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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 μg 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.

Contents

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_2 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_2 (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 us 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^{-1} 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^{-1})	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	$8.0x10^{-6}$ 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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buffer solution was prepared from sodium tetraborate puriss. p.a. standard substance (Riedel-de Haën, Seelze, Germany) adjusted to the appropriate pH (9.0) by adding diluted hydrochloric acid or sodium hydroxide solution. Fresh buffer solution was prepared daily.

A 1% (m/v) sodium tetrahydroborate solution was prepared by dissolving the $NaBH_4$ powder (Sigma-Aldrich, St. Louis, USA). Solutions were stabilized in 0.5% (m/v) NaOH (Merck) and filtered before use through Whatman no. 42 paper to eliminate turbidity. Solutions were prepared daily.

Welding argon from Praxair (Buenos Aires, Argentina) was found to be sufficiently pure for Zn determination.

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.

2.2. Instruments

The measurements were performed with a sequential ICP spectrometer [Baird (Bedford, MA, USA) ICP2070]. The 1 m Czerny-Turner monochromator had a holographic grating with 1800 mm^{-1} groove. The operating conditions of the ICP-OES equipment are listed in Table 2. The hydride unit used was a PS Analytical LTD hydride generator and the flow speeds of the reagents were controlled by a Watson-Marlow 303X peristaltic pump. The Zn vapor generated was swept out by Ar connected directly to the inlet tube of the plasma torch. The operating conditions are also listed in Table 2. The pH was determined by using a pH-meter (Orion Research, Inc., Orion 230 A, Beverly, MA, USA) equipped with a 9107 BN Orion glass electrode.

The flow injection system used in this work is shown in Fig. 1. Several Minipuls 3 peristaltic pumps [Gilson (Villiers-Le-Bel, France)] were used. Sample injection was achieved using a Rheodyne (Cotati, CA, USA) Model 50, four-way rotary valve. A home-made column was used as the EVA holder. Pump tubes-Tygon type (Ismatec, Cole-Parmer Instrument Company, Niles. IL, USA) were employed to propel the sample, buffer solution, eluent, and reducing agent. The 213.856 nm spectral line for Zn was used and FI system measurements were expressed as peak height emission, which was corrected against the reagent blank.

2.3. Column preparation

EVA is a flexible (rubbery), transparent polymeric material with good low temperature flexibility, good chemical resistance (to acids, alkalis, and alcohols), and high friction coefficient. This material was employed as follows: the column was prepared by placing 100 mg approximately of EVA turnings (small shavings with a media length of 1.5 mm and a media width of 0.45 mm) into an empty cylindrical EVA tubing (85 mm long and 4.0 mm i.d.) using the dry packing method. Further increase in column length generated elution tails without improving the analytical response. A small amount of quartz wool was placed on both ends of the column. Finally, the column was connected with PTFE tubing to the peristaltic pump to form the preconcentration system. This column was used for around 1000 cycles and the retention capacity did not change.

Table 2
Instrumental parameters employed for zinc determination.

Plasma	
Forward power	1.0 kW
RF generator	40.68 MHz
Plasma gas flow rate	8.5 L min^{-1}
Auxiliary gas flow rate	1.0 L min^{-1}
Carrier gas flow rate	0.75 L min^{-1}
Observation height	15 mm
Analytical line for Zn	213.856 nm
Hydride generation	
Sample and reagent flow rate	2.0 mL min^{-1}
Sample acidity (hydrochloric acid)	10% v/v
$NaBH_4$ concentration	1% m/v

2.4. Sample preparation

Tap and river water samples (from San Luis, Argentina and La Carolina River, San Luis, Argentina; respectively) were filtered through 0.45 μm pore size membrane filters immediately after sampling and were adjusted to pH 2.0 with nitric acid solution and stored in Nalgene bottles at 4 °C (Nalge, Rochester, NY, USA).

The on-line preconcentration method required the samples' pH to be within the range from 4 to7 to avoid the precipitation of Zn as hydroxide before the load step. The pH of the samples was adjusted off-line using a NaOH solution, thus precipitation and retention (pH 9) of Zn in the EVA column was assured.

