



Analytical Methods

Novel method for determination of zinc traces in beverages and water samples by solid surface fluorescence using a conventional quartz cuvette



María Carolina Talio^b, María Gimena Acosta^b, Mariano Acosta^b, Roberto Olsina^{a,b}, Liliana P. Fernández^{a,b,*}

^aÁrea de Química Analítica, Facultad de Química, Bioquímica y Farmacia, Universidad Nacional de San Luis, San Luis, Argentina

^bInstituto de Química de San Luis (INQUISAL-CONICET), Chacabuco y Pedernera, 5700 San Luis, Argentina

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"In memoriam" of Dr. Adriana Masi, prominent researcher, dear colleague and friend, who passed away prematurely, as a consequence of public insecurity, killed by a shot in the head at the door of her house.

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ABSTRACT

A new method for zinc pre-concentration/separation and determination by molecular fluorescence is proposed. The metal was complexed with *o*-phenanthroline and eosin at pH 7.5 in Tris; a piece of filter paper was used as a solid support and solid fluorescent emission measured using a conventional quartz cuvette. Under optimal conditions, the limits of detection and quantification were 0.36×10^{-3} and $1.29 \times 10^{-3} \mu\text{g L}^{-1}$, respectively, and the linear range from 1.29×10^{-3} to $4.50 \mu\text{g L}^{-1}$. This method showed good sensitivity and selectivity, and it was applied to the determination of zinc in foods and tap water. The absence of filtration reduced the consumption of water and electricity. Additionally, the use of common filter papers makes it a simpler and more rapid alternative to conventional methods, with sensitivity and accuracy similar to atomic spectroscopies using a typical laboratory instrument.

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1. Introduction

Zinc is a metal with great nutritional importance, necessary in cellular replication and immune response development, with catalytic and regulatory actions on more than 300 enzymes (Seiler, Sigel, & Sigel, 1994, chap. 58; Terres-Martos et al., 2002). Growth retardation, altered immune response, premature birth, weight loss, and anorexia are some of the consequences of zinc deficiency (Gruber & Pista, 2013; Katz et al., 1987). Deficiency can be the result of low dietary intake of bioavailable zinc, but it can also be caused by illness, which impairs food intake (Haase, Overbeck, & Rink, 2008; Salgueiro et al., 2002). On the other hand, a diet with excess zinc can cause disturbances in energy metabolism or an

increase in oxidative stress (Tupe, Tupe, Tarwadi, & Agte, 2010; Yanagisawa et al., 2009).

The recommended zinc intake values are between 5 and 15 mg L^{-1} per day depending on sex and age (NRC, National Research Council, & National Academy of Sciences, 1999). Foods represent the main intake source of zinc as well as tap water. Although tap water should not have toxic levels of zinc, this metal can be present due to corrosion processes in pipes. (Alam & Sadiq, 1989). High levels of zinc associated to other toxic metals have been recently found to be present both in ground and tap water (Almeida, Chan, Pettigrove, Catrall, & Kolev, 2014; Patterson, Pehrsson, & Perry, 2013).

The determination of zinc in foods and tap water is one of the most difficult and complex analytical tasks, especially at trace levels. Different analytical techniques have been applied to the determination of low concentrations of zinc, such as atomic absorption spectrometry with flame (FAAS) (Abdolmohammad-Zadeh & Sadeghi, 2009; Carletto, Roux, Maltez, Martendal, & Carasek, 2008; Zhu, Liang, Zhao, Yan, & Han, 2008) and electrothermal

* Corresponding author at: Área de Química Analítica, Facultad de Química, Bioquímica y Farmacia, Universidad Nacional de San Luis, San Luis, Argentina. Tel.: +54 02664 425385.

E-mail address: lfernand@unsl.edu.ar (L.P. Fernández).

atomization (ETAAS) (Batista et al., 2008; Kiptoo, Ngila, & Silavwe, 2008), inductively coupled plasma optical emission spectrometry (ICP-OES) (Chang et al., 2008; Khajeh, 2009; Salonia, Wuilloud, Gásquez, Olsina, & Martinez, 2000; Suvardhan et al., 2007; Salonia, Cerutti, Martinez, Fernández Turiel, & Gásquez, 2008), and spectrofluorimetry (Haase et al., 2008).

