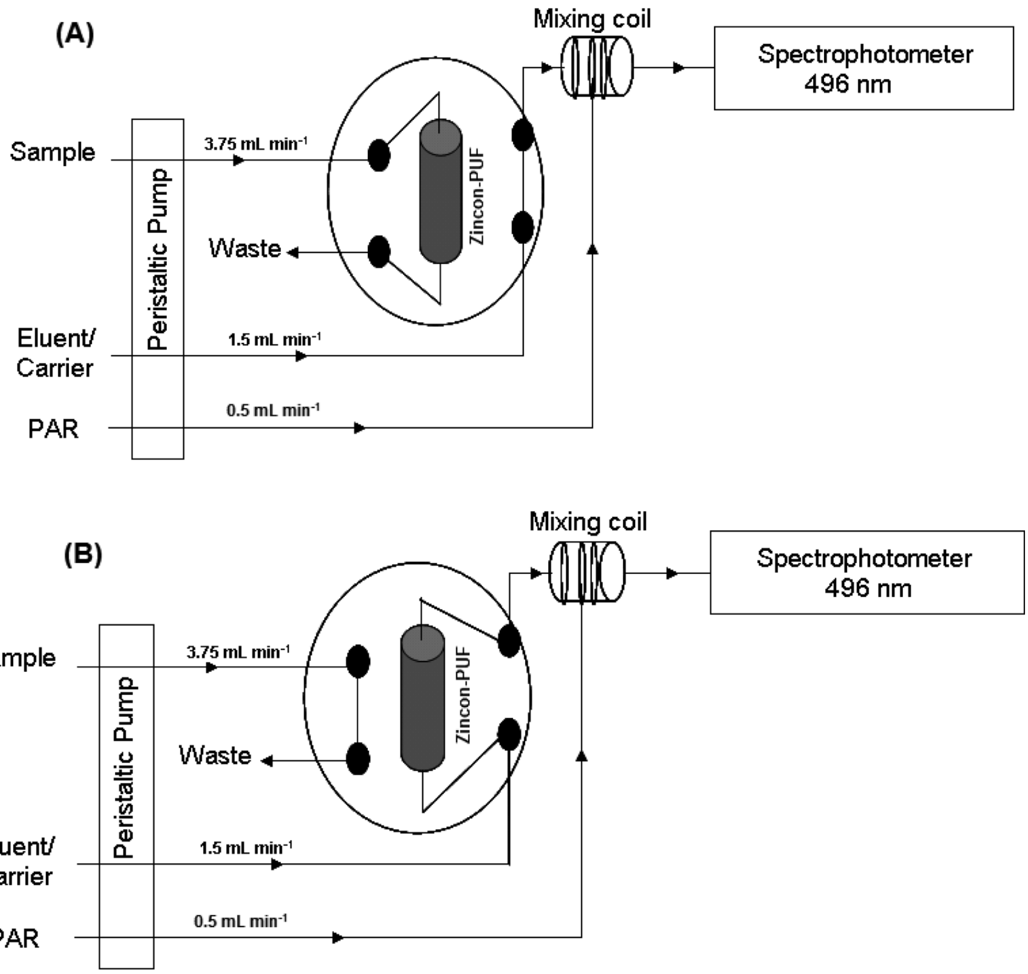

Fig. 1 Proposed chemical structure of zincon-PUF sorbent.

of this reaction can be proposed by two steps involving the exchange of water molecules of salvation.

$$[Zn[H_2O)_n]^{2+} + HPAR^- ======= [Zn(H_2O)_{n-2}(HPAR)]^+ + 2\ H_2O \quad \text{(Slow)}$$

$$[Zn(H_2O)_{n-2}(HPAR)]^+ + HPAR^- ======= [Zn(H_2O)_{n-4}(HPAR)_2] + 2\ H_2O \quad \text{(Fast)}$$