2.5. Analytical procedure

As mentioned above, a diagram of the on-line separation/preconcentration and determination system is shown in Fig. 1, which consisted of three peristaltic pumps (P_1, P_2 and P_3) fitted with Tygon tubes, a four-way valve (V), and a column (C) packed with EVA coupled to the gas/liquid separator and ICP-OES.

Before loading, the minicolumn was conditioned for the precipitation/preconcentration at the correct pH value (9.0) with a buffer solution (5 s). The water sample containing Zn was mixed with the buffer solution after passing the injection valve and before entering the column, so the mixed solutions were loaded on the EVA column at flow rates of 4.0 mL min^{-1} and 2.5 mL min^{-1} (120 s), respectively with the peristaltic pump P_1 and valve V in load position (a). The remaining solution was discharged (W) at the same time as a 10% (v/v) HCl solution was passed throughout the manifold directly to the gas/liquid separator and mixed with the $NaBH_4$ solution at 8.0 mL min^{-1} and 3.0 mL min^{-1}; respectively (pump P_2 and P_3). Then, the vapor formed was carried by Ar to the ICP-OES system and the analytical response was recorded. Finally, after loading the sample, the peristaltic pump P_1 was stopped.

Following the loading time, the injection valve V was switched to the injection position (b) and the retained metal was quantitatively eluted with a 10% (v/v) HCl solution at a flow rate of 8 mL min^{-1} directly into the detection system (20 s). After zinc determination, the injection valve was switched back to the loading position with the purpose of eliminating the remaining acid solution and ultrapure water (30 s) was pumped through the tubing lines and the column.

The emission measures expressed as peak height were used for quantification purposes because they are reproducible and proportional to the Zn concentration in the sample, which was corrected against the reagent blank. The operating conditions were established and the determination was carried out.

2.6. Optimization strategy

The optimization process for the vapor generation strategy was carried using a two-level full factorial design and a central composite design (CCD). All the experiments were carried out in duplicates using a 50 μg L^{-1} zinc solution. Four variables: sample flow rate, reagent flow rate, eluent concentration, and reagent concentration were considered as factors.

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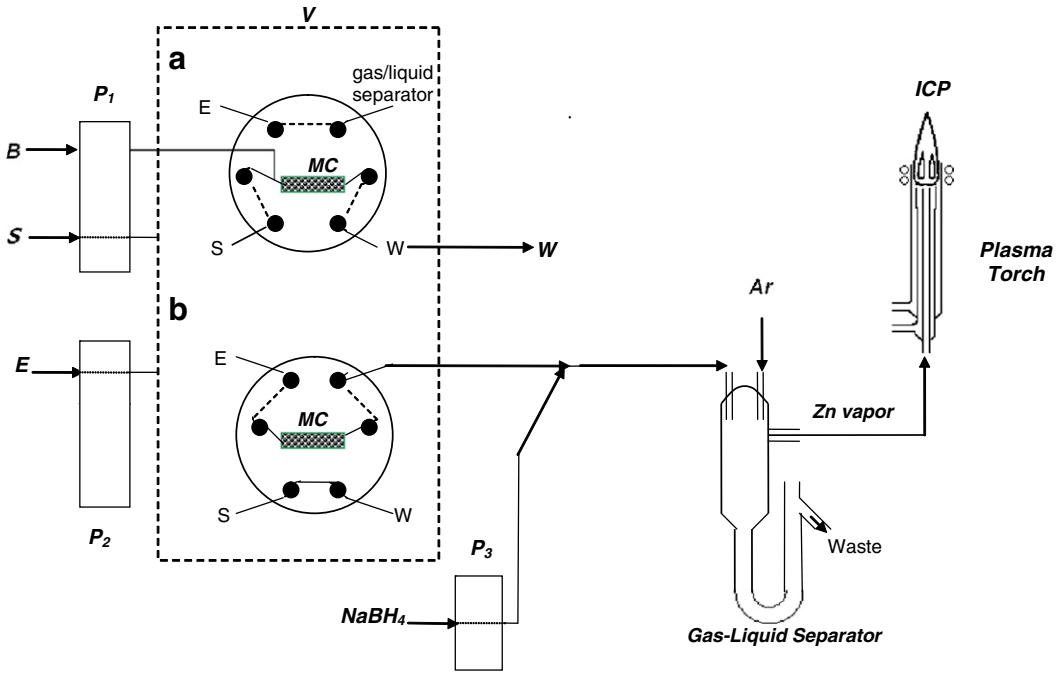

