Determination of Zn(II) in natural waters by ICP-OES with on-line preconcentration using a simple solid phase extraction system

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ABSTRACT

An on-line zinc preconcentration and determination system implemented with inductively coupled plasma optical emission spectrometry (ICP-OES) was developed. The zinc was precipitated and retained on a minicolumn filled with ethyl vinyl acetate (EVA) at pH 9.0, without using any complexing reagent. The zinc ions were eluted from the minicolumn with 10% (v/v) hydrochloric acid. Experimental conditions including pH and sample loading and eluting variables were evaluated and established.

An enrichment factor (EF) of 44 was obtained for Zn^{2+} with a preconcentration time of 120 s. Under the optimal conditions, the value of the limit of detection (3σ) for the preconcentration of 10 mL of sample was 0.08 µg L^{-1}. The sampling frequency was about 24 h^{-1}. The precision for six replicate determinations (repeatability conditions) at 50 µg L^{-1} Zn level was 3.94% relative deviation standard (RSD), calculated from the peak heights obtained. The methodology was successfully applied to the determination of zinc in tap water samples and in a certified VKI reference material QC Metal LL1 DHI (Water & Environment) Denmark.

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1. Introduction

Zinc is one of the most important essential tracer metals of human nutrition, and its deficiency is a world nutritional problem [1]. It has several functions due to play a role as a co-factor in more than 200 enzymes [1,2]. Also, zinc plays an essential role in the biological processes of plants and animals. However, an excess of this metal can also play an important role in the progression of several damages to human body, including disturbances in energy metabolism or increasing in oxidative stress, growth retardation, altered immune response, disturbed pregnancy, weight loss, and anorexia; among others [3].

The determination of low concentration of zinc in water samples has been successfully carried out by different analytical techniques, such as flame atomic absorption spectrometry (FAAS) [4–14], electrothermal atomization (ETAAS) [15,16], inductively coupled plasma optical emission spectrometry (ICP-OES) [17–21], and spectrofluorimetry [3].

Although the two techniques extensively used for Zn determination are FAAS and ICP-OES, they are not suitable for the direct analysis of trace zinc levels in well water, tap water, river water, etc. Therefore, preconcentration is an effective means for extending the detection capabilities of the analytical methodologies mentioned above. However, when practiced manually in the batch mode, the operations are usually too laborious and time-consuming. To overcome these limitations, an on-line preconcentration step prior the instrumental analysis is mandatory. Of the several enrichment procedures, the combination of the solid phase extraction (SPE) and flow injection (FI) in an on-line system is one of the most effective methods due to the low consumption of samples and reagents, high analytical throughput and minimal waste production [21,22].

The proper choice of an adsorbent material for SPE can provide simple operation and more flexible working condition. Several SPE methods for zinc preconcentration have been reported in the literature, they utilize solid materials such as: alumina [10], mesoporous silica [11], PVC [14], magnetic nanoparticles [18], silica gel [21,23], amberlite XAD-4 [24], zeolite [25,26], chelate resin [4,27], microcrystalline triphenilmethane [28], and multiwalled carbon nanotube [29]; in all of the cases the material has been modified. Table 1 shows a comparison regarding the use of SPE for preconcentration of Zn and its determination in water samples between this work and some recent literature articles.

Minicolumns packed with ethyl vinyl acetate (EVA) as sorbent material have been used for the SPE of As [30], Se and Te with good results [31]. This material exhibits good chemical resistance and unlimited lifetime; it does not need any regeneration, and remains unaltered after the preconcentration or elution steps.

Our research group has previously reported an on-line methodology which included the molybdenum preconcentration by solid phase extraction with EVA and ICP-OES detection [32]. To the best of our knowledge, no SPE approach using EVA for the preconcentration of Zn without utilizing any complexing agent or chemical modifier has yet been reported.

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Table 1
Comparative data from some recent studies (researches) on preconcentration systems for Zn determination in sample waters.

Preconcentration system	LD ($\mu g\ L^{-1}$)	R.S.D (%)	EF	PF	SV (mL)	Technique	References
Chelate resin modified	0.28	–	–	50	500	ICP-AES	[27]
Magnetic nanoparticles modified	0.8	0.8	30	–	50	ICP-OES	[18]
Modified mesoporous silica	8.0×10^{-6} mM	<4.0	–	200	1000	FAAS	[11]
Chitosan (chelating resin) modified	0.8	2.7	17.6	–	–	FAAS	[4]
Silica gel modified	1.3	<5.0	50(?)	–	–	ICP-OES	[21]
Multiwalled carbon nanotubes	0.35	<5.0	–	80	400	FAAS	[29]
Triton X-100-coated PVC	1.23	<4.0	–	90	450	FAAS	[14]
Modified clinoptilolite zeolite	–	0.92	–	170	–	FAAS	[25]
Modified alumina coated with sodium dodecyl sulfate	0.69	1.2–1.4	–	292	–	FAAS	[10]
Microcrystaline triphenilmethane modified	0.05	3.1	–	–	200	FAAS	[28]
Modified zeolite	0.006	1.3	–	160	800	FAAS	[26]
Modified amberlite XAD-4	–	1.2–1.8	–	–	–	ICP-MS	[24]
Ethyl vinyl acetate (EVA)	0.08	3.94	44	–	8	ICP-OES	This work

LD: limit of detection; R.S.D: relative standard deviation; EF: enrichment factor; PF: preconcentration factor (ratio of sample volume to eluent volume); SV: sample volume; mM: milimolar.