Sample preparation

Three certified reference materials were analyzed for their zinc content by the proposed procedure namely SRM 1463d river water, sewage sludge BCR 144R (domestic origin), and bovine liver NIST 1577b. The river water sample (40 mL) was adjusted to pH 8.5 with 5 mL of 0.5 mol L^{-1} borate buffer then analyzed directly after dilution to 50 mL with deionized water. Sewage sludge and bovine liver samples were prepared according to the reported method.[22] A 0.5 g amount of standard reference material was mixed with 10 mL of aqua regia solution at room temperature for 24 h, and then heated to 95°C. After the evaluation of NO_2 fumes had ceased, the mixture was evaporated almost to dryness and mixed with 10 mL of aqua regia. The mixture was again evaporated to dry. A few milliliter of deionized water were added to the residue and the resulting suspension was filtered through a filter paper and the insoluble part was washed with deionized water. The final solution was adjusted to pH 8.5 and diluted to 50 mL with deionized water then subjected to analysis. Blanks were prepared in the same manner, after omitting the sample.

A tap water sample was obtained from our research laboratory at Ain Shams University and Nile River water was taken directly from a nearby place in Cairo City. Aliquots of 50 mL from each sample were filtered through cellulose membrane filters of pore size 0.45 μm. Next, they were acidified to pH 2 with 0.5 mol L^{-1} nitric acid. Finally, these solutions were adjusted to pH 8.5 and passed through the mini-column at a flow rate of 4.0 mL min^{-1}. The adsorbed zinc in the mini-column was eluted with 0.1 mol L^{-1} HCl solution and analysis was carried out in four replicates.

Results and Discussion

Characterization of zincon-PUF sorbent

The IR spectrum of zincon-PUF material was recorded by the KBr disc technique. Characteristic absorption band appeared at 1723.09 cm^{-1} whereas the urethane C=O group in PUF showed absorption peak at 1710 cm^{-1} which might be attributable to C=O stretching in the COOH group of zincon reagent. Furthermore, two absorption bands were observed at 1602 and 1548.5 cm^{-1} that could be due to N=N and C=N groups, respectively. This confirmed chemical bonding of zincon onto the backbone of PUF *via* -N=N- groups as shown in Fig. 2.

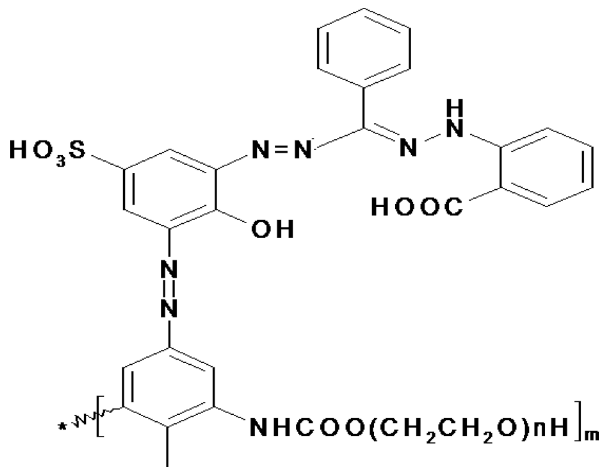

Fig. 2 Setup of the on-line preconcentration manifold used for determination of zinc ions. Preconcentraion mode (A) and elution mode (B).