Fig. 1. Schematic diagram of the instrumental setup. S: sample (flow rate: 4.0 mL min^{-1}); B: buffer solution (flow rate 2.5 mL min^{-1}); E: eluent (flow rate 8.0 mL min^{-1}); $NaBH_4$ solution (flow rate: 3.0 mL min^{-1}); W: waste; P_1, P_2 and P_3: peristaltic pumps; MC: minicolumn; V: injection valve. Valve positions: (a) sample loading; (b) injection.

3. Results and discussion

3.1. Argon carrier gas flow rate

The carrier gas affects the transport and extraction of vapor from the gas–liquid separator in the chemical vapor generation system. The Ar flow rate used to transport zinc volatile compounds into the gas–liquid separator and then into the plasma torch was varied over the range 0.10 to 1.0 L min^{-1}. The most proper Ar flow rate was about 0.6 L min^{-1} for this system. Above or below this value, the Zn signal decreased.

3.2. Transfer line

The length of the transfer tubing between the gas–liquid separator and the ICP-torch is an important factor in zinc vapor generation. The emission intensity decreases as the transport distance increases, reflecting the additional losses of the analyte due to collisions with the inner wall surfaces of the tubing. In order to obtain high transfer efficiency, the length of the tubing between the gas–liquid separator and the ICP should be kept as short as possible. For our experimental set-up, a transfer line of 0.3 m length to transport Zn volatile compounds from liquid-separator to plasma torch was used.

3.3. Factorial design

Following the optimization made by our group in a previous work [2], the variables used in the precipitation/preconcentration system were as follows: loading sample flow rate fixed at 4 mL min^{-1}, buffer flow rate at 2.5 mL min^{-1},buffer pH value of 9.0, and the eluent was hydrochloric acid.

On the other hand the factors that could influence the Zn chemical vapor generation system and, as a consequence, the analytical response, were evaluated. The following factors, sample flow rate (*Sample FR*, from 4 to 8 mL min^{-1}), reagent flow rate (*Reagent FR*, from 2 to 4 mL min^{-1}), eluent concentration (*Eluent conc.*; from 5 to 15% v/v), and reagent concentration (*Reagent conc.*; from 0.8 to 1.2% m/v) were studied. It is important to notice that the sample flow rate for the zinc chemical vapor generation is the same as the eluent flow rate for the preconcentration system. Then, a 2^4 level full factorial design consisting of 16 runs and four central points was performed in order to determine the influence of the factors and their interactions in the system. All the experiments were carried out in random order. The experimental data were processed using the STATISTICA software [38]. Minimum, maximum, and central point levels are shown in Table 3. The matrix design and the relative analytical signals obtained are shown in Table 4. Analysis of variance (ANOVA) and p-value were used to evaluate the significance of the effects on the vapor generator system.

Main effects and their interactions can be seen in the Pareto chart depicted in Fig. 2. This graphical representation demonstrated that sample flow rate and reagent flow rate were statistically significant at 95% confidence level. Eluent and reagent concentrations showed no influence and were fixed at 10% (v/v) and 1.0% (m/v); respectively.

3.4. CVG-final optimization using a central composite design

The significant variables indicated by the full factorial design (sample flow rate and reagent flow rate) needed further optimization. Thus, a central composite design (CCD) involving them was developed for such purpose. The experiment required by CCD was a cube with five central points and four axial points. Table 5 shows the matrix as coded and real values and relative analytical signal (%) obtained in the CCD.

Table 3
Factors and levels used in the 2^4 factorial design.

Variable	Low (−)	Central point (0)	High (+)
Sample flow rate (mL min^{-1})	2.0	5.0	8.0
Reagent flow rate (mL min^{-1})	2.0	3.0	4.0
Eluent concentration (%)	5.0	10.0	15.0
Reagent concentration (%)	0.8	1.0	1.2

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Table 4
Design matrix and results of the 2^4 level full factorial design (16 runs and 4 central points); low level (−); central point (0); high level (+); the factor levels (−, 0, and +) correspond with the ones present in Table 3.

