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# Determination of selenium in selected food samples from Argentina and estimation of their contribution to the Se dietary intake

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#### Abstract

An optimized FI-HGAAS method was applied to determine the total selenium concentrations in selected high consumption food (fish, beef, chicken, milk, rice, wheat flour, egg) and to estimate their contribution to the Argentinean dietary intake, whose information is scarce nowadays. Through several optimization steps a suitable method was achieved showing satisfactory figures of merit for all matrices. Average recovery was 96%, RSD < 5%, LODs ranged 2.0 - 7.0  $\mu$ g kg<sup>-1</sup> and the accuracy was assessed using DOLT-3 NRC certified reference material. Meat and eggs showed the highest values (in  $\mu$ g kg<sup>-1</sup>, beef: 42-153; chicken; 62-205; fish: 94-314; canned tuna: 272-282; eggs: 134-217), minor values were found for wheat flour (22-42), rice: (< 22), pasta (47-64) and milk (< 7-9). An estimated intake of 32  $\mu$ g day<sup>-1</sup> and 24  $\mu$ g day<sup>-1</sup> for adult men and women, respectively, suggested a deficient Se intake, leading to further comprehensive surveys of Se occurrence in Argentina.

Keywords: selenium; food; FI-HGAAS; Argentinean dietary intake.

#### 1. Introduction

Selenium is an essential micronutrient for human beings. Diet is the major source of this element to the organism. Intake depends on its food concentration and the amount of food consumption. Its bioavailability varies according to the biochemical nature, being significantly higher for organic chemical forms (Dumont, Vanhaecke, & Cornelis, 2006). Selenium acts as an antioxidant showing enzymatic redox activity through essential enzymes as glutathione peroxidase. This enzyme in junction with vitamin E catalyzes the reduction of hydrogen peroxide and other hydroperoxides from oxidative degradation by means cell protective processes. Furthermore, selenium has roles in several critical metabolic pathways and within immune and endocrine systems (Williams & Harrison, 2010; Beckett & Arthur, 2005). Several diseases have been associated to Se deficiency, such as cardiopathies, hepatopathies and some cancer types (Navarro-Alarcon & López- Martínez, 2000). Excessive intake can result in the appearance of toxic syndromes, such as dermatitis, gastrointestinal disturbances, hair, nail, teeth and skin changes. Selenium Recommended Dietary Allowance (RDA) for adults is set at 55 µg day<sup>-1</sup> while the tolerable upper intake level for adult is established at 400 µg day<sup>-1</sup> (Food and Nutrition Board, 2000). The adverse consequences to health of both deficient and excessive intake of selenium have been well demonstrated. Thresholds between these two undesirable effects are very close, giving complexity to the definition of the optimal intake, that need to be completely understood (Rayman, 2008). Consequently it is nowadays of high concern to increase the knowledge about abundance and deficiency of Se in foods and to estimate actual intakes of population. Amount and availability of Se in soils reflect generally Se status in food produced in a region. Se concentrations in soils are widely variable around the world (Kabata-Pendias, 1998; Cuvardic, 2003). Low levels of Se in soils ( $< 0.05 \text{ mg kg}^{-1}$ ) were reported in several

regions such as parts of China, Finland and New Zealand. High Se concentrations in soils (> 5 mg kg<sup>-1</sup>) are found in some regions of western USA, Canada, France and Germany. So, similar food may have very different concentrations of Se depending on agricultural region of growing or production. Consequently, nutrient regional databases may reflect such variations and be more appropriate than those reporting average nutritional data (Smrkoli, Pograjc, Hlastan-Ribič, & Stibilj, 2005). However, currently the information about Se content in soil and food from most parts of Africa, Southern Asia and South America, particularly Argentina, is scarce or absent (Navarro-Alarcon & Cabrera-Vique, 2008; Sammán & Portela, 2010). Use of fertilizers enriched with selenium (Dumont, Vanhaecke, & Cornelis, 2006; Aro, Alfthan, & Varo, 1995), addition of Se to the farm animal diet (Pappa, Pappas, & Surai, 2006; Tinggi, 2003; Muñiz-Naveiro et al, 2006; Lyons, Papazyan, & Surai, 2007) and the direct consumption of dietary supplements (Dumont, Vanhaecke, & Cornelis, 2006) have been strategies employed in order to increase the amount of Se in diet of population living in regions with deficient selenium soils. However, the population should be warned about the ingestion of Se supplements for prevention of diseases, because its benefits are still uncertain and their indiscriminate use could generate a risk increase of Se toxicity (Stoedter, Schweizer, & Schomburg, 2010).