In this present work, a simple on-line procedure for the preconcentration and determination of trace levels of zinc in natural water samples by ICP-OES is proposed. Zinc was preconcentrated using a minicolumn filled with EVA as sorbent material without any modification.

2. Experimental

2.1. Instrumentation

The measurements were performed with a sequential ICP spectrometer [BAIRD (Beldford, MA, USA) ICP2070]. The 1 m Czerny–Turner monochromator had a holographic grating with 1800 grooves mm^{-1}. The operating conditions of the ICP-OES equipment are listed in Table 2.

The pH was determined using a portable pHmeter (ORION RESEARCH, INC., Orion 230 A, Beverly, MA, USA) equipped with a 9107 BN Orion glass electrode. For sorption of the analyte, a minicolumn (85 mm length × 3.0 mm inner diameter) was prepared using turnings small particles of spiraled shape cross-linked ethyl vinyl acetate. Minipuls™ 3 peristaltic pumps (Gilson, Villiers-Le-Bel, France) were used. Sample injection was achieved using a Reodyne® (Cotati, CA, USA), Model 50 four way rotary valve.

2.2. Reagents and solutions

Working standard solution was prepared by stepwise dilution from 1000 mg L^{-1} Zn(II) stock standard solution [TraceCERT® (Fluka, Buchs, Switzerland)]. Ultrapure water with a maximum resistivity of 18.2 MΩ cm was obtained from an EASY pure RF (Barnstedt, Dubuque, IA, USA). Hydrochloric acid, puriss. p.a. ACS (FLUKA, Switzerland) was used. A buffer solution was prepared from Tris(hydroxymethyl) aminomethane puriss. p.a. standard titrimetric substance (FLUKA).

All solvents and reagents were of the highest available purity and at least of analytical grade, and the presence of Zn was not detected in the working range.

Table 2
ICP-OES instrumental parameters.

RF generator power plasma	0.8 kW
Frequency of RF generator	40.68 MHz
Gas flow rate	8.5 L min^{-1}
Auxiliary gas flow rate	1.0 L min^{-1}
Observation height (above load coil)	15 mm
Wavelength	213.856 nm

2.3. Column preparation

Ethyl vinyl acetate is a flexible (rubbery), transparent polymeric material with good low temperature flexibility, chemical resistance (to acids, alkalis, and alcohols) and high friction coefficient properties. This material was employed to create the preconcentration mini-column as follows: the minicolumn was prepared by placing 100 mg approximately of EVA turnings (small shaving with a media length of 1.5 mm and a media wide of 0.45 mm) into an empty cylindrical EVA tubing using the dry packing method. Small amount of quartz wool was placed on both ends of the minicolumn. Finally, the column was connected with PTFE tubing to the peristaltic pump to form the preconcentration system. This method was used for around 500 cycles and changes in the retention capacity were no observed.

2.4. Sample preparation

The natural water samples were filtered through 0.45 μm pore size membrane filters immediately after collection, and were acidified to pH 2 with nitric acid and stored at 4 °C in bottles (Nalgene, Nalge, Rochester, NY, USA.).

2.5. On-line preconcentration step

Before loading the minicolumn, it was conditioned for the preconcentration with a buffer solution adjusted to pH 9.0. The water sample containing Zn to pH 2.0 was mixed with buffer solution after passing the injection valve and before entering the minicolumn.

A schematic of the preconcentration manifold is shown in Fig. 1.

2.6. Loading step

Aqueous sample solution containing zinc and buffer solution was loaded on the EVA minicolumn at flow rates of 5.0 mL min^{-1} and 2.5 mL min^{-1}, respectively with the peristaltic pump P_1 and valve V in load position (a); while a 10% (v/v) HCl solution was passing throughout the manifold directly to the detection system (pump P_2). Finally, after loading the sample, the peristaltic pump P_1 was stopped.

2.6.1. Injection step
After the loading time (120 s), the injection valve V was switched to the injection position (b) and the retained metal was quantitatively eluted with the 10% (v/v) HCl solution at a flow rate of 1.5 mL min^{-1} directly into the detection system (20 s).

2.6.2. Conditioning
After zinc determination, the injection valve was switched back to the loading position and ultrapure water was pumped through the