Experiment	Sample FR	Reagent FR	Eluent conc.	Reagent conc.	Relative analytical signal (%)[a]
1	−	−	−	−	44.19
2	+	−	−	−	83.90
3	−	+	−	−	80.15
4	+	+	−	−	68.91
5	−	−	+	−	51.69
6	+	−	+	−	82.40
7	−	+	+	−	55.43
8	+	+	+	−	95.51
9	−	−	−	+	47.79
10	+	−	−	+	63.97
11	−	+	−	+	88.39
12	+	+	−	+	100.00
13	−	−	+	+	59.93
14	+	−	+	+	54.16
15	−	+	+	+	56.93
16	+	+	+	+	52.43
17	0	0	0	0	44.94
18	0	0	0	0	52.43
19	0	0	0	0	32.96
20	0	0	0	0	37.45

[a] Analytical signal resulted from the instrumental peak height measurements. Once these values were obtained, the highest one was considered the 100 (Experiment 12) and the others as a percentage of this maximum (relative analytical signal (%)).

The CCD data was used to create the surface response shown in Fig. 3, which is described by the following quadratic equation (Eq. (1)).

$$Z = -67.4884 + 32.6570^{*}X - 3.1266^{*}X^{2} + 37.1320^{*}Y - 8.8525^{*}Y^{2} + 3.0448^{*}X^{*}Y \quad (1)$$

Where X represents the sample flow rate, Y the reagent flow rate, and the term X×Y their interactions. Thus the optimal conditions for a maximum analytical response value were obtained. As a result, a sample flow rate of 8.0 mL min^{-1} and a reagent flow rate of 3.0 mL min^{-1} were used for further experiments.

3.5. Interference studies

One of the sources of interference in chemical vapor generation systems is the presence of transition metals. In addition, the catalytic effect of metals over the decomposition of BH_4^- [20] has been documented. In this work, the effect of Al (III), As (III), Cd (II), Cr (III), Ge (IV), Mn (II), Sb (III), Sn (IV), Ni (II), Te (IV), Ti (IV), V (V), Bi (III), Co (II), Cu (II), Fe (III), Mn (II), Pb (IV), and Se (IV), at 2500 μg L^{-1} concentration level each, was tested; no variation of Zn signal was observed.

Other elements that could be present in the water sample matrices such as alkali and alkaline earth were not retained on the column. In addition the hydride forming elements were not retained under the optimal conditions applied for Zn preconcentration on EVA.

These results show that the elements that are commonly found in natural waters (at the concentration levels at which they may occur) do not interfere with the analyte's preconcentration and/or generation of its chemical vapor.

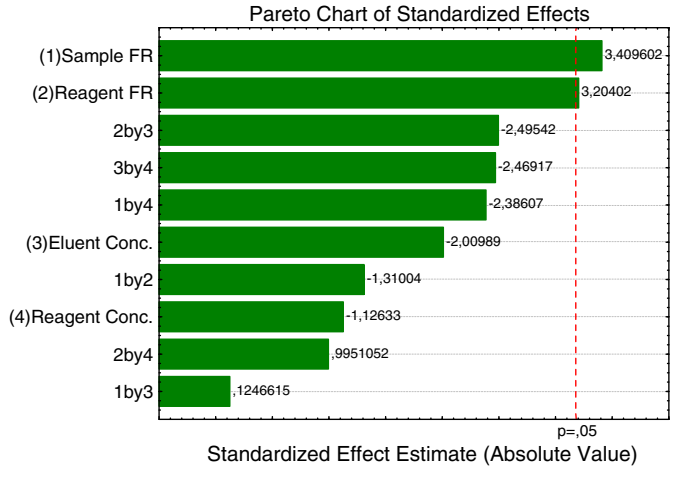

Fig. 2. Pareto chart of standardized effects for variables related to zinc solid phase extraction. (1) Sample flow rate (mL min^{-1}). (2) Reagent flow rate (mL min^{-1}). (3) Eluent concentration. (4) Reagent concentration.

Table 5
Central composite design matrix used to obtain the response surface.