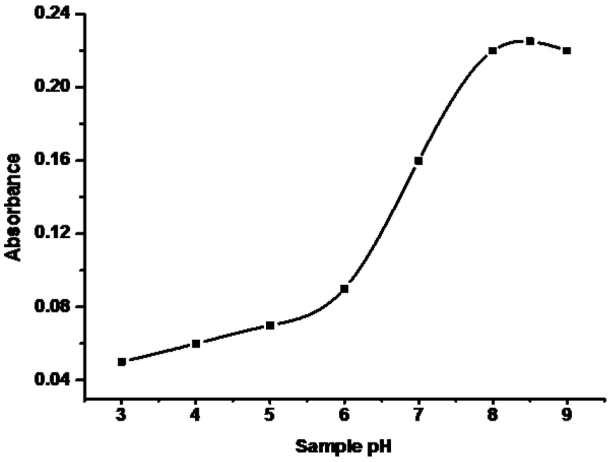

Fig. 4 Influence of sample pH on the sorption of zinc by zincon-PUF sorbent. Zinc concentration of 100 ng mL^{-1}, preconcentration time of 1 min, carrier flow rate at 3 mL min^{-1}, PAR flow rate of 0.5 mL min^{-1} and measurement wavelength at 496 nm.

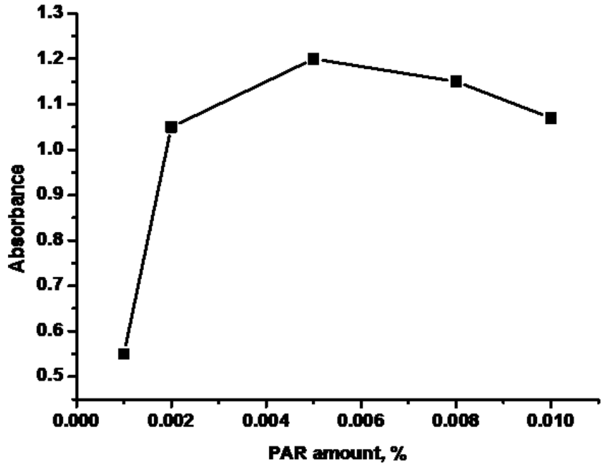

Fig. 3 Influence of PAR amount on the peak height absorbance. Zinc metal ion concentration of 100 ng mL^{-1}, preconcentration time of 1 min, carrier flow rate at 3 mL min^{-1}, PAR flow rate of 0.5 mL min^{-1} and measurement wavelength at 496 nm.

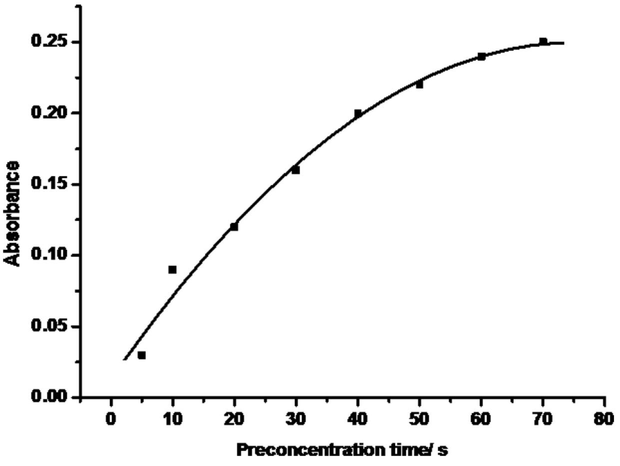

Fig. 5 Influence of preconcentration times of the sample on the peak height absorbance. Zinc concentration of 100 ng mL^{-1}, preconcentration time of 1 min, carrier flow rate at 3 mL min^{-1}, PAR flow rate of 0.5 mL min^{-1} and measurement wavelength at 496 nm.

Chemical and flow optimization

In order to determine the best chemical and hydrodynamic conditions for zinc preconcentration, a standard solution containing 100 ng mL^{-1} of Zn was employed. The effect of PAR content was tested ranging from 0.001 to 0.01% at sample preconcentration time of 1 min and flow rate of 3 mL min^{-1}. The results shown in Fig. 3 indicated that signals were maximum for PAR concentration at 0.005%. Therefore, the PAR concentration chosen was 0.005%.

The PAR flow rate was examined within the range 0.1 – 2.5 mL min^{-1}. The analytical signal was maximum and constant at a flow rate of 0.5 mL min^{-1}. Flow rates faster than 0.5 mL min^{-1} revealed weak analytical signals which could be due to the short time of interaction between the analyte and zincon. Thus, the PAR flow rate was selected and kept fixed at 0.5 mL min^{-1}.