Selenium is able to replace sulphur in the amino acids due to their physicochemical similarity, so protein-rich food such as eggs, meat, chicken, fish and cereals contain high levels of Se, especially as organic compounds (Klapec et al., 2004; Ventura, Freitas, Pacheco, Van Meerten, & Wolterbeek, 2007; Sager, 2006). These food groups contribute the major part of dietary Se. The highest levels of Se in food have been reported in fish with a wide variation between different species. However, it is usually a poor source of available Se, due to the high levels of Hg and other heavy metals, which bind to Se forming insoluble inorganic complexes. Through this way selenium reduces the toxicity of several trace metals

(Pappa, Pappas, & Surai, 2006). Vegetables rich in sulphur compounds such as members of the *Cruciferae* family (broccoli, Brussel sprouts, cauliflowers and cabbage) and the *Liliaceae* family (garlic, chives and onion) could become in a good dietary source of Se depending the magnitude of its consumption. In general, fruits and vegetables content low Se concentrations (10-20 µg kg<sup>-1</sup>) possibly due to the low protein proportion (Klapec, 2004; Combs, 2001; Ventura, Stibilj, Freitas, & Pacheco, 2009) so they make only a small contribution to the dietary intake of selenium. The highest concentrations were found in Brazil nuts (3800 ng g<sup>-1</sup>) (Manjusha, Dash, & Karunasagar, 2007). Se content in cow's milk becomes a considerable contribution to the total dietary intake, mainly for infants (Pappa, Pappas, & Surai, 2006; Klapec et al., 2004; Zand et al., 2011). An important collection of data relating Se content in foods in the world can be found in Navarro-Alarcon & Cabrera-Vique, 2008.

Several analytical methods with low limits of detection have been applied to determine Se ultratrace levels in food. Hydride generation atomic absorption spectrometry (HGAAS) (Murphy & Cashman, 2001; Klapec et al., 2004, Diaz-Alarcón, Navarro-Alarcón, Lopez-G de la Serrana, & Lopez-Martínez, 1996; Smrkolj, Pograjc, Hlastan-Ribič, & Stibilj, 2005; Hussein & Bruggeman, 1999), hydride generation atomic fluorescence spectrometry (HGAFS) (Pappa, Pappas, & Surai, 2006; Smrkolj, Pograjc, Hlastan-Ribič, & Stibilj, 2005, Ventura, Stibilj, Freitas, & Pacheco, 2009), electrothermal atomic absorption spectrometry (ETAAS) (Hussein & Bruggeman, 1999; Manjusha, Dash, & Karunasagar, 2007), inductively coupled plasma-mass spectrometry (IPC-MS) (Nardi et al. 2009; Al-Ahmari, 2009) have been the most frequently reported. Determination of selenium trace in complex matrices, same to other elements or heavy metals, usually requires extensive pre-treatments before instrumental quantification. Residues of acids and organic matter frequently remaining after wet digestion of the samples, seem to present no interferences in ETAAS

and ICP-MS determinations, due to the high atomization temperature. However, when HGAAS or HGAFS are used, those residues could interfere with the hydride generation reaction, which is strongly dependent on the selenium redox status, despite that both techniques present the advantage of being free from spectral interferences. In this sense, a careful study on the matrix effects becomes critical in order to evaluate the analytical performance. However, usually this is not observed in the literature referred to the total Se determination in food samples using wet sample digestion and HGAAS methodologies. Dry ashing digestion provides lower LOD due to the preconcentration of samples and cleaner blanks, although Se losses during the ashing procedure may occur if the use of ashing aids is not successfully optimized. Wet digestion procedures present less probability of analyte losses, although a careful optimization is necessary in order to avoid raising LODs due to high dilution factors (Matos-Reyes, Cervera, Campos, R., & de la Guardia, 2010). The inclusion of flow injection (FI) facilitates the implementation of the hydride generation technique, giving rise to automated systems with important advantages regarding sensitivity, selectivity, reproducibility and samples throughput (Burguera & Burguera, 1997).