Solid phase extraction (SPE) is an alternative rapid, simple, more environmentally-friendly, and economic pre-concentration step, which has advantages over the traditional liquid-liquid extraction. SPE followed by ETAAS, ICP-OES or ICP-mass spectrometry have been shown to be suitable for analysis of trace metal (Karbasia, Jahanparast, Shamsipur, & Hassan, 2009; Suleiman, Hu, Huang, & Zhang, 2008). Investigators are interested in improving the selectivity of the sorbents used in SPE. Several solid materials, such as silica gel, exchange resins, aluminum oxide, poly(vinylalcohol), C₁₈ membranes, cyclodextrines, filter papers, and nylon membranes, among others, have been employed successfully as solid supports for SPE (Correa & Escandar, 2006; Peralta, Fernández, & Masi, 2010).

The application of molecular fluorescence in zinc determination has shown several analytical advantages, such as sensitivity, selectivity and a wide dynamic range in association with separation/pre-concentration step (Vega, Augusto, Talio, & Fernández, 2011).

The aim of present work was to propose an alternative method for zinc determination in real-world samples, using instruments accessible in quality control laboratories. Considering economic aspects and operating simplicity, filter papers were used as a solid support for Zn(II)-complex retention for determination by solid surface fluorescence (SSF). A conventional 10 mm cuvette adapted to SSF was used for the measurement step.

2. Experimental

2.1. Reagents

Blue Ribbon Filter papers (Whatman, UK) of 2–5 µm pore size and 12.5 cm diameter were used in retention studies.

Stock solutions of Zn(II) 6.54 mg L⁻¹ were prepared by dilution of 100 µg mL⁻¹ standard solution plasma-pure (Leeman Labs, Inc., Hudson, NH, USA).

Tris-(hydroxymethyl)-aminomethane (Mallinckrodt Chemical Works, St. Louis, USA – 1 mmol L⁻¹), sodium tetraborate (Merck & Co., Inc., – 1 mmol L⁻¹), potassium phthalate acid (Merck & Co., Inc., – 1 mmol L⁻¹) and acetic acid/acetate (Mallinckrodt Chemical Works) buffer solutions were prepared.

The desired pH was obtained by adding HClO₄ (Merck & Co., Inc., Darmstadt, Germany) or NaOH, with the assistance of a pH meter (Orion Expandable Ion Analyzer Model EA 940, Orion Research, Cambridge MA, USA).

Stock solutions of eosin (H.E Daniel Ltd., UK – 1 × 10⁻³ mmol L⁻¹) and o-phenanthroline (Merck & Co., Inc., – 1 × 10⁻² mmol L⁻¹) were prepared weekly by dissolving the appropriate amount of each reagent in ultrapure water. The stability of the solutions was checked using a spectrophotometer. All glass materials were previously rinsed with a 10% (v/v) HNO₃, and then with Millie-Q ultrapure water. All reagents were analytical grade.

2.2. Apparatus

Spectrofluorimetric measurements were made using a Shimadzu RF-5301 PC spectrofluorometer equipped with a 150 W Xenon lamp and 1.00 cm quartz cells adapted to SSF.

Measurements were performed with a Shimadzu Model AA-6800 atomic absorption spectrometer (Tokyo, Japan) equipped with a deuterium background corrector, an EX7-GFA electrothermal

atomizer and an ASC-6100 autosampler. L'vov graphite tubes (Shimadzu, Tokyo, Japan) were used in all experiments. A zinc hollow-cathode lamp (Hamamatsu, Photonics K., Japan) was employed as the radiation source. The wavelength used was 213.9 nm using a pyrolysis time of 13 s at 450 °C, and an atomization time of 3 s at 1800 °C.

A Milestone STARTD microwave furnace (Italy) and Milestone polytetrafluoroethylene (PTFE) reactors hermetically sealed (internal volume 100 mL and 1 cm wall thickness) were used for microwave digestion.

2.3. Sampling procedure and sample preparation

Tap water samples (1000 mL), from the locations specified in Table 4, were collected in sampling bottles, after being allowed to run for 10 min, and transported to the lab in refrigerated boxes. Tap water samples were processed once they arrived in the laboratory, without previous treatment.