The influence of sample pH on sorption of zinc onto the zincon-PUF mini-column was investigated within the pH range from 3.0 to 9.0. The obtained results are shown in Fig. 4. Weak absorbance signals were observed at pH $\leq$ 6 and the signals increased within the pH range 6 – 8 then reached a maximum and remained relatively constant at pH 8 – 9. Thus, borate buffer of pH 8.5 was recommended for further experiments since this allowed for the achievement of the highest signals.

The preconcentration time during which zinc solution is flowing through zincon-PUF was studied in the range from 5 to 70 s at a sample flow rate of 4.0 mL min^{-1}. The absorbance increased linearly up to 40 s as shown in Fig. 5. For longer preconcentration times, the analytical signal increased slightly with smaller rates but a non-linear. This might be due to the effect from partial leaching of the retained Zn(II) ions from the mini-column that becomes significant. Finally, a 60 s preconcentration time corresponding to sample volume of 4 mL was chosen as a compromise between adequate sample consumption and sample throughput.

The influence of sample rate flow on metal extraction was studied by varying the flow rate from 0.75 to 6.5 mL min^{-1}. Results demonstrated that the analytical signal reached a maximum at a flow rate of 4.0 mL min^{-1}. High flow rates showed a decrease in the signal height as well because it is limited by the back-pressure produced by the mini-column. Conversely, slower flow rates would decrease the ultimate number of sample throughput leading to long analysis periods. Therefore, a flow rate of 4.0 mL min^{-1} was selected for the subsequent studies to adapt the efficiency and stability of the procedure.

The effect of eluent concentration was studied by testing hydrochloric acid solutions at various concentrations in the range 0.01 – 0.50 mol L^{-1} as eluents for Zn ions. It was found that with 0.1 mol L^{-1} HCl solution, the analytical signal was maximum. Also, the analytical signal remained constant even at acid concentrations higher than 0.1 mol L^{-1}. However, strong acidic eluents were excluded in order to avoid the extrapolation of the borate buffering capacity in the PAR stream. Consequently, in the subsequent experiments, 0.1 mol L^{-1} hydrochloric acid solution was utilized as the eluent.

The carrier flow rate has a significant effect on eluent efficiency. Deionized water was used as a carrier solvent to bring the eluent into the mini-column for desorption. It was tested within the range from 0.75 to 4.5 mL min^{-1}. Best analyte signals were obtained at a carrier flow rate of 3.0 mL min^{-1}. Thus, this flow rate value was considered suitable to elute zinc quantitatively with high sensitivity. Moreover, displacing the retained zinc ions from the mini-column required passing of the eluent for 1 min while recording the analytical signal. Thus, the consumed eluent volume was 3 mL. Applying higher flow rates was found to cause dispersion in the eluate and consequently reduced, to some extent, the analytical signal.

The interference due to coexisting ions in the determination of 100 ng mL^{-1} zinc was studied systematically using the proposed on-line preconcentration procedure in the presence of a series of diverse ions under the optimal experimental conditions. Relatively high concentrations with ratios of 100-fold for some diverse ions and 500-fold for the alkali and alkaline earth metals *e.g.* Ni^{2+}, Mn^{2+}, Fe^{2+}, Cu^{2+}, Cd^{2+}, Co^{2+} and Cr^{2+}, SO_4^{2-}, PO_4^{3-} *e.g.* Na, Ca and Mg were added. The recovery value of zinc was evaluated with each addition and the amount of foreign ion causing a relative error of ±5% was considered to be within the allowed interfering error. The examined diverse ions revealed good recovery percentages in the range of 94 – 98% for zinc which indicated the negligible effects of most added foreign ions at given concentrations. Finally, the developed zincon-PUF showed good selectivity, suggesting it can be applied successfully to the determination of zinc in real samples since the interference by these elements that might compete with zinc was found to be rather low.