The aim of this work was to develop and optimize a suitable FI-HGAAS method to determine selenium concentrations in a selected group of food frequently consumed in Argentina, with emphasis on the influence of matrix effect in the quantification process. The food analyzed may contribute in a major proportion to the population dietary Se intake which was estimated from the obtained data. Resulting information is not available yet in this country and contributes to the necessary collection of global information about selenium status in food and environment.

#### 2. Experimental

#### 2.1. Instrumentation

A Perkin-Elmer Model 3110 flame atomic absorption spectrometer (Connecticut, USA) was used as detector. It was equipped with a selenium hollow cathode lamp Photron (Victoria, Australia) set at 196.0 nm wavelength, 12 mA lamp current and 0.7 nm slit width. A Perkin-Elmer FIAS 100 flow injection hydride generation system (Connecticut, USA) with a heated quartz tube atomizer (10 mm i.d. x 160 mm length) was used for hydride generation and coupled to the AAS. The rotation speed of the multichannel peristaltic pump and the process timing were programmed and automatically controlled by software Perkin-Elmer AA WinLab version 3.2. PTFE tubing was used to transfer sample and solutions. Peak height was used for the measurements of the analytical signal. Statistical software Statgraphics Centurion XV (StatPoint Inc., USA) was utilized for chemometric data evaluation and graphic outputs.

#### 2.2. Reagents, solutions and samples

All reagents used were of high purity or at least of analytical reagent grade. Deionizeddistilled water (resistivity 18 M $\Omega$  cm) was used to prepare all solutions in the work. Working selenium solutions for external calibration curve were prepared from a 1000 mg L<sup>-1</sup> Se(IV) standard in 0.5 mol L<sup>-1</sup> nitric acid (Merck, Germany) using 2.4 mol L<sup>-1</sup> hydrochloric acid as diluent. A 5 mg L<sup>-1</sup> Se(VI) working stock solution prepared from a 1000 mg L<sup>-1</sup> Se(VI) standard in 0.5 mol L<sup>-1</sup> nitric acid (Merck, Germany) was used for recovery assays.

Hydrochloric acid solutions at range 1-15% (v/v) were prepared from concentrated HCl (S.G. 1.18 g mL<sup>-1</sup>; J. T. Baker, USA) for use as carrier solutions. Sodium tetrahydroborate solutions (NaBH<sub>4</sub>) as reductant at range 0.008-0.5% (m/v) were prepared

daily by dissolving NaBH<sub>4</sub> (Merck, Germany) in 0.025% (m/v) sodium hydroxide solution (Merck, Germany) to minimize its decomposition. Nitrogen 99.998 % purity was obtained from Linde, Argentina.

Food samples (cow's milk, beef, chicken breast, fish muscle, canned fish, eggs, rice, wheat flours and pasta) were purchased from markets in Santa Fe, province located in the central region of Argentina. The samples selected were representative of the Argentina diet since all correspond to trademarks whose market products from a large region that includes the food-producing provinces analyzed in the work. Beef, chicken breast, fish, eggs, and pasta were milled and homogenized in a food processor and then sub-sampled for analysis. Rice and wheat flour were sampled by mixing and quartering.

#### 2.3. Wet digestion procedures of food samples

The sample digestion was carried out in beakers of 50 mL capacity which were soaked previously overnight in 50% (v/v) nitric acid, rinsed with distilled-deionized water and left to air-dry. The digestion procedure used was based on the method proposed by Foster & Sumar (1996). A volume of 5 ml of concentrated nitric acid (S.G. 1.42 g mL<sup>-1</sup>; J. T. Baker, USA) were added to 5.0 g of milk sample and to approximately 1.0 g of other processed foods accurately weighed. The samples were left overnight and then heated in a block digestion system (laboratory made) at 90 °C for approximately 2 hours until the evolution of brown fumes of NO<sub>2</sub> had ceased; then, 5 ml of a mixture solution of nitric acid and perchloric acid (S.G. 1.70 g mL<sup>-1</sup>; J. T. Baker, USA) (4:1) were added. The digests were heated until the appearance of white fumes of perchloric acid and the volume was reduced up to approximately 1 mL taking care to avoid complete dryness.