Experiment	Sample flow rate (mL min^{-1})	Sample flow reagent (mL min^{-1})	Relative analytical signal (%)[a]
1	4,00 (−1)	2,00 (−1)	65.56
2	8,00 (+1)	2,00 (−1)	67.78
3	4,00 (−1)	4,00 (+1)	70.51
4	8,00 (+1)	4,00 (+1)	97.09
5	3,17 (−α)	3,00 (0)	71.20
6	8,83 (+α)	3,00 (0)	95.30
7	6,00 (0)	1,59 (−α)	94.27
8	6,00 (0)	4,41 (+α)	86.84
9	6,00 (0)	3,00 (0)	112.31
10	6,00 (0)	3,00 (0)	105.47
11	6,00 (0)	3,00 (0)	100.00
12	6,00 (0)	3,00 (0)	99.23
13	6,00 (0)	3,00 (0)	95.13

The negative (−1), positive (+1), zero (0), (+)α and (−)α sign are coded values of the factors/variables used for the optimization of the method at low, high and medium (central point) levels and star points.

[a] Analytical signals resulted from the instrumental peak height measurements. Once these values were obtained, the highest one was considered the 100 (Experiment 11) and the others as a percentage of this maximum (relative analytical signal (%)).

3.6. Evidence for vapor generation specie

To eliminate the possibility that transport of zinc, and hence final response, was due to the formation of a chemical vapor from the gas/

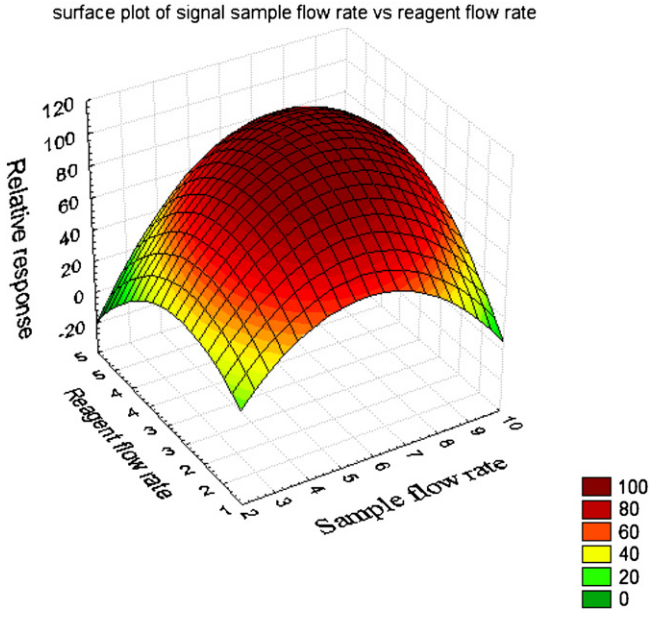

Fig. 3. Response surface obtained using central composite design.

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Table 6
Concentration of zinc in water samples and certified VKI reference material QC Metal LL1 DHI (95% confidence interval; n = 3).

Sample	Zn(II) conc. Base ($\mu g\ L^{-1}$)	Zn(II) conc. Added ($\mu g\ L^{-1}$)	Zn(II) conc. Found ($\mu g\ L^{-1}$)	Recovery[a] (%)
River water	6.1 ± 1.25	0.00	6.1 ± 1.25	–
(La Carolina, San Luis, Arg.)	6.10	10.00	16.40	103.00
	6.10	20.00	25.80	98.50
	6.10	30.00	36.08	99.93
	6.10	40.00	47.00	102.25
Tap water	20.20 ± 1. 31	0.00	20.20 ± 1. 31	–
(San Luis, Arg.)	20.20	10.00	30.00	98.00
	20.20	20.00	40,50	101.50
	20.20	30.00	50.30	100.33
	20.20	40.00	59.70	98.75
QC metal L1	50.1 ± 1.5	0.00	48.9 ± 1.9	–

[a] Recovery (%) = [(found − base) / added] × 100.

liquid separator, a 50 $\mu g\ L^{-1}$ Zn spiked solution containing 1 $mg\ L^{-1}$ of Mg and Ca; respectively, was evaluated and emission from these ion lines at 279.55 and 396.85 nm was monitored. Magnesium and calcium are nonhydride forming elements and they are unlikely to form a volatile compound during the conditions mentioned above. Besides, these elements are several orders of magnitude more sensitive than zinc in the ICP-OES. No signal of Ca or Mg was obtained.

