



Analytical Methods

Development of a FI-HG-ICP-OES solid phase preconcentration system for inorganic selenium speciation in Argentinean beverages

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ABSTRACT

A preconcentration system has been developed to determine inorganic selenium species. Selenium was retained by a column filled with polyvinyl chloride (PVC) with lanthanum hydroxide co-precipitation. Speciation was achieved by selective photoreduction previous Se preconcentration. The retention pH was optimized at 10.0. Two multivariate calibrations and a central composite design were employed for optimization of the system. Sample, reagents and acid flow rates are significant variables affecting the system. Employing HG-ICP-OES as detection, the optimized system reached a detection limit of 0.03 µg/L, and an enhancement factor of 14875 (25 for preconcentration system, 595 for hydride generation). To verify the method accuracy, two certified reference materials, BCR[®] 414 Plankton & IRMM-804 Rice Flour, were analysed. The system was applied to inorganic selenium speciation in several Argentinean beverages to estimate their selenium contribution to diet.

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1. Introduction

Selenium is an essential micronutrient for human beings and diet is the major source of this element. Selenium acts as an antioxidant in the human body showing redox activity through essential enzymes as glutathione peroxidase (Berger et al., 2004). This enzyme, along with vitamin E, is involved in cellular protection processes and catalysis of peroxides reduction, generated by oxidative degradation. Furthermore, Selenium has a significant role in metabolic pathways, and in immune and endocrine system (Beckett & Arthur, 2005; Williams & Harrison, 2010).

Selenium intake depends on its concentration and chemical form in food. Organic selenium is more bioavailable than inorganic forms (Sigrist, Brusa, Campagnoli, & Beldoménico, 2012). The Recommended Dietary Allowance (RDA) for adults is 55 µg of Selenium per day while the tolerable upper intake level for adult is established at 400 µg of Selenium per day (Food and Nutrition Board, USA, 2000). Thresholds between these two undesirable effects are very close. In addition, under equal intake, selenite is more toxic than selenate at concentrations higher than RDA, (Moreno, Pérez-Conde, & Cámara, 2000). Considering the presence

of this different species in beverages, it is important to be able to determine the concentration of individual species, and not only total concentrations. Beverages are an integral part of the diet. Fluids (drinking water and other beverages) provide over 80 percent of the daily intake of total water, which is necessary for life (Randy, Rhonda, Cecilia Wilkinson Enns, & Goldman, 2011). Beverages are also a source of micronutrients like selenium, which is found at trace levels concentrations (µg/L) (Ulusoy, Yilmaz, & Gürkan, 2013). Nowadays researches point to determine selenium concentration in foods and beverages to estimate actual population intakes (Rayman, 2008).

The detection limits of some atomic spectrometries like inductively coupled plasma optical emission spectrometry (ICP OES) (Tyburska & Jankowski, 2011) and electrothermal atomic absorption spectrometry (ETAAS) (Ghasemi, Najafi, Raofie, & Chassempour, 2010; Tuzen, Saygi, & Soylak, 2007) are not suitable for selenium quantification at µg/L levels. In this sense several solid sorbents have been used for selenium preconcentration and speciation (Pyrzynska, 1995). Huang et al. employed mercapto-silica-Fe₃O₄ nanoparticles for Se speciation in environmental samples (Huang et al., 2012). Chen et al. reached selenium speciation with Mg-FeCO₃ layered double hydroxides loaded cellulose fibre (Chen & An, 2012). Lemos et al. propose the preconcentration based on the sorption of species formed between Se(IV) and ammonium pyrrolidinedithiocarbamate (APDC) in a minicolumn packed with polytetrafluoroethylene (PTFE) and hydride generation-atomic

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absorption spectrometry (HG-AAS) determination (Lemos & Maciel, 2013). Other preconcentration strategies for Se determination by HG-AAS, consist in a collection of Se coprecipitation with $\text{La}(\text{OH})_3$ on ethyl vinyl acetate (EVA), (Gil, Kaplan, Salonia, Gásquez, & Martínez, 2007). Several solid phase extraction (SPE) methods also introduced lanthanum hydroxide for selenium coprecipitation (Nielsen, Sloth, & Hansen, 1996; Tang, Xu, & Wang, 2005; Tao & Hansen, 1994). For the last 7 years, a new material has been employed for SPE: minicolumns packed with poly(vinyl chloride) (PVC) (Su, Lee, & Sun, 2012; Su, Li, & Sun 2008). This sorbent exhibit: (i) high distribution coefficients for the analytes, but not for the possible salt from matrix, (ii) appropriate capacity, and (iii) fast kinetics of sorption and elution (Eboatu, Diete-Spiff, Ezenweke, & Omalu, 2002).

