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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.

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, & Ghassempour, 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-Fe_3O_4 nanoparticles for Se speciation in environmental samples (Huang et al., 2012). Chen et al. reached selenium speciation with Mg-$FeCO_3$ 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 $La(OH)_3$ on ethyl vinyl acetate (EVA), (Gil, Kaplan, Salonia, Gásquez, & Martinez, 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, & Escaleira, 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, $La(OH)_3$. 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 MΩ cm was obtained from an EASY pure RF (Barnstedt, Dubuque, IA, USA). Hydrochloric acid, puriss, p.a. ACS (FLUKA, Switzerland) was used. A buffer solution was prepared from 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 Minipulse 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 ($\mathbf{P_1}$). Sample (S) (supplemented with the optimized $La(NO_3)_3$ concentration) and buffer (B) solution were merged at 8.0 mL/min and 1.5 mL/min, respectively, with peristaltic pump ($\mathbf{P_1}$) 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 $\mathbf{P_2}$ and $\mathbf{P_3}$, 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 $\mathbf{P_1}$ 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.