#### 2.4. Pre-reduction treatment of Se(VI)

When the digest was cooled, a volume of 15 ml of 6 mol L<sup>-1</sup> HCl solution was added. The mixture was heated in a digestion block at 90 °C for 30 min to reduce Se(VI) to Se(IV); then, the cooled sample digest was transferred into a 25 mL volumetric flask and made up with distilled-deionized water.

#### 2.5. Total Se determination by FI-HGAAS

The sample solution flowed into a 500  $\mu$ L sample loop. Then, the sample was released from the loop using a directional valve by HCl carrier solution and transported to the chemifold where it was mixed with the NaBH<sub>4</sub> reductant in the reaction coil to produce selenium hydride (SeH<sub>2</sub>). The reaction coil is formed by two different sections between which is located the nitrogen entrance. The liquid/vapor mixture flowed to a gas-liquid membrane separator and the gaseous hydride was transported by the nitrogen carrier stream to the quartz atomizer heated with an air-acetilene flame. The remaining liquid was removed from the separator by the peristaltic pump. An external calibration curve at Se(IV) concentration levels ranged from 2.5 to 40.0  $\mu$ g L<sup>-1</sup> was used for quantification of Se content in the samples. Background analytical levels tested by running blank acid digestions were insignificant.

#### 3. Results and discussion

3.1. Optimization of the hydride generation conditions for Se determination by FI-HGAAS

Different experiments were carried out to study the effect of FI-HG system variables on the signal. The selenium absorbance increased with the acid concentration up to 1.2 mol  $L^{-1}$  HCl. A 0.1% (m/v) NaBH<sub>4</sub> concentration was chosen as the optimum. The signal showed a strong dependence with the reductant agent concentration. A nitrogen flow rate of 125 mL min<sup>-1</sup> was selected. At higher flow rates, a decrease of the sensitivity was observed probably due to the major dilution of hydride in the gas stream and the smaller time of residence of the analyte in the quartz tube. Flow rates of 10 mL min<sup>-1</sup> and 5 mL min<sup>-1</sup> were selected for carrier and reductant solutions, respectively. The effect of the different sample sizes was also studied. An increase in the sample loop volume from 500  $\mu$ L to 1000  $\mu$ L produced an increase in the aqueous standard solution signal of 25% approximately. However, when a 1000  $\mu$ L sample loop was used for measurements of sample solutions a double peak signal was obtained. Thus, a 500  $\mu$ L sample loop was selected. The instrumental and operating conditions used for determination of selenium in the food samples are shown in Table 1.

#### 3.2. Matrix effect and recovery studies

A study on the combined effect of matrix enhancement/suppression interferences and analyte recovery related to the methodology used was tested by analysis of fortified sample matrix prior to digestion, compared with instrumental responses obtained from aqueous standard solutions. The analytical slopes of standard addition lines on wheat flour, rice, milk, beef and egg samples were compared to the Se(IV) aqueous standard calibration line. The results obtained showed that the standard addition line slopes (wheat flour, 0.01770 L  $\mu$ g<sup>-1</sup>; rice, 0.01713 L  $\mu$ g<sup>-1</sup>; milk, 0.01699 L  $\mu$ g<sup>-1</sup>; beef, 0.01694 L  $\mu$ g<sup>-1</sup>; egg, 0.01580 L  $\mu$ g<sup>-1</sup>) were statistically comparable with the aqueous standard line (0.01733 L  $\mu$ g<sup>-1</sup>). Beef was selected as a representative matrix of meat. While standard addition was not made for pasta,

their major ingredients, namely wheat flour and eggs, were tested. From results found it can be seen that no significant matrix effects were observed. The recovery obtained for each food matrices at a fortification level of 500 μg kg<sup>-1</sup> using an aqueous standard calibration curve are shown in Figure 1. The average selenium recovery was 96%. The precision expressed as RSD% (n=3) was 4% for wheat flour, rice and beef, 3% for chicken and eggs, 2% for pasta, cow's whole milk and fish. Selenium quantification in the food samples using a Se(IV) aqueous standard calibration line allowed a significant simplification of the methodology.

#### 3.3. Ruggedness test

As mentioned above, the residues of organic matter and oxidizing acids from the digestion procedure could interfere seriously with the hydride generation reaction. A two-level Plackett-Burman design consistent of twelve experiment and eleven factors was used to evaluate the digestion procedure ruggedness by examining significant effects. The factors selected were tested at nominal level corresponding to that detailed in *2.3.* and at extreme level, which exceptionally might be attained in the practice. Usually, the latter is defined in a slightly exaggerated way to make sure that one measures a representative effect. The standard error on  $E_x$  (effect on the factor X), (SE)<sub>e</sub>, estimated from the dummy factor effects represents the experimental error in the design. A dummy factor is an imaginary variable for which the variation between both levels does not cause a response change. Enough dummies have to be considered and minimal three has been suggested previously (Vander Heyden, 1995). Statistical significance of the effects was determined using a *t*-test. A factor was considered as significant if the  $E_x$  value is higher than a critical effect value,  $E_{critical}$ :  $E_x \ge E_{critical} = t_{critical} \cdot (SE)_e$  where  $t_{critical}$  is the tabulated two-sided critical *t*-value at  $\alpha$ 

confidence level and  $n_{dummy}$  degrees of freedom. The factors and levels examined using rice samples, effects and critical effect are detailed in Table 2. Selected variables did not show statistically significant effects as it was expected, owing to the previous optimization assays carried out during method development stages.

#### 3.4. Analytical figures of merit

Limits of detection (LOD) and quantification (LOQ) calculated as three and ten times standard deviation of the absorbance signal of 10 reagent blanks divided by the calibration slope were 2 and 7  $\mu$ g kg<sup>-1</sup> of selenium for milk and 7 and 22  $\mu$ g kg<sup>-1</sup> of selenium for other matrices, respectively. Average recovery at fortification level of 500  $\mu$ g kg<sup>-1</sup> of selenium was 96%. The precision was less 5% (*n* = 3) expressed as RSD%. The accuracy of the method was evaluated by analysis of a certified sample DOLT-3 NRC (dogfish liver certified reference material for trace metals). Comparison between the found and certified concentration values (Maroto, Riu, Boqué, & Rius, 1999), was statistically non-significant (*t* test, 95% significance level) for a certified value with an expanded uncertainty of 7.06 ± 0.48  $\mu$ g g<sup>-1</sup> and a found value with an uncertainty from CRM measurement intermediate precision of 7.34 ± 0.32  $\mu$ g g<sup>-1</sup>.

3.5. Analysis of food samples by FI-HGAAS

The total contents of Se in the food samples analyzed are shown in Table 3. Mean and range data are presented. The results are expressed in micrograms of Se per kg (wet weight) for all foods. The concentrations found in the present work are compared with those reported previously in the literature. Unfortunately, data on the Se content in foods

11

consumed in Argentina have not been reported at this time, so it is not possible to carry out a comparison of the results obtained in this study.

The analyzed retail wheat flours showed a low variation in the Se concentration in the range from 22 to 42  $\mu$ g kg<sup>-1</sup>, despite that the samples were collected from several trademarks without specification of agricultural land of origin. Gluten-free flours which have lower Se due to its lower protein content (Murphy, & Cashman, 2001) were not analyzed here. Rice showed to be a poor source of dietary Se. The concentration range of Se in pasta from 47 to 64  $\mu$ g kg<sup>-1</sup> was comparable to those reported in other works.

Cow's whole milk showed to be a relatively poor source of Se (infant population excepted) with a mean concentration of 7  $\mu$ g kg<sup>-1</sup>, slightly lower than those found in other countries. Eggs had an average content of 178  $\mu$ g kg<sup>-1</sup>, which could explain the higher Se content in pasta in comparison with wheat flours.

Meats selenium concentrations ranged from 42 to 314  $\mu$ g kg<sup>-1</sup>. As can be seen in Table 3, the content of Se en beef, which is a food highly consumed in Argentina, was comparable to those found in several countries but much lower than US. Studies on soil Se levels of grazing areas and surveys of animal feeding practices would be key tools in order to identify the causes of this difference. The mean Se content in fish (233  $\mu$ g kg<sup>-1</sup>) was significantly higher than those found in latter two meats. However, as mentioned above, fish is not usually a good source of available Se, due to the high levels of heavy metals binding Se to insoluble inorganic complexes.