Food samples (beverages) were purchased from supermarkets popular with consumers and typically sold throughout Argentina. Samples were selected taking into account the main products consumed by segments of the population with different dietary requirements due to their age and lifestyle. In order to guarantee representative samples, a randomize strategy sampling was used; a total of three examples of the same brand for each product were acquired. Entire products were homogenized and reserved for sample preparation.

About 0.5 g of each solid sample (milk powder, express coffee, cocoa powder) was digested using a microwave furnace. Then resulting solutions were transferred to 100 mL volumetric flask and made to volume with Millie-Q ultrapure water. Portions of 100 µL of each sample were put into 100 mL volumetric flask and diluted with Millie-Q ultrapure water (*n* = 4). These solutions were kept for Zn(II) determination.

Beverages (cola drink, instant coffee, energy and hydrating drinks) were diluted and analyzed for Zn(II) directly. Solid and liquid samples were analyzed using the same method subsequently.

2.4. Analysis

Sample and standards Zn(II) (1.29 × 10⁻³ to 4.50 µg L⁻¹, pH7.5) and 1 mL methanol were put in a crystallizer flask, and the mixture diluted to 10 mL with ultrapure water. Pieces of Blue Ribbon filter paper (1 × 3 cm) were impregnated through contact with each solution for 1 min (*n* = 4). The filter papers were dried at room temperature and kept in a dried ambient (20 °C–25 °C) atmosphere until analysis. Sample filter paper were arranged in a conventional quartz cell, adapted for solid support, and SSF determined at λ_{em} = 440 nm (emission), using λ_{ext} = 370 nm (excitation).

2.5. Interferences study

Different amounts of zinc, which may be present in water samples (1/1, 1/10, 1/100 and 1/1000 Zn(II)/interference ratio) were added to a test solution containing 32.6 × 10⁻³ µg L⁻¹ Zn(II), and analyzed.

2.6. Accuracy study

Tap water samples were spiked with increasing amounts of Zn(II) (1.29 × 10⁻³ to 4.50 µg L⁻¹) and analyzed using the proposed SSF method.

2.7. Precision study

The repeatability (within-day precision) of the SSF method was tested for replicate samples ($n = 4$) spiked with $32.6 \times 10^{-3} \mu\text{g L}^{-1}$ of Zn(II) and content determined with other samples and the standards.

2.8. Validation

Zinc in tap water samples were determined by ETAAS, under the operational conditions described in Section 2.2.

3. Results and discussion

Previous research has shown the feasibility of o-phen/eo/metal ions ternary complexes (Mudakavi, 1984; Rauf, Ikram, & Ahmad, 2002; Talio, Luconi, Masi, & Fernández, 2009; Talio, Luconi, Masi, & Fernández, 2010) and their determination by molecular fluorescence. The fluorescence of the eo/o-phen/Zn(II) system was initially explored in an aqueous medium without satisfactory results in relation to enhanced fluorescent signal and stability.

Then, the fluorescent emission of the eo/o-phen/Zn(II) system was explored by SSF using different solid supports and determination of the fluorescent signal of the eo/o-phen/Zn(II) complex. The results obtained showed an important enhancement of the signal when Blue Ribbon filter paper was employed in the retention process; this fact reinforces the formation of a eo/o-phen/Zn(II) complex, with the additional advantage sensitivity for the luminescent response (Fig. 1).

The feasibility of using common filter paper substantially reduces the cost per assay compared to nylon membranes (Vega et al., 2011). With respect to sampling time, this parameter was minimized (previous work) by eliminating the filtration step, thus also enabling sampling *in situ*.

A conventional quartz cuvette was used for SSF with the aim of making the method easier for quality control laboratories.

A plastic device was placed diagonally in the cuvette to accommodate the filter paper during SSF measurements. The results were

highly satisfactory and equivalent to those obtained using a commercial device for solid supports.

In order to assure quantitative metal retention, assays were carried out with o-phen and eo concentrations ranging from 1×10^{-9} to $1 \times 10^{-6} \text{ mol L}^{-1}$, and $32.6 \times 10^{-3} \mu\text{g L}^{-1}$ Zn(II). Concentrations of o-phen and eo of $5 \times 10^{-7} \text{ mol L}^{-1}$ and $5 \times 10^{-8} \text{ mol L}^{-1}$, respectively, were selected as optimal because above these conditions the eo/o-phen/Zn(II) complex produced maximum fluorescent emission at all concentrations.