Analytical figures of merit

Applying the manifold depicted in Fig. 1 under the optimum chemical and flow variables resulted in the calibration graph shown in Fig. 6 which could be represented by the regression equation: $A = 0.0036$ [Zn(II), ng mL^{-1}] + 0.0096 ($R = 0.9986$). The analytical range varied from 10 to 120 ng mL^{-1}. Direct determination of Zn(II) without preconcentration mini-column showed a linear regression line in the range 0 – 600 ng mL^{-1} Zn(II) defined by a linear equation, $A = 0.000116$ [Zn(II), ng mL^{-1}] + 0.00142 ($R = 0.998$). The experimental enrichment factor (EF),[12] calculated as the ratio of the slopes of the calibration graphs with and without preconcentration was found to be 31 at 60 s preconcentration time. The time needed for complete analysis is 3 min and consequently the sampling frequency was 20 h^{-1}. The concentration efficiency, defined as the product of the EF and the sampling frequency per number of samples analyzed per minute, was found to be 10.

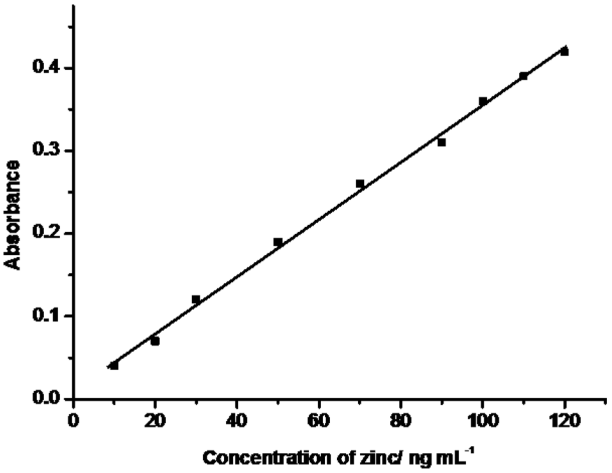

Fig. 6 Analytical curve for zinc determination by the developed zincon-PUF procedure. Sample flow rate of 3.0 mL min^{-1}, preconcentration time of 1 min, carrier flow rate 3 mL min^{-1}, desorption with 0.1 mol L^{-1} hydrochloric acid, 0.01% PAR flow rate of 0.5 mL min^{-1}, measurement wavelength of 496 nm, and 100 mg sorbent.

Table 1 Determination of zinc in certified reference materials using the proposed zincon-PUF procedure

Reference sample	Certified value	Found (mean ± SD)	Recovery, %	RSD, %
SRM 1463d river water[a]	72.48 ± 0.65	69.7 ± 3.4	96.1	4.9
BCR144R-sewage sludge[b]	932 ± 23	1014 ± 11	109.8	1.1
NIST 1577b-bovine liver[b]	127	119.2 ± 4.1	93.8	3.4

a. Value in μg L^{-1}.
b. Value in μg g^{-1}.

The limits of detection was calculated by the 3 s criterion as the concentration that gives a response equivalent to three times the standard deviation (SD) of the blank ($n = 5$). The limits of quantification were calculated as the concentration that gives a response equivalent to 10 times the SD of the blank ($n = 5$), and define the lower limit of the range. The limit of detection found was 3 μg L^{-1} and the limit of quantification was found to be 10 μg L^{-1}.

The precision of the procedure was defined as the relative standard deviation, RSD% ($n = 5$) for measurement of sample solutions containing 20 and 110 ng mL^{-1} Zn(II) which represent the point near the lower and higher limits of the analytical range. The obtained RSD% values were 4.8 and 6.7% at 20 and 110 ng mL^{-1}, respectively.