Multivariate techniques have been used for analytical methods optimization (Bezerra, Santelli, Oliveira, Villar, & Escalera, 2008). These techniques allow several variables to be optimized simultaneously. Speed of analysis, practicality, economy, and reduction in the number of experiments that need to be carried out, are some advantages obtained after multivariate optimization (Ferreira, Dos Santos, Quintella, Neto, & Bosque-Sendra, 2004). The statistical significance and relevance of the studied variables are estimated by mathematical models. Furthermore, interactions between variables can also be defined. Factorial design is one of the mathematical models for multivariate optimization and is widely applied in chemistry. However, in order to determine the real functionality established among the analytical response and the significant variables, second order designs eventually are also needed.

In this work, an on-line preconcentration procedure using SPE of inorganic selenium species in water samples, energy drinks, wine and tea by HG-ICP-OES is proposed. The extraction and preconcentration steps were performed using a column of PVC and coprecipitation with lanthanum hydroxide, $\text{La}(\text{OH})_3$. Se speciation was achieved by selective photoreduction with an UV lamp. A two-level fractional factorial design was used to evaluate the experimental variables including buffer flow rate and concentration; sample flow rate; NaBH_4 flow rate and concentration; and acid flow rate and concentration. The experiments for the final system optimization were performed according to a central composite response surface experimental design. To the best of our knowledge, this is the first time that PVC and the optimized preconcentration methodology are proposed for Se inorganic speciation.

2. Experimental

2.1. Reagents and solutions

Unless otherwise stated, the chemicals used were of analytical reagent grade and, therefore, no further purification was required. A 1000 mg/L Se(VI) and Se(IV) standard solution were obtained from Sigma–Aldrich, respectively. A 1% (w/v) sodium borohydride solution (Sigma–Aldrich, St. Louis, USA) was prepared in 0.5% (w/v) sodium hydroxide (Merck) solution and was filtered through Whatman No. 42 filter paper to remove possible undissolved solids. This solution was prepared daily. Lanthanum nitrate hexahydrate solution, 0.5% (m/v), was made by dissolving 0.6662 g of lanthanum nitrate hexahydrate in 100 mL of distilled water.

Ultrapure water with a resistivity of 18.2 M Ω 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 ammonium chloride to appropriate pH by addition of ammonia. Welding argon from Praxair (Buenos Aires, Argentina) was found to be sufficiently pure (at least 99.996%) for Se determination.

2.2. Instrumentation

Measurements were performed with a sequential ICP spectrometer Baird ICP 2070 (Bedford, MA, USA.). The ICP operating conditions are listed in Table 1 (Supplementary Material). The FI system used is shown in Fig. 1 (Supplementary Material). A Mini-pulse 3 peristaltic pump Gilson (Villiers-Le-Bell, France) was used. Sample injection was achieved using a Rheodyne (Cotati, CA, USA) Model 50, four-way rotary valve. The hydride generator unit used was from PS Analytical Ltd. and the flow rate of the reagents was controlled by a Watson Marlow 303X peristaltic pump. The column was prepared as follows: an aliquot (ca. 100 mg) of PVC beads was pre-weighed and packed into 8 cm long, 0.4 cm i.d. PTFE tubing (Alltech Associates, Inc., Deerfield, Illinois, USA). To avoid filling losses when the sample solution passed through the column, a small amount of quartz wool was placed at both ends of column. The column was then connected to a peristaltic pump with PTFE tubing to form the preconcentration system. Tygon-type pump tubing (Ismatec, Cole Parmer, Vernon Hills, IL, USA) was employed to propel the sample, reagents and eluent. The Se 196.026 nm spectral line was used. UV photoreduction was achieved with a 400 W Hg vapour lamp (15W G15T8 UV-C long life high pressure Hg, Philips) that ignited with a suitable starter and chock, surrounded by 10 m PTFE tubing.