The results obtained showed that Zn(II) retention began at pH 3.5 achieving a plateau pH 4–7.8; Zn(II) retention suffered a sharp decrease at higher pH (Fig. 2). A Tris buffer (pH 7.5) was chosen as optimal for subsequent experiments. In order to obtain the maximum fluorescent signal for the system, the influence of Tris buffer concentration was tested in the range of 1×10^{-5} to 0.5 mol L^{-1} ; $5 \times 10^{-4} \text{ mol L}^{-1}$ was optimal and used in subsequent analyses.

Drying the filter papers was among the experimental steps that impacted the most the time taken for analysis. With the aim of accelerating drying, volatile organic solvents were added to the solution used for solid support pre-treatment. Among the solvents studied, 10% methanol in water produced the best results in terms of sensitivity and the highest Zn(II) retention.

Another optimized parameter was the contact time in the preparation of the solid support. Filter papers were prepared by immersion in a o-phen/eo/buffer/methanol/Zn(II) solution for different periods of time. The optimal immersion time selected was 1 min, which was also the minimum time enabling quantitative metal retention. Table 1 shows the main experimental advantages with respect to previous research (Vega et al., 2011).

3.1. Analytical parameters

3.1.1. Calibration curve

A calibration curve for different concentrations of Zn(II) from 1.29×10^{-3} to $4.50 \mu\text{g L}^{-1}$ was realized by applying the method developed (described in Section 2.4). Table 2 summarizes the main characteristics of the calibration plot and the optimized experimental conditions for the quantification of Zn(II) traces.

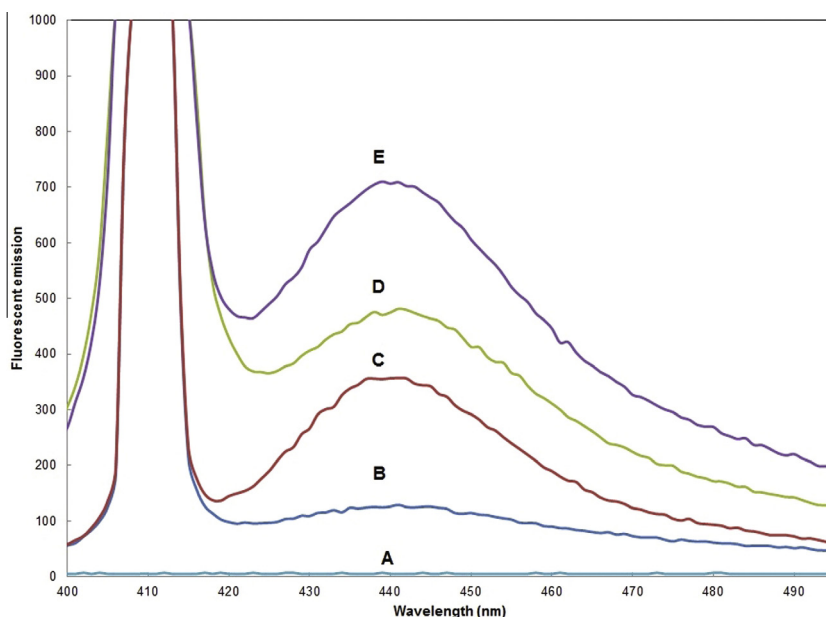


Fig. 1. Solid surface fluorescence of o-phen/eo/Zn(II) system. (A) Filter papers. (B) Blank signal-filter paper with o-phen and eo. (C) Idem B with Zn(II) $32.6 \times 10^{-3} \mu\text{g L}^{-1}$. (D) Idem B with Zn(II) $65 \times 10^{-3} \mu\text{g L}^{-1}$. (E) Idem B with Zn(II) $97 \times 10^{-3} \mu\text{g L}^{-1}$. Conditions: $\lambda_{\text{em}} = 440 \text{ nm}$; $\lambda_{\text{exc}} = 370 \text{ nm}$; $C_{\text{o-phen}} = 5 \times 10^{-7} \text{ mol L}^{-1}$, $C_{\text{eo}} = 5 \times 10^{-8} \text{ mol L}^{-1}$; $C_{\text{buffer Tris}} = 5 \times 10^{-4} \text{ mol L}^{-1}$, pH 7.5. Other experimental conditions are described under procedure.