On the other hand the presence of an aerosol containing the Zn species should produce a variation in the background signal in all cases and this was not observed. One may confidently conclude that no significant amount of Zn is being transported to the plasma in the form of an aerosol. This is according to the results obtained by Smitchowski et al. [1].

3.7. Figures of merit

The calibration curve obtained was linear between values closer to the limit of quantification (LOQ) and 300 $\mu g\ L^{-1}$. The F-test demonstrated that linear regression was statistically acceptable in the working range and this model showed goodness of fit. The determination coefficient (R^2) was 0.9950. The limit of detection (LOD) and LOQ where calculated as $3\sigma/S$ and $10\sigma/S$, respectively (n = 10); where S is the slope of the calibration curve and σ is the standard deviation of six consecutive measurements of the blank solution. The LOD and LOQ values were 0.06 $\mu g\ L^{-1}$ and 2.01 $\mu g\ L^{-1}$, respectively. The precision of a 50 $\mu g\ L^{-1}$ zinc solution, calculated as the relative standard deviation of six consecutive measurements (repeatability condition), was 3.7%. An enhancement factor of 230-fold (23 for the preconcentration and 10 for the vapor generation system, in reference to pneumatic nebulization) for a sample volume of 16 mL, was obtained. The throughput sample was approximately 17 samples per $hour^{-1}$.

4. Validation and analytical application

The proposed method was successfully applied to the determination of traces of Zn in tap (San Luis City, Argentina) and river (La Carolina, San Luis, Argentina) water samples, the mentioned river is important because it is used to purify the water supply of the city of San Luis. In order to evaluate the methodology, a recovery study was conducted. The samples were divided into 10 aliquots, the preconcentration/vapor generation/determination method was applied to six portions and the average quantity of the Zn obtained was taken as the base value. Then, increasing quantities of Zn were added to other aliquots of the sample and the element was determined by the same method. In all cases the recoveries were close to 100%. This method was also verified by determining Zn in a certified reference material VKI QC Metal LL1 DHI (Water & Environment) Denmark; the results are listed in Table 6.

5. Conclusions

This study has demonstrated for the first time the possibility of associating an on-line preconcentration procedure, using ethyl vinyl acetate as sorbent, with the generation of volatile species of zinc. The procedure offers a preconcentration system with satisfactory accuracy and precision. Besides, this methodology is simple and economical since only EVA, without modification, is used for Zn preconcentration. Such an approach could certainly enhance the analytical features of the spectrometric techniques by increasing the sample throughput, reducing the reagents consumption, lowering the risk of the sample contamination. In addition, the application of the optimized procedure was suitable for the analysis of zinc in water samples and a reference material.

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References

[1] P. Smichowski, S. Farías, S. Pérez Arisnabarreta, Chemical vapour generation of transition metal volatile species for analytical purposes: determination of Zn by inductively coupled plasma-optical emission spectrometry, Analyst 128 (2003) 779–785.
[2] L. Escudero, L.D. Martinez, J.A. Salonia, J.A. Gasquez, Determination of Zn(II) in natural waters by ICP-OES with on-line preconcentration using a simple solid phase extraction system, Microchem. J. 95 (2010) 164–168.
[3] S.A. Luna, R.E. Sturgeon, R.C. de Campos, Chemical vapor generation: atomic absorption by Ag, Au, Cu, and Zn following reduction of aquo ions with sodium tetrahydroborate(III), Anal. Chem. 72 (2000) 3523–3531.
[4] E. Peña-Vázquez, J. Villanueva-Alonso, P.R. Bermejo-Barrera, Optimization of a vapor generation method for metal determination using ICP-OES, J. Anal. At. Spectrom. 22 (2007) 642–649.
[5] A.S. Luna, H.B. Pereira, I. Takase, R. Araújo Goncalves, R.E. Sturgeon, R.C. de Campos, Chemical vapor generation–electrothermal atomic absorption spectrometry: new perspectives, Spectrochim. Acta B 57 (2002) 2047–2056.
[6] Y.L. Feng, R.E. Sturgeon, J.W. Lam, Chemical vapor generation characteristics of transition and noble metals reacting with tetrahydroborate(III), J. Anal. At. Spectrom. 18 (2003) 1435–1442.
[7] M. Ghaedi, K. Niknam, A. Shokrollahi, E. Niknam, H.R. Rajabi, M. Soylak, Flame atomic absorption spectrometric determination of trace amounts of heavy metal ions after solid phase extraction using modified sodium dodecyl sulfate coated on alumina, J. Hazard. Mater. 155 (2008) 121–127.
[8] D. Pérez-Quintanilla, A. Sánchez, I. del Hierro, M. Fajardo, I. Sierra, Preconcentration of Zn(II) in water samples using a new hybrid SBA-15-based material, J. Hazard. Mater. 166 (2009) 1449–1458.
[9] M. Ghaedi, K. Niknam, A. Shokrollahi, E. Niknam, H. Ghaedi, M. Soylak, A solid phase extraction procedure for Fe3+, Cu2+ and Zn2+ ions on2-phenyl-1H-benzo [d] imidazole loaded on TritonX-100-coated polyvinyl chloride, J. Hazard. Mater. 158 (2008) 131–136.