2.3. Sample preparation

Tap water samples were obtained directly from San Luis city (Argentina) water system. The tap was opened for 5 min before collecting the sample. River water samples were collected from Trapiche and Carolina rivers, San Luis, Argentina. Tea, wines and energy drinks were purchased from local markets from San Luis city. Tea infusions were prepared in 100 mL distilled water at 100 °C. All samples were filtered through 0.45 μm pore size membrane filters immediately after sampling.

2.4. Preconcentration procedure

Fig. 1 (Supplementary material) shows the manifold representation of the preconcentration system. The loading steps starts with valve **V** in position **a**. First the column is conditioned at the optimized pH value (9.0) with a buffer solution, at pump (**P**₁). Sample (S) (supplemented with the optimized $\text{La}(\text{NO}_3)_3$ concentration) and buffer (B) solution were merged at 8.0 mL/min and 1.5 mL/min, respectively, with peristaltic pump (**P**₁) and then directed to the column. The excess of solution, after loading the column, is directed to waste (**W**). At the same time a 40% (v/v) HCl solution at 7.0 mL/min was passed throughout the manifold directly to the gas/liquid separator and mixed with the NaBH_4 solution at 3.0 mL/min with pump **P**₂ and **P**₃, respectively.

After loading, injection valve **V** was switched to injection position (**b**) and the retained analyte was quantitatively eluted with a 40% (v/v) HCl solution at a flow rate of 7.0 mL/min. Eluted Se is transported to the HG system. The hydride formed was carried by Ar to the ICP-OES system and the analytical response was recorded. Finally, after sample injection, peristaltic pump **P**₁ was stopped. At the same time the injection valve was switched back to the loading position to eliminate the remaining acid solution and ultrapure water was pumped through the tubing lines and column.

When the UV photoreactor is off only Se (IV) is determined. If the photoreactor is on, then Se (VI) is reduced to Se (IV) and both selenium species are preconcentrated, as Se (IV). Se (VI) concentration is calculated by difference.

2.5. Optimization strategy

The optimization process was carried using a two-level fractional factorial design and a central composite design (CCD) involving seven, four and three variables, respectively. All the experiments were carried out in duplicates using a 20 µg/L selenium (IV) solution. The variables influencing Se retention/elution and Se hydride generation are: sample, reagent and acid flow rates; and acid, buffer and reagent concentration. These variables were chosen for optimization. The experimental data was processed by using the MINITAB® 15 computer software (1972–2003, Minitab Inc., USA).

3. Results and discussion

3.1. Argon carrier gas flow rate

The carrier gas affects hydride transport and extraction from the gas-liquid separator in the hydride generation system. The Ar flow rate used to transport selenane from the gas liquid separator to the plasma torch was varied from 0.10 to 1.0 L/min. The most suitable Ar flow rate was 0.60 L/min in this system. Above or below this value Se 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 selenane 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 tubing length 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 was used to transport the hydride from the gas liquid-separator to the plasma torch.

3.3. pH studies

Preliminary experiments showed that pH and La(NO₃)₃ concentration were critical parameters for Se coprecipitation and retention on PVC column. According to this, standards containing 20 µg/L of Se (IV) were evaluated varying pH from 2 to 12. Results can be observed in Fig. 1. Retention efficiency improved with additions of 20 mg/L La(NO₃)₃ in 20 µg/L Se (IV) solutions at pH values ranging from 6 to 8. This fact is in good agreement with Su et al. studies (Su et al., 2012) where Cu, Co, Zn, Cd and Pb retention was higher at pH values from 6–7 employing a PVC column. In order to increase the system automatization and to avoid sample modification, it was decided to include a buffer carrier line into the FI manifold. Different buffers were tested like sodium tetraborate, tris(hydroxymethyl)aminomethane and ammonia. The best results were obtained with ammonia buffer. For the consequence studies, a pH value of 10 was selected.

