



Depósito de Investigación de la Universidad de Sevilla

<https://idus.us.es/>

This is an Accepted Manuscript of an article published by Taylor & Francis in

INTERNATIONAL JOURNAL OF ENVIRONMENTAL ANALYTICAL  
CHEMISTRY, Vol. 91, Issue 5 on 2011,

available at: <https://doi.org/10.1080/03067310903045489>

# Optimisation and assessment of an innovative high sensitivity 90-degree reflecting ICP-MS ion optics system for the validation of simultaneous determination of Arsenic and Selenium in water matrices

EUSEBIO ÁLVAREZ VÁZQUEZ, RAMÓN BOUZA DEAÑO, MIGUEL TERNERO RODRÍGUEZ, ANTONIO J FERNÁNDEZ ESPINOSA \*

Department of Analytical Chemistry, Faculty of Chemistry, University of Seville.  
C. Profesor García González 1, Campus of Reina Mercedes, E-41012 Seville, Spain

\*Corresponding author. Tel.: +34 954554368; fax: +34 954557168  
*E-mail:* [anjose@us.es](mailto:anjose@us.es)

A routine ICP-MS method for the determination of As and Se in fresh and sewage water has been developed. After a first phase of optimization, where the torch alignment, flow of gases and ion optic adjustments were calibrated, the method was validated successfully. The parameters limits of detection and quantitation, linearity, working range, sensitivity and the interferences, precision and accuracy were studied with three procedures for the method: measuring two SRMs, spiking four different matrices at three levels of concentration and doing a proficiency test. The limits of detection obtained were 0.2 and 0.8 µg/L for As and Se respectively. The percentages of linearity obtained were 99.2 for As and 99.8% for Se. All recovery values were according to the AOAC intervals, from 95.3 % for As in the wastewater matrix to 106.4 % for Se in the seawater matrix. The accuracy was also studied determined via a proficiency testing resulting in acceptable Z-scores of 0.65 and 0.4 respectively for As and Se. The complete method allowed analysis of water samples according to the European Directive 2000/60 EC and the different guides for method validation.

*Keywords:* ICP-MS; Arsenic; Selenium; optimisation; validation; fresh water; wastewater

## 1. Introduction

There has been great interest over the last years in the determination of As and Se levels in environmental, foods and biological samples [1,2]. As and Se are two essential elements that must be present in the human diet; however their presence in high concentrations is detrimental to health. There is a great similarity between these elements as both maintain a natural balance between their different chemical forms in the earth's crust, air and water phases. Human activities are altering these cycles in a manner that the elements finally accumulate in the surface and groundwaters [3,4]. This fact implies a risk of direct contact with the population that could cause damage and adverse health symptoms. Therefore, appropriate analytical methods are essential to quantify the

presence of these pollutants in water in order to avoid hazardous contamination of potable water systems, such as that occurred in Bangladesh [5,6], East Bengala [7] or Nepal [8].

Regarding the toxicological aspect, the effects of acute poisoning caused by a large intake of As would be different from those of small doses spread over a long period of time. A punctual high dosage produces vomiting or diarrhoea while small amounts continued over time would cause diseases of the circulatory system, hyperkeratosis or cancer of the skin, bladder or kidney [9]. High amounts of Se in a short space of time can cause dizziness, fatigