



## Review article

# On-line preconcentration of zinc on ethyl vinyl acetate prior to its determination by CVG-ICP-OES

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## ABSTRACT

A separation/preconcentration procedure using solid phase extraction coupled to zinc vapor generation associated to inductively coupled plasma optical emission spectrometry determination in water samples was studied. The solid phase material was ethyl vinyl acetate (EVA) contained in a column, where the analyte ions were retained without using any complexation agent. The variables involving the preconcentration and the chemical vapor generation (CVG) were optimized using both full factorial and central composite designs, respectively. Volatile species of zinc were generated by merging the acidified eluent and sodium tetrahydroborate in a continuous flow system. The gaseous analyte was introduced via a stream of Ar carrier into the inlet tube of the ICP torch. An enhancement factor of 230-fold for a sample volume of 16 mL was obtained. The detection limit was  $0.06 \mu\text{g L}^{-1}$ . The proposed method was successfully applied to the determination of traces of zinc in a Certified Reference Material and tap and river water samples.

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## 1. Introduction

Essential trace elements need to be present in the human diet to maintain normal physiological functions. As an essential micronutrient, zinc plays an important role in the environment and human

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health. However, an excess of this metal can effect the progression of several damages to human body, including disorders in energy metabolism or increase in oxidative stress, growth retardation, altered immune response, disturbed pregnancy, weight loss, and anorexia; among others [1–6].

Considering the low content of zinc in environmental samples, sensitive analytical techniques are required to obtain low limits of detection (LODs). However, the LODs of some atomic spectroscopic techniques, such as inductively coupled plasma optical emission spectrometry (ICP-OES), are not always compatible with the low levels of Zn in these samples. In order to achieve accurate, reliable, and sensitive results, preconcentration and separation steps are needed. In this sense, preconcentration strategies are effective means of extending the LODs. Several solid phase extraction (SPE) methods for zinc preconcentration have been reported in the literature, they utilize modified solid materials such as: alumina [7], mesoporous silica [8], PVC [9], magnetic nanoparticles [10], silica gel [11,12], Amberlite XAD-4 [13], zeolite [14,15], chelate resin [16,17], microcrystalline triphenylmethane [18], and multiwalled carbon nanotubes [19]. A comparison between the results obtained in this work and some recent literature articles regarding the use of SPE for preconcentration/determination of Zn in water samples is presented in Table 1.

The chemical vapor generation (CVG) technique has been used in analytical chemistry because the production of gaseous analytes and their introduction into atomization cells can offer for some of the detectors significant advantages, which include separation of the analyte from the undesirable matrix components that lead to improved selectivity and accuracy, significant reduction of interferences in the liquid phase during vapor generation from the sample; analyte transport efficiency; elimination of the need for a nebulizer, and the possibility of coupling preconcentration steps to vapor generation approaches because homogeneous vapor is delivered to the atomizer and automation of the method can be easily achieved [20–24]. Traditionally, the application of vapor generation has been limited to the conventional group of elements such as Hg (cold vapor generation), As, Sb, Bi, Se, Te, Ge, and Sn. In recent years, use of hydride generation techniques has expanded in scope to encompass the generation of “unconventional” volatile species (possibly as hydrides, vapors, or other unidentified species) of different noble and transition metals and noticeable efforts have been dedicated to clarification of mechanistic aspects [25–28]. The evidence of the volatile species for Zn is not fully clarified. Besides, ZnH<sub>2</sub> synthesis has been performed previously [29] and the compound is reported as moderately stable. Recent works assume that the reaction between Zn and tetrahydroborate produces relatively stable species of ZnH<sub>2</sub> (as dihydrides) that are released into the vapor phase. That is the mechanism of formation of vapor phase this being more accepted [30,31].

On the other hand, multivariate techniques have been used for optimization of analytical methods. They allow more than one variable to be optimized simultaneously and have several advantages, such as speed of analysis, practicality, economy, and reduction in the number of experiments that need to be performed [32,33]. In addition, these methods are able to generate mathematical models that permit estimating the relevance as well as statistical significance of the factors' effects on the processes and also evaluating the interactions' effects among the factors. Factorial design is one of the available statistical processes for multivariate optimization and is widely applied in chemistry due to its usefulness in the identification of the significant variables and the best conditions of an experiment. However, in order to determine the real functionality established among the analytical response and the significant factors, second order designs are used.

Our research group had worked with different materials for solid phase extraction; among others columns packed with ethyl vinyl acetate (EVA) were used for preconcentration of various analytes, such as Cu [34], As [35], Mo [36], Se and Te [37] with satisfactory results. In the present work, an on-line separation/preconcentration procedure using EVA has been coupled to the zinc vapor generation. The variables involving preconcentration and vapor generation, such as sample flow rate, buffer flow rate, type of acid and content, effect of pH on analytical performance, reducing agent flow rate, were preliminary evaluated and further optimized using full factorial and central composite designs. The zinc trace content was separated from the sample matrix and preconcentrated on a column packed with ethyl vinyl acetate (EVA). The analyte retained was removed from the column with hydrochloric acid. After that, volatile species of zinc were generated by merging the acidified eluent and sodium tetrahydroborate in a continuous flow system. The gaseous analyte was subsequently introduced via a stream of Ar carrier into the inlet tube of the inductively coupled plasma torch. Finally the formation of a Zn vapor and, as a consequence, the absent transport of Zn to the plasma torch in the form of an aerosol was demonstrated.

## 2. Experimental

### 2.1. Reagents

The chemicals used in this work were of analytical reagent grade. Working standard solution was prepared by stepwise dilution from 1000 mg L<sup>-1</sup> Zn(II) stock standard solution [TraceCERT® (Fluka, Buchs, Switzerland)]. Ultrapure water with a 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

**Table 1**  
Comparative data on Zn preconcentration/determination in water samples.

Preconcentration system	LOD (μg L <sup>-1</sup> )	RSD (%)	EF	PF	SV (mL)	Technique	References
Chelate resin modified	0.28	–	–	50	500	ICP-OES	[17]
Magnetic nanoparticles modified	0.8	0.8	30	–	50	ICP-OES	[10]
Modified mesoporous silica	8.0x10 <sup>-6</sup> mM*	<4.0	–	200	1000	FAAS**	[8]
Chitosan (chelating resin) modified	0.8	2.7	17.6	–	–	FAAS	[16]
Silica gel modified	1.3	<5.0	50	–	–	ICP-OES	[11]
Multiwalled carbon nanotubes	0.35	<5.0	–	80	400	FAAS	[19]
Triton X-100-coated PVC	1.23	<4.0	–	90	450	FAAS	[9]
Modified clinoptilolite zeolite	–	0.92	–	170	–	FAAS	[14]
Modified alumina coated with sodium dodecyl sulfate	0.69	1.2–1.4	–	292	–	FAAS	[7]
Microcrystalline triphenylmethane modified	0.05	3.1	–	–	200	FAAS	[18]
Modified zeolite	0.006	1.3	–	160	800	FAAS	[15]
Modified Amberlite XAD-4	–	1.2–1.8	–	–	–	ICP-MS***	[13]
Ethyl vinyl acetate (EVA)	0.06	3.7	223	23	25	CVG-ICP-OES	This work

LOD: limit of detection; RSD: relative standard deviation; EF: enhancement factor; PF: preconcentration factor; SV: sample volume; \*mM: millimolar, \*\*FAAS: Flame Atomic Absorption Spectroscopy, \*\*\*ICP-MS: inductively coupled plasma-mass spectrometry.

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