3.4. Factorial design

There is a limited number of works devoted to elemental preconcentration employing PVC packed in columns (Su et al., 2008, 2012). In those studies the retention efficiency was optimized by changing different variables such as pH and sample flow rate. In this sense, preliminary tests were performed to investigate the factors that could influence Se retention on the PVC column. The sample flow rate (SFR), buffer flow rate (BFR) and buffer concentration (BC) were studied. Selenium hydride generation also requires opti-

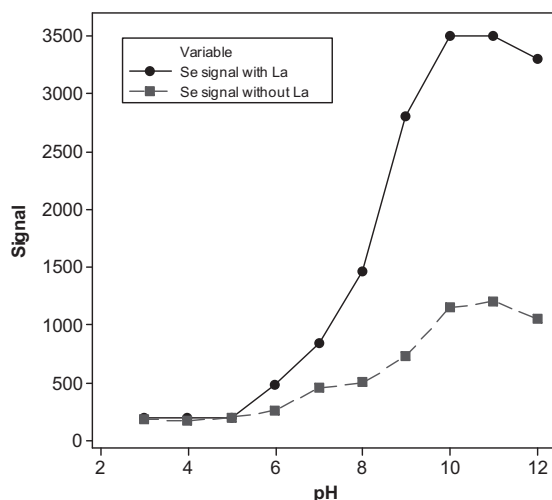


Fig. 1. Influence of pH and La(OH)₃ addition on the retention of Se. Se(IV) concentration: 20 µg/L; sample volume: 10 mL; La(OH)₃ 20 mg/L.

mization of NaBH₄ flow rate (RFR) and concentration (RC); and acid flow rate (AFR) and concentration (AC) (Moscoso-Pérez et al., 2004). The mentioned variables were chosen as factors in a 2⁷⁻³ fractional factorial design (Table 2, Supplementary Material). Minimum, maximum, and central point levels of each factor were chosen according to data from preliminary experiments. Table 3 (Supplementary Material) shows the experimental design and their respective relative analytical signal. Analysis of variance (ANOVA) and *p*-value were used to evaluate the significance of the effects, main effects and their interactions on the preconcentration system as depicted in the Pareto chart shown in Fig. 2. Results of the factorial design demonstrated that the variables SFR, RFR, AFR and AC (A, B, C and E respectively) and their interactions are significantly affecting the system (95% confidence level). On the other hand, AC is affecting the system in a lower proportion compared to SFR, RFR and AFR, close to the significance level. According to this, a second optimization was performed including only SFR, RFR, AFR and AC to evaluate the most important effects on the system. This approach will allow a definitive identification of the factors controlling Se preconcentration system by PVC with HG-ICP OES as detection. Factors and values employed in this design are depicted in Table 4 (Supplementary Material). Table 5 (Supplementary Material) shows the experimental matrix design and the

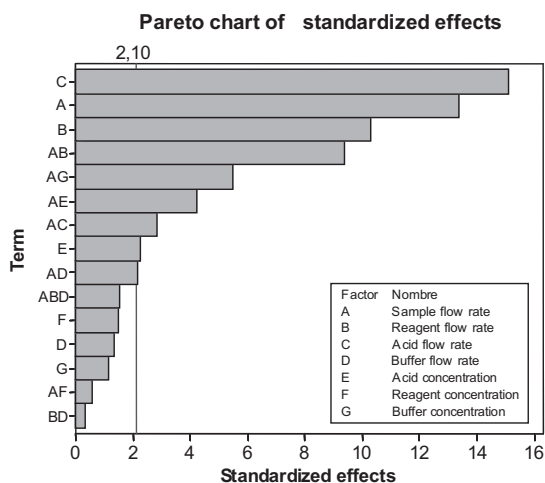


Fig. 2. Pareto chart obtained from the 2⁷⁻³ fractional factorial design used as first optimization approach for Se determination.