Accuracy of the method was validated by analysis of the certified reference materials namely SRM 1463d river water, sewage sludge BCR 144R from domestic origin, and NIST 1577b bovine liver and (Table 1). The obtained recovery values were in the range 93.8 – 109.8% with corresponding RSD% in the range 1.1 – 4.9%. Thus, the developed procedure proved to be highly sensitive and accurate so that it is deemed quite sufficient for analysis of real samples.

Finally, the sorbent durability could be investigated since only one mini-column was used in conducting all experiments. The total number of analytical cycles reached more than 100 for sorption-desorption without a noticeable decrease in the mini-column efficiency. This conveyed the high stability and long lifecycle of the sorbent.

Application to water and urine samples

The presented zincon-PUF method was applied to the analysis of tap water, Nile River water and human urine and the obtained results are compiled in Table 2. Results showed good accuracy of the data confirmed by the satisfactory values of RSD which ranged from 1.1 to 6.3%. Also, the values of recovery of spiked samples varied from 94 and 107% which are considered relevant results. This confirmed the applicability of the developed method for the selective sorption and determination of zinc ions in real samples.

Comparison to other on-line preconcentration procedures

Comparison of the proposed procedure with other on-line methods for determination of zinc using several sorbents is presented in Table 3. Enrichment factor was found to be higher than other sorbents even that involving the use of Dowex 1X8 resin modified with 1% (w/w) of zincon coupled to FI-FAAS system. Detection limits are comparable to some of those described in the literature. However, all these methods used more expensive FAAS detection techniques. The simplicity and low cost of the developed procedure underscore that it is available alternative approach for the determination of zinc in water and human urine.

Conclusions

The development of zincon-PUF sorbent as an alternative procedure for the separation, preconcentration and determination of zinc ions was established. Using a less expensive spectrophotometric determination method is an advantage. The method is fast and offers high accuracy which makes it an attractive alternative to already existing procedures. The preconcentration factor and detection limit of the procedure is quite sufficient for quantification of trace amounts of zinc from several real samples even in the presence of complex matrices.

Table 2 Analysis of zinc in water and human urine samples using the developed zincon-PUF procedure

Sample	Amount added/ μg L^{-1}	Found (mean ± SD, n = 4)/μg L^{-1}	Recovery, %	RSD, %
Tap water	0.0	7.9 ± 0.5	—	6.3
	50	61.4 ± 3.3	107	5.3
	100	106.3 ± 2.1	98	2.0
Nile river water	0.0	27.5 ± 0.3	—	1.1
	50	75.8 ± 1.3	97	1.7
	100	121.3 ± 4.7	94	3.4
Human Urine	0.0	0.6 ± 0.05	—	8.3
	50	47.5 ± 1.4	94	2.9
	100	95.3 ± 2.2	95	2.3

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Table 3 Comparison of analytical features for zincon-PUF and other reported on-line preconcentration procedures for zinc determination

Sorbent	Detection technique	Correlation coefficient (R)	Analytical range/ μg L^{-1}	EF[a]	LOD/ μg L^{-1}	Analyzed sample
Zincon-PUF This work	Spectropho-tometry	0.997	10 - 120	31	3.0	River water, Tap water, human urine
Unloaded PUF[17]	FAAS	0.999	20 - 100	8	3.0	Sea, underground waters
Zincon-Dewex 1X8[23]	FAAS	—	—	10	0.67	Beverages
XAD-HVMC[b][9]	FAAS	0.999	10 - 100	14	1.1	Sea, underground, river waters
TDMS[c][24]	FAAS	0.998	5 -500	40	2.2	Well water, liver
DPTH-gel[d][11]	ICP-AES	0.999	2 - 500	—	1.7	Sea water

a. Enrichment factor, b. (S)-2-[hydroxy-bis(4-vinylphenyl)methyl]pyrrolidine-1-carboxylic acid ethyl esther, c. Poly(2-thiozylmethacrylamide-*co*-divinylbenzene-*co*-2-acrylamido-2-methyl-1-propane sulfonic acid), d. 1,5-bis(di-2-pyridyl)methylene thiocarbohydrazide.

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