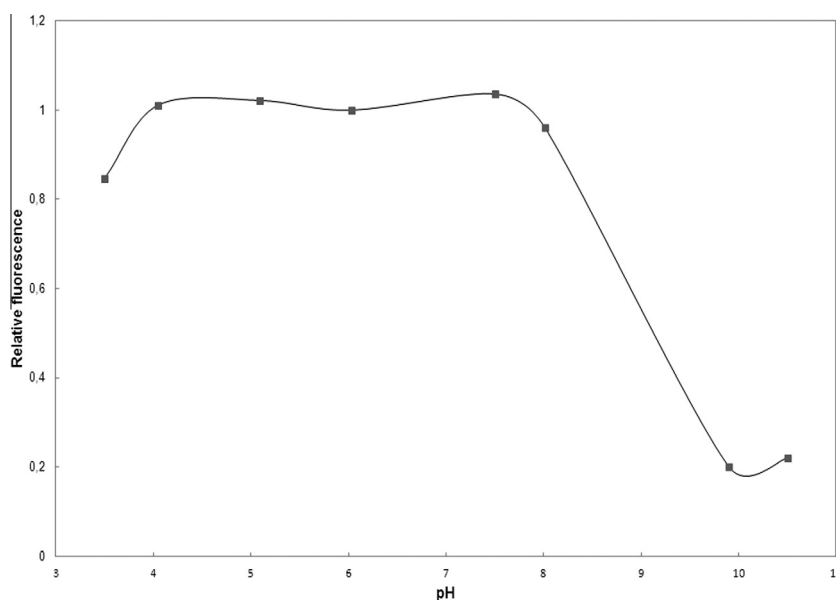


Fig. 2. Influence of pH on Zn(II) retention. Conditions: $\lambda_{em} = 440$ nm; $\lambda_{exc} = 370$ nm; $C_{o-phen} = 5 \times 10^{-7}$ mol L⁻¹, $C_{eo} = 5 \times 10^{-8}$ mol L⁻¹; $C_{buffer\ Tris} = 5 \times 10^{-4}$ mol L⁻¹, pH 7.5; $C_{Zn(II)} = 32.6 \times 10^{-3}$ μ g L⁻¹. Other experimental conditions are described under procedure.

Table 1

Comparative table of experimental conditions between Vega et al. and present works.

	Vega et al.	This work
Solid support	Nylon membrane	Filter paper
Performance/ assay	1	4
Support pretreatment		Yes (5 min)
Dry step	2	1
Analyte retention	Filtration using peristaltic pump (0.1 mL/min)	Simple immersion (1 min)
SSF	Solid sample holder with quartz window	Conventional quartz cuvette
Sampling time	75 min	15 min

Table 2

Experimental conditions and analytical parameters for zinc determination using the proposed methodology.

Parameters	Studied range	Optimal conditions
pH	3.5–10.5	7.5
Buffer Tris	1×10^{-5} to 0.5 mol L ⁻¹	5×10^{-4} mol L ⁻¹
O-phen concentration	1×10^{-9} to 1×10^{-6} mol L ⁻¹	5×10^{-7} mol L ⁻¹
Eo concentration	1×10^{-9} to 1×10^{-6} mol L ⁻¹	5×10^{-8} mol L ⁻¹
Immersion time	10–120 s	60 s
LOD	–	0.36×10^{-3} μ g L ⁻¹
LOQ	–	1.29×10^{-3} μ g L ⁻¹
LOL	–	1.29×10^{-3} to 4.50μ g L ⁻¹
r ²	–	0.9989

Table 3

Tolerance limits of interfering species in Zn(II) determination.

Interferent/Zn(II) mole ratio	Interferent species
10,000:1	Na ⁺ , K ⁺ , Cl ⁻
1000:1	Cd ²⁺ , Ca ²⁺ , Mg ²⁺ , Mn ²⁺ , Ni ²⁺ , Pb ²⁺ , Co ²⁺ , Cu ²⁺ , F ⁻ , CO ₃ ²⁻ , SO ₄ ²⁻ , CH ₃ COO ⁻ , NO ₃ ⁻
100:1	Hg ²⁺ , Fe ³⁺ , Ba ²⁺ , Sr ²⁺ , Cr ³⁺

Conditions: $\lambda_{em} = 440$ nm; $\lambda_{exc} = 370$ nm; $C_{o-phen} = 5 \times 10^{-7}$ mol L⁻¹, $C_{eo} = 5 \times 10^{-8}$ mol L⁻¹; $C_{buffer\ Tris} = 5 \times 10^{-4}$ mol L⁻¹, pH 7.5; $C_{Zn(II)} = 32.6 \times 10^{-3}$ μ g L⁻¹. Other experimental conditions are described under procedure.

Table 4

Water samples. Recuperation and validation studies.

Sample	Zn(II) added (μ g L ⁻¹)	Proposed methodology		ETAAS Zn(II) found \pm CV (μ g L ⁻¹)
		Zn(II) found \pm CV (μ g L ⁻¹)	Recovery (%; n = 4)	
1	–	1.81 \pm 0.08	–	–
	1.00	2.87 \pm 0.03	101.25	–
	2.00	3.76 \pm 0.02	98.97	–
2	–	4.77 \pm 0.04	–	4.80 \pm 0.001
	1.00	5.80 \pm 0.01	100.44	–
	2.00	6.74 \pm 0.03	99.56	–
3	–	2.32 \pm 0.01	–	–
	1.00	3.31 \pm 0.05	99.81	–
	2.00	4.30 \pm 0.05	99.63	–
4	–	2.98 \pm 0.06	–	3.00 \pm 0.002
	1.00	4.01 \pm 0.03	100.60	–
	2.00	4.97 \pm 0.04	99.80	–
5	–	1.72 \pm 0.03	–	–
	1.00	2.75 \pm 0.02	101.74	–
	2.00	3.69 \pm 0.04	98.25	–
6	–	1.39 \pm 0.02	–	1.44 \pm 0.004
	1.00	2.41 \pm 0.01	101.44	–
	2.00	3.38 \pm 0.08	99.30	–
7	–	2.39 \pm 0.07	–	–
	1.00	3.42 \pm 0.04	101.25	–
	2.00	4.36 \pm 0.03	98.75	–

1 – Tap water (San Luis city, Argentina).

2 – Tap water (Potrero de los Funes, San Luis, Argentina).

3 – Tap water (Campus Universidad Nacional de San Luis, San Luis, Argentina).

4 – Tap water (Córdoba city, Argentina).

5 – Tap water (Huinca Renancó, Córdoba, Argentina).

6 – Tap water (Riocuarto, Córdoba, Argentina).

7 – Tap water (Mendoza city, Argentina).

The limits of detection (LOD) and quantification (LOQ) were calculated in accordance to formulas given by the official compendia methods (Miller & Miller, 1994), using the equation $k(SD)/m$, where $k = 3$ for LOD, and 10 for LOQ; SD represents the standard deviation from 15 replicate blank responses, and m is the slope of the calibration curve.

Table 5
Food samples. Recuperation study.

Sample	Zn(II) added ($\mu\text{g L}^{-1}$)	Proposed methodology		Zn(II) content (mg/100 g)	
		Zn(II) found \pm CV ($\mu\text{g L}^{-1}$)	Recovery (%; $n = 4$)	This methods	Others
1	–	0.086 ± 0.02	–	4.79	7.640 ^a
	0.05	0.135 ± 0.01	98.84		
	0.10	0.188 ± 0.04	102.32		
2	–	0.022 ± 0.03	–	10.10	2.482 ^{b,c}
	0.05	0.071 ± 0.05	95.45		
	0.10	0.122 ± 0.05	100.00		
3	–	0.145 ± 0.06	–	0.14	0.262 ^b
	0.05	0.194 ± 0.07	99.31		
	0.10	0.246 ± 0.03	102.22		
4	–	0.064 ± 0.03	–	0.06	0.057 ^b
	0.05	0.115 ± 0.02	101.56		
	0.10	0.164 ± 0.01	100.00		
5	–	0.154 ± 0.05	–	0.15	0.027 ^b
	0.05	0.203 ± 0.05	99.35		
	0.10	0.255 ± 0.08	100.65		
6	–	0.073 ± 0.02	–	0.07	WD
	0.05	0.122 ± 0.01	98.64		
	0.10	0.172 ± 0.02	98.64		
7	–	0.075 ± 0.03	–	0.08	WD
	0.05	0.126 ± 0.02	101.33		
	0.10	0.175 ± 0.07	100.00		
8	–	0.060 ± 0.04	–	0.06	WD
	0.05	0.109 ± 0.06	98.33		
	0.10	0.161 ± 0.02	101.66		
9	–	0.047 ± 0.03	–	0.05	0.03 ^c
	0.05	0.100 ± 0.07	106.40		
	0.10	0.145 ± 0.04	95.75		
10	–	0.033 ± 0.02	–	0.025	0.03 ^c
	0.05	0.085 ± 0.05	106.06		
	0.10	0.132 ± 0.05	97.00		