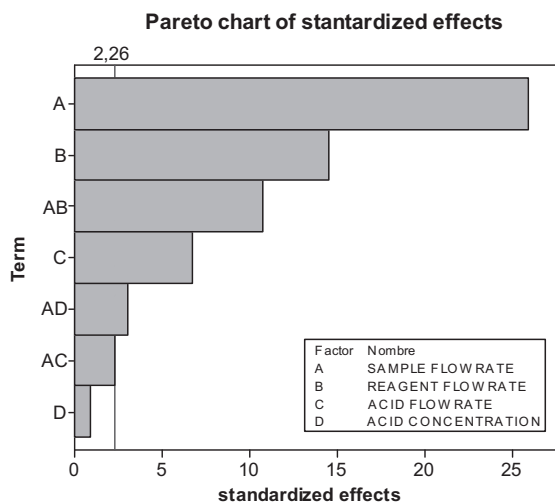


Fig. 3. Pareto chart obtained from the 2^{4-1} fractional factorial design used as second optimization approach for Se determination, involving the significance factors on the system.

respective relative analytical signal. The interpretation of the factorial design by the Pareto chart (shown in Fig. 3) and ANOVA demonstrate that SFR, RFR (NaBH_4 flow rate) and AFR (A, B and C, respectively) were statistically significant at 95% confidence level. However the acid concentration (E) showed poor influence and was fixed at 40% v/v.

3.5. Final optimization using a central composite design

From the first and second factorial design optimization, it was demonstrated that the SFR, RFR and AFR (A, B and C, respectively)

were the variables controlling the system. A central composite design was developed for a final optimization of these variables.

The experiment was cube central with six central points in cube and six axial points. The experiment design and Se relative response can be observed in Table 6 (Supplementary Material). SFR and AFR ranged from 1.63 to 8.36 mL/min, and RFR ranged from 1.31 to 4.38 mL/min. With the information obtained by the presented CCD, surface responses were built and they can be observed in Fig. 4. As a general outcome from these graphics it can be observed that at higher flow rates, Se response increase. For this reason the selected optimal values for these factors were: 8.0 mL/min for SFR; 3.0 mL/min for RFR and 7.0 mL/min for AFR.

3.6. Interferences studies

The effects of potentially interfering species (at the concentration levels at which they may occur in the samples) were tested under optimal Se preconcentration conditions. The tolerance limits of the coexisting ions, defined as the largest amount of ion that produces a recovery of Se(IV) less than 90%, were evaluated. The results showed that As(III), Ge (IV), Sb (III), Sn (IV), Te (IV), Ti (IV), V (V), Bi (III), Co (II), Cu (II), Pb (IV), Zn(II), Cd(II), Ni(II), Cr(III), Mn(II), Al(III), Fe(III), Cu(II) could be tolerated up to at least 2500 $\mu\text{g/L}$. Other common matrix components such as alkaline and alkaline-earth elements were not retained on the PVC column.

3.7. Analytical performance

The proposed methodology reaches a precision of 0.17% expressed as percentage relative standard deviation (RSD%; $n = 6$; repeatability conditions). The detection limit (DL) corresponds to 0.03 $\mu\text{g/L}$ and the quantification limit to 0.09 $\mu\text{g/L}$. The preconcentration system was lineal from the LOQ up to at least 200 $\mu\text{g/L}$ ($r^2 = 0.997$). No significant difference (95% confidence) in