#### 3.6. Estimation of the food contribution to the selenium daily intake

Given the lack of information on the estimated Se daily intake from previous studies in Argentina, was of great interest to reach an approximation based on data obtained in this

study. Calculation of adult Se daily intake was achieved by adding the weighted contributions of different foods, by multiplying the average of the selenium concentration determined in each group by its mean consumption per person day<sup>-1</sup> (Hussein, & Bruggeman, 1999). Values of dietary consumption in Argentina were taken from available databases. Results led to an estimation of the average intake of Se in Argentina of 32 ug day <sup>1</sup> and 24  $\mu$ g day<sup>-1</sup> for adult men and women, respectively (from database reported by Pacin, Martínez, Pita Martín de Portela, & Neira, 1999). An estimated value of 23 µg day<sup>-1</sup> for women between 10-49 years old was also obtained regardless milk, chicken and fish consumption (these foods were not included in the survey) from database reported by Encuesta Nacional de Nutrición y Salud of Ministerio de Salud de Argentina in 2007. These values appear being lower than literature information from other countries, for example: Austria (48 µg day<sup>-1</sup>), Egypt (49 µg day<sup>-1</sup>), UK (50-60 µg day<sup>-1</sup>), Germany (37-47 µg day<sup>-1</sup>), USA (105  $\mu$ g day<sup>-1</sup>). The lowest value has been reported in China (7  $\mu$ g d<sup>-1</sup>) (Hussein, & Bruggeman, 1999). Beef meat explains the major contribution of selenium to Argentinean dietary intake. The distribution of percent contribution of each analyzed food is illustrated in Figure 2.

#### Conclusions

In the present work, a suitable FI-HGAAS method was optimized and applied to the determination of selenium in selected food from Argentinean diet (different meat, milk and cereal based samples) using a wet digestion pre-treatment. The developed methodology provides a very good performance for the various matrices studied using an aqueous standard calibration line for quantification, with low detection levels, good precision and accuracy, recoveries averaging 96%. Levels found are informed as a first approach reported

for the region under study. Animal food like meat (fish, chicken, beef) and eggs showed highest concentrations and average values were comparable with those reported in other countries, despite that maximum values in our study were frequently lower than maximum concentrations reported in literature, suggesting a moderate status regarding occurrence of Se in Argentinean foods. An approximate estimation of the daily intake of Se through our results was  $32 \ \mu g \ day^{-1}$  and  $24 \ \mu g \ day^{-1}$  for adult men and women, respectively, with main contribution from meat (beef, chicken, fish). These values are relatively low in comparison with literature data from other countries and RDA (55  $\mu g \ day^{-1}$ ), suggesting a deficient Se intake in Argentina. Further more comprehensive survey to establish the selenium status in this country is strongly recommended.

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#### Table 1

Instrumental and operating conditions used for determination of selenium in food samples by FI-HGAAS. Parameter

	Spectrometer	
	Resonance wavelength (nm)	196.0
	HCL current (mA)	12
	Pandnass (nm)	0.7
	Danupass (IIII) Dead time (a)	0.7
	Near time (S)	10 Dealt height
	Measurement mode	Peak neight
	YY 1 - 1 .	
	Hydride generation	
	Reagent concentration	
	HCl carrier solution (mol 1 <sup>-</sup> )	1.2
	NaBH <sub>4</sub> reducting solution (% $m/v$ )	0.1
	Reagent flow rate	
	HCl carrier solution/Sample (ml min <sup>-1</sup> )	10.0
	NaBH <sub>4</sub> reducting solution (ml min <sup>-1</sup> )	5.0
	Nitrogen carrier gas (ml min <sup>-1</sup> )	100
	Sample loop volume (µl)	500
	Reaction coil length I (mm)	115
	Reaction coil length II (mm)	310
	Prefill time (s)	15
	Fill time (s)	10
	Injection time (s)	15
	•	
v		

#### Table 2

	Low Level (nominal level)	High Level	Effect
HNO <sub>3</sub> volume (mL) (A) HNO <sub>3</sub> -H <sub>3</sub> ClO <sub>4</sub> mix volume (mL) (B) Digestion temperature (°C) (C) Digestion time with HNO <sub>3</sub> (min) (D) HCl concentration (mol L <sup>-1</sup> ) (E) Pre-reduction temperature (°C) (F) Pre-reduction time (min) (G) d1 d2 d3 d4	5.0 5.0 90 120 6.0 90 30	10.0 8.0 110 150 8.0 110 50	0.0027 0.0083 -0.0263 -0.0040 0.0107 0.0173 0.0037 -0.0013 0.0007 -0.0087 -0.0180
Standard error, (SE) <sub>e</sub> E critical calculated from $t_{(5,95)}$	0.01002		0.0278
	2 m		

Factors and levels examined in the ruggedness test and effects calculated.