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[10] M. Khajeh, Application of Box–Behnken design in the optimization of a magnetic nanoparticle procedure for zinc determination in analytical samples by inductively coupled plasma optical emission spectrometry, J. Hazard. Mater. 172 (2009) 385–389.
[11] J.A. Salonia, E.S. Cerutti, L.D. Martinez, J.L. Fernández Turiel, J.A. Gásquez, On-line preconcentration and analysis of zinc in water by flow injection–knotted reactor: application to geological and environmental exploration, Instrum. Sci. Technol. 36 (2008) 302–308.
[12] X. Zhu, X. Chang, Y. Cui, X. Zou, D. Yang, Z. Hu, Solid-phase extraction of trace Cu (II) Fe(III) and Zn(II) with silica gel modified with curcumin from biological and natural water samples by ICP-OES, Microchem. J. 86 (2007) 189–194.
[13] D. Kara, A. Fisher, S.J. Hill, Comparison of some newly synthesized chemically modified amberlite XAD-4 resins for the preconcentration and determination of trace elements by flow injection inductively coupled plasma-mass spectrometry (ICP-MS), Analyst 131 (2006) 1232–1240.
[14] S. Hajialigol, M.A. Taher, A. Malekpour, Determination of trace amounts of zinc by flame atomic absorption spectrometry after preconcentration with modified clinoptilolite zeolite, J. AOAC Int. 91 (2008) 1446–1452.
[15] A. Mostafavi, D. Afzali, M.A. Taher, Atomic absorption spectrometric determination of trace amounts of copper and zinc after simultaneous solid phase extraction and preconcentration onto modified natrolite zeolite, Anal. Sci. 22 (2006) 849–853.
[16] J.S. Carletto, K.C.D.P. Roux, H.F. Maltez, E. Martendal, E. Carasek, Use of 8-hydroxyquinoline-chitosan chelating resin in an automated on-line preconcentration system for determination of zinc(II) by FAAS, J. Hazard. Mater. 157 (2008) 88–93.
[17] S. Kagaya, E. Maeba, Y. Inoue, W. Kamichatani, T. Kajiwara, H. Yanai, M. Saito, K. Tohda, A solid phase extraction using a chelate resin immobilizing carboxymethylated pentaethylenehexamine for separation and preconcentration of trace elements in water samples, Talanta 79 (2009) 146–152.
[18] Q. Li, X. Zhao, Q. Lv, G. Liu, The determination of zinc in water by flame atomic absorption spectrometry after its separation and preconcentration by malachite green loaded microcrystalline triphenylmethane, Sep. Purif. Technol. 55 (2007) 76–81.
[19] M. Tuzen, K.O. Saygi, M.M. Soylak, Solid phase extraction of heavy metal ions in environmental samples on multiwalled carbon nanotubes, J. Hazard. Mater. 152 (2008) 632–639.
[20] R.E. Sturgeon, J. Liu, V.J. Boyko, V.T. Luong, Determination of copper in environmental matrices following vapor generation, Anal. Chem. 68 (1996) 1883–1887.
[21] H. Sun, R. Suo, Enhancement reagents for simultaneous vapor generation of zinc and cadmium with intermittent flow system coupled to atomic fluorescence spectrometry, Anal. Chim. Acta 509 (2004) 71–76.
[22] R.E. Sturgeon, X. Guo, Z. Mester, Chemical vapor generation: are further advances yet possible? Anal. Bioanal. Chem. 382 (2005) 881–883.
[23] T. Matousek, The efficiency of chemical vapor generation of transition and noble metals, Anal. Bioanal. Chem. 388 (2007) 763–767.