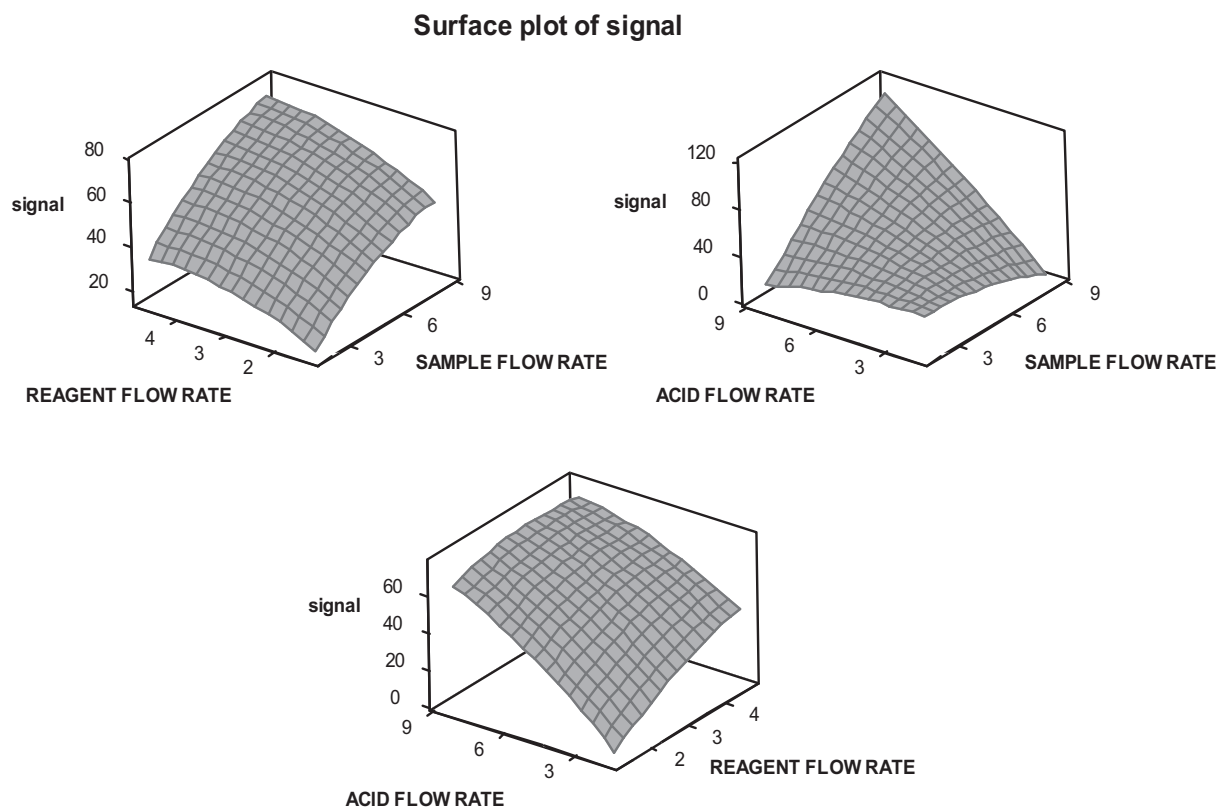


Fig. 4. Response surfaces obtained using central composite design.

background signals were observed between Se (IV) and Se (VI) determination conditions.

The calculated enhancement factor correspond to 14875 (25 for preconcentration system, 595 for hydride generation) for a preconcentration time of 3 min and a sample volume of 21 mL regard selenium determination by ICP-OES without preconcentration. The throughput sample was of 15 samples/h.

The obtained enrichment factor is acceptable regarding the low sample volume employed and compared with those reported by Latorre, García, Martín, and Crecente (2013) in his review of different studies involving SPE procedures for Se speciation (retained as oxyanions) using different types of polymers and silica gel-based sorbents.

3.8. Validation studies

The accuracy of selenium analysis was also monitored and checked using recovery tests to control possible analyte matrix effect (Ulusoy et al., 2013) and results can be observed in Table 1. As it can be observed recoveries were quantitative for the studied samples, ranged 96–103% for Se(VI) analysis and 97.00–104.00 for Se(IV) analysis. The RSDs spiked of samples at three concentration levels were lower than 5.71%.

This method was also verified by determining Se in two certified reference materials, BCR[®] 414 Plankton and IRMM 804 Rice Flour; results are listed in Table 7 (Supplementary Material).

Table 1
Analytical results for the determination of Se(VI) and Se(IV) in different beverages by FI-HG-ICP-OES previous preconcentration with PVC column.