#### Table 3

Se concentrations (wet weight) in food samples from Santa Fe, Argentina by FI-HGAAS.

Food sample	Se concentration ( $\mu g k g^{-1}$ )		Se concentration reported	Reference
	Mean (n=5)	Range	by other authors (μg kg <sup>-</sup> )	
Cereals and derivatives				
Wheat flour	28	22-42	50 ± 3 13-99 193 (mean) 627-870	Spain <sup>a</sup> Ireland <sup>b</sup> Egypt <sup>c</sup> USA <sup>b</sup>
Rice	< LOQ (22)		$67 \pm 2$ $19.1 \pm 1.4$ $20.1 \pm 45.3$ 14.5 - 34.6	Spain <sup>a</sup> Greece <sup>d</sup> Italy <sup>e</sup> China (Suzhou) <sup>f</sup>
Pasta	55	47-64	$     \begin{array}{c}       10-100 \\       49-78 \\       5.8 \pm 0.2     \end{array} $	Spain <sup>g</sup> Ireland <sup>b</sup> Greece <sup>d</sup>
Milk and dairy product	ts			
Cow's whole milk	7	5-9	13.1-21.9 14 -22 28.7 12.5	Greece <sup>d</sup> Ireland <sup>b</sup> Croatia <sup>h</sup> Slovenian <sup>e</sup>
Eggs	178	134-217	172.8 90-260 56-81 (egg white) 222-282 (egg yolk) 81.7-242.0	Greece <sup>d</sup> Australian <sup>i</sup> Ireland <sup>b</sup> China (Suzhou) <sup>f</sup>
Meat				
Beef	86	42-153	48.8-94.1 80-200 33-155 61-105 190-1000 66.8-116.1	Greece <sup>d</sup> Australian <sup>i</sup> Slovenian <sup>e</sup> Ireland <sup>b</sup> USA <sup>b</sup> China (Suzhou) <sup>f</sup>
Chicken	120	62-205	97-154 86-147 62.1-150.4	Slovenian <sup>e</sup> Ireland <sup>b</sup> China (Suzhou) <sup>f</sup>
Fish	243	94-314	62.7-506.7 120.0-632.0 153-686 233-299 20-761 88.4-214.2	Greece <sup>d</sup> Australian <sup>j</sup> Slovenian <sup>e</sup> Ireland <sup>b</sup> France <sup>k</sup> China (Suzhou) <sup>f</sup>
Canned fish (tuna)	277	272-282	637-789 (in brine) 810 (in oil) 170(mean); 448 (max)	Ireland <sup>b</sup> Egypt <sup>c</sup> France <sup>k</sup>

<sup>a</sup> Matos-Reyes, Cervera, Campos, & de la Guardia, 2010; <sup>b</sup> Murphy, & Cashman, 2001; <sup>c</sup> Hussein, & Bruggeman, 1999; <sup>d</sup> Papa, Papas, & Surai, 2006; <sup>e</sup> Smrkolj, Pograjc, Hlastan-Ribič, & Stibilj, 2005; <sup>f</sup> Gao et al., 2011; <sup>g</sup> Díaz-Alarcón, Navarro-Alarcón, López-G de la Serrana, & López-Martínez, 1996; <sup>h</sup> Klapec et al., 2004; <sup>i</sup> Tinggi, 1999; <sup>j</sup> McNaughton, & Marks, 2002; <sup>k</sup> Guerin et al., 2011.

Figure(s)

# **ACCEPTED MANUSCRIPT**





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Fig. 2. Percent contribution of Se for each food to daily intake.

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#### Highlights

- We optimize a methodology for determining total selenium in food matrices.
- We study selenium content in selected high consumption food from Argentinean diet.
- We estimate their contribution to the Se dietary intake.
- This information is currently scarce or absent in Argentina.
- More survey is strongly recommended from results suggesting a deficient Se intake.