[24] P. Smichowski, S. Farías, Advantages and analytical applications of chloride generation. A review on vapor generation methods in atomic spectrometry, Microchem. J. 67 (2000) 147–155.
[25] A. D'Ulivo, Z. Mester, R.E. Sturgeon, The mechanism of formation of volatile hydrides by tetrahydroborate derivatization: a mass spectrometric study performed with deuterium labeled reagents, Spectrochim. Acta B 60 (2005) 423–438.
[26] A. D'Ulivo, Z. Mester, J. Meija, R.E. Sturgeon, Mechanism of generation of volatile hydrides of trace elements by aqueous tetrahydroborate(III). Mass spectrometric studies on reaction products and intermediates, Anal. Chem. 79 (2007) 3008–3015.
[27] A. D'Ulivo, Mechanism of generation of volatile species by aqueous boranes: towards the clarification of most controversial aspects, Spectrochim. Acta B 65 (2010) 360–375.
[28] P. Pohl, B. Prusisz, Chemical vapor generation of noble metals for analytical spectrometry, Anal. Bioanal. Chem. 388 (2007) 753–762.
[29] D.F. Shriver, G.J. Kubas, J.A. Marshall, Zinc hydride complexes $NaZn_2(CH_3)_2H_3$ and $NaZnH_3$, J. Am. Chem. Soc. 93 (1971) 5076–5079.
[30] P. Pohl, Recent advances in chemical vapor generation via reaction with sodium tetrahydroborate, Trends Anal. Chem. 23 (1) (2004) 21–27.
[31] P. Pohl, P. Jamroz, Recent achievement in chemical hydride generation inductively coupled and microwave induced plasmas with optical emission spectrometry detection, J. Anal. At. Spectrom. 26 (2011) 1317–1337.
[32] M. Zougagh, P.C. Rudner, A.G. de Torres, Jose M. Cano Pavon, Application of Doehlert matrix and factorial designs in the optimization of experimental variables associated with the on-line preconcentration and determination of zinc by flow injection inductively coupled plasma atomic emission spectrometry, J. Anal. At. Spectrom. 15 (2000) 1589–1594.
[33] S.L.C. Ferreira, W.N.L. Dos Santos, C.M. Quintella, B.B. Neto, J.M. Bosque-Sendra, Doehlert matrix: a chemometric tool for analytical chemistry—review, Talanta 63 (2004) 1061–1067.
[34] L.A. Escudero, S. Cerutti, R.A. Olsina, J.A. Salonia, J.A. Gasquez, Factorial design optimization of experimental variables in the on-line separation/preconcentration of copper in water samples using solid phase extraction and ICP-OES determination, J. Hazard. Mater. 183 (2010) 218–223.
[35] R.A. Gil, N. Ferrúa, J.A. Salonia, R.A. Olsina, L.D. Martinez, On-line arsenic coprecipitation on ethyl vinyl acetate turning-packed mini-column followed by hydride generation-ICP OES determination, J. Hazard. Mater. 143 (2007) 431–436.
[36] L. Escudero, R.A. Gil, J.A. Gasquez, R.A. Olsina, L.D. Martinez, Trace molybdenum determination in drinking waters by USN-ICP OES after solid phase extraction on ethyl vinyl acetate turnings-packed minicolumn, At. Spectrosc. 29 (2008) 21–26.
[37] R.A. Gil, M.M. Kaplan, J.A. Salonia, J.A. Gasquez, L.D. Martinez, Total inorganic Se and Te preconcentration and their determination by on-line coupling of a solid-phase extraction procedure with HG-AAS, At. Spectrosc. 28 (2007) 67–72.
[38] Statistica for Windows, StatSoft, Inc., 2300 East 14th Street, Tulsa, OK 741014, USA, 1999.

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