Sample	Se (VI) µg/L				Se (IV) µg/L				Se total
	Found	Added	Sum	Recovery ^c (%)	Found	Added	Sum	Recovery ^c (%)	
Tap water	1.17 ± 0.04	0.00	1.17	–	0.37 ± 0.05	0.00	0.37	–	1.54
		1.00	2.19	102.00		0.50	0.89	104.00	
		1.50	2.63	97.33		1.00	1.36	99.00	
		2.00	3.20	101.50		1.50	1.90	102.00	
Mineral water	0.84 ± 0.03	0.00	0.84	–	0.29 ± 0.01	0.0	0.29	–	1.13
		1.00	1.81	97.00		0.50	0.81	104.00	
		1.50	2.37	102.00		1.00	1.27	98.00	
		2.00	2.83	99.50		1.50	1.80	100.66	
River water (1)	1.5 ± 0.06	0.00	1.50	–	0.49 ± 0.03	0.00	0.49	–	1.99
		1.00	2.52	102.00		0.50	1.01	104.00	
		1.50	2.93	95.33		1.00	1.47	98.00	
		2.00	3.58	104.00		1.50	2.00	100.60	
River water (2)	0.65 ± 0.02	0.00	0.65	–	0.46 ± 0.03	0.00	0.46	–	1.11
		1.00	1.67	102.00		0.50	0.95	98.00	
		1.50	2.12	98.00		1.00	1.47	101.00	
		2.00	2.68	101.5		1.50	1.95	99.33	
Energy drink	1.43 ± 0.07	0.00	1.43	–	0.36 ± 0.02	0.00	0.36	–	1.79
		1.00	2.42	99.00		0.50	0.87	102.00	
		1.50	2.95	101.33		1.00	1.37	101.00	
		2.00	3.40	98.50		1.50	1.84	98.66	
Soda (coca-cola)	0.70 ± 0.03	0.00	0.70	–	0.49 ± 0.03	0.00	0.49	–	1.19
		1.00	1.67	97.00		0.50	1.01	104.00	
		1.50	2.23	102.00		1.00	1.47	98.00	
		2.00	2.65	97.50		1.50	2.01	101.33	
White wine-chablis	0.56 ± 0.04	0.00	0.56	–	1.04 ± 0.09	0.00	1.04	–	1.60
		1.00	1.53	97.00		0.50	1.53	98.00	
		1.50	2.10	102.66		1.00	2.08	104.00	
		2.00	2.58	101.00		1.50	2.53	99.33	
White wine-sauvignon	2.05 ± 0.09	0.00	2.05	–	0.64 ± 0.05	0.00	0.64	–	2.69
		1.00	3.01	96.00		0.50	1.13	98.00	
		1.50	3.60	103.33		1.00	1.65	101.00	
		2.00	4.03	99.00		1.50	2.11	98.00	
Red wine malbec	0.21 ± 0.01	0.00	0.21	–	1.70 ± 0.08	0.00	1.70	–	1.91
Yerba-mate extract (2 g)	1.05 ± 0.06	0.00	1.05	–	0.47 ± 0.05	0.00	0.47	–	1.52
		1.00	2.02	97.00		0.50	0.98	102.00	
		1.50	2.58	96.33		1.00	1.46	99.00	
		2.00	3.03	99.00		1.50	1.98	100.66	
Black tea (2 g)	1.70 ± 0.04	0.00	1.70	–	0.77 ± 0.03	0.0	0.77	–	2.47
		1.00	1.81	97.00		0.50	0.81	104.00	
		1.50	2.37	102.00		1.00	1.27	98.00	
		2.00	2.83	99.50		1.50	1.80	100.66	
Green tea (2 g)	0.94 ± 0.04	0.00	0.94	–	0.79 ± 0.05	0.0	0.79	–	1.73
		1.00	1.95	101.00		0.50	1.30	102.00	
		1.50	2.42	98.66		1.00	1.76	97.00	
		2.00	2.95	100.5		1.50	2.29	100.00	
Red tea (2 g)	2.66 ± 0.03	0.00	2.66	–	0.76 ± 0.05	0.0	0.76	–	3.42
		1.00	3.69	103.00		0.50	1.27	102.00	
		1.50	4.13	98.00		1.00	1.73	97.00	
		2.00	4.65	99.50		1.50	2.25	99.33	

(1) La Carolina river water, (2) Trapiche river water.

^c Recovery (%) = [(found-base)/added] x 100.