1 – cocoa; 2 – milk power; 3 – instant coffee; 4 – cola drink; 5 – mineral water; 6 – hydrating beverage; 7 – energizing beverage; 8 – energy beverage; 9 – tea instant; 10 – tea black.

WD: without date.

^a <http://wholefoodcatalog.info/nutrient/zinc/beverages/>.

^b Olivares, Pizarro, de Pablo, Araya, and Uauy (2004).

^c <http://www.dietandfitnesstoday.com/drinks-high-in-zinc.php>.

3.1.2. Interference

The effect of other ions on the recovery of Zn(II) was tested using different amounts of ions commonly present in water, which were added to the test solution containing $32.6 \times 10^{-3} \mu\text{g L}^{-1}$ Zn(II). An ion was considered to interfere when it caused a variation in the fluorescence signal greater than $\pm 5\%$. The tolerance limits for the various ions are given in Table 3. These results demonstrate that even large amounts of some common ions do not interfere with the determination of Zn(II) at trace levels, and confirms the selectivity of the method developed.

3.2. Applications

The proposed method was applied to Zn(II) in tap water from Córdoba, San Luis and Mendoza (Argentina) to establish its applicability for real-world samples. The accuracy of the method was assessed by using the standard addition method and validated by ETAAS. Different sample aliquots were spiked with increasing amounts of Zn(II) (1.29×10^{-3} to $4.50 \mu\text{g L}^{-1}$). The results obtained showed an adequate precision, $\text{CV} \leq 0.08$ (see Tables 4 and 5).

Robustness of the assay was evaluated by repeating the analysis four times for each sample. Table 4 shows the recovery results

achieved. The results obtained indicate that the proposed method is suitable for Zn(II) determination in tap water.

The levels of Zn(II) found in the tap water samples were 100-fold lower than those established by the National Food Code (Segura Muñoz et al., 2003). But, given the limited number of samples studied and considering these regions have not been thoroughly sampled in this study, these results are an indication of low levels. Subsequent studies would be necessary and desirable in order to establish levels Zn(II) bases in this region.

With the aim of determining the incidence of low Zn-content, foods and beverages widely consumed by the population were analyzed using the method developed (Table 5), and compared with declared Zn content (<http://wholefoodcatalog.info/nutrient/zinc/beverages/>; Olivares, Pizarro, de Pablo, Araya, & Uauy, 2004; <http://www.dietandfitnesstoday.com/drinks-high-in-zinc.php>).

Results were similar for most of the foods studied, except milk and mineral water. Despite the results obtained showing, generally, low levels of Zn, further more in-depth studies should be conducted in order to establish baseline values of this element in the region.

4. Conclusions

The proposed method represents a valuable contribution to green chemistry since the absence of the filtration step reduces the consumption of water and electricity. Filter paper, a cheap material, was shown to be an adequate solid support for Zn(II) retention by simple immersion, thus enabling *in situ* sample preparation. Additionally, a conventional 10 mm cuvette was used for SSF with results similar to those obtained with a commercial device for solid supports, which makes the approach a simpler, more economic and rapid alternative to conventional methods. The level of sensitivity attained was comparable to those of atomic spectroscopies. The good tolerance at common constituents suggests high selectivity and versatility of the new method. Precision and accuracy were tested; validation was performed against ETAAS with satisfactory results. The method developed was successfully applied to Zn(II) quantification in tap water samples from different locations (Córdoba and San Luis) in Argentina, and beverages of consumed widely throughout the country. Considering the low Zn(II) concentrations present in water samples, at-risk groups may need dietary supplements containing zinc to prevent deficiency of this important element. However, further studies are necessary to confirm this.

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