3.9. Application to real samples

Selenium is an essential micronutrient for human beings and diet is the major source of this element. Recent studies revealed an estimation of the average Se intake in Argentina from foods, corresponding to 32 and 24 $\mu\text{g}/\text{day}$ for adult men and women, respectively (Sigrist et al., 2012). However these values appear being lower than literature information from other countries, for example: Austria (48 $\mu\text{g}/\text{day}$), Egypt (49 $\mu\text{g}/\text{day}$), UK (50–60 $\mu\text{g}/\text{day}$), Germany (37–47 $\mu\text{g}/\text{day}$), USA (105 $\mu\text{g}/\text{day}$). Considering that 46% of Argentinean diet corresponds to food, and 54% correspond to beverages (Chamorro, 2013), becomes important to determine Se concentrations in beverages, to estimate their contribution of this metalloid to Argentinean diet. In this work determinations were made to speciate inorganic selenium in some beverages of regular consumption in Argentina and results can be observed in Table 1.

3.9.1. Water

Rivers, mineral and tap water samples were analysed. Results ranged from 0.65 to 1.17 $\mu\text{g}/\text{L}$ of Se(VI) and 0.29 to 0.49 of Se(IV). These values are in good agreement with Tyburska and Jankowski (2011) determinations in mineral waters of 2.0 $\mu\text{g}/\text{L}$.

3.9.2. Sodas and energy drinks

Selenium concentrations ranged from 0.70 to 1.43 $\mu\text{g}/\text{L}$ for Se(VI) and 0.36 to 0.49 $\mu\text{g}/\text{L}$ for Se(IV).

3.9.3. Wines

Lower Se concentrations were found in different types of wines (white and red) compared to 28.4 $\mu\text{g}/\text{L}$ and 35.6 $\mu\text{g}/\text{L}$ respectively obtained by Ulusoy et al. (2013). Se(VI) concentrations correspond to 0.56–2.05 $\mu\text{g}/\text{L}$ and Se(IV) concentrations corresponds to 1.04–0.64 $\mu\text{g}/\text{L}$ for white wines. Regard red wines, selenium species concentration found were of 0.21 $\mu\text{g}/\text{L}$ and 1.70 $\mu\text{g}/\text{L}$ for Se (VI) and Se (IV), respectively.

3.9.4. Infusions

Black tea, red tea, green tea and yerba-mate tea infusions were analysed. Yerba mate infusion is the most consumed beverage in Argentina (100 L per person per year) according to Instituto Nacional de Yerba Mate (GEA, 2009). Selenium species concentrations in infusions were of 1.05 $\mu\text{g}/\text{L}$ for Se (VI) and 0.47 for Se (IV) respectively. These concentration values are in good agreement with those reported by Musa Özcan, Ünver, Uçar, and Arslan (2008).

Table 1 shows total inorganic selenium concentrations present in the analysed samples. Considering that Argentineans consume 2.05 L of liquids per day and that infusions, water, sodas and other beverages correspond to 38%, 21%, 18% and 22% of that quote (Chamorro, 2013), these beverages contributes approximately with 3.89 μg of inorganic selenium per day to their diet.

4. Conclusion

A novel flow injection preconcentration and speciation system employing PVC as sorbent for inorganic selenium using HG-ICP-OES has been described. PVC column became a suitable substrate for Se retention when this was coprecipitated with $\text{La}(\text{OH})_3$. Inorganic selenium speciation was successfully achieved introducing a selective photoreduction step previous preconcentration with an UV lamp.

Factorial design was introduced as a mathematical model for multivariate optimization. In a first approach it was revealed that the sample flow rate, reagent flow rate (NaBH_4 flow rate), acid flow

rate and acid concentration were significant parameters affecting the system, however a second optimization defined sampling flow rate, reagent flow rate (NaBH_4 flow rate) and acid flow rate as the most significant. A central composite design defined their optimal values according to the best response of the system reaching higher enrichment factors, improving the detection limit, reaching ng/L levels. The introduction of solid phase extraction by means of the PVC column into the system conducted to an acceptable enrichment factor and an overall remarkable enhancement factor.

The developed system was successfully applied to inorganic selenium speciation in several Argentinean beverages. Selenium determination in local beverages samples contributed to a better understanding of selenium incorporation into Argentinean diet.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.foodchem.2014.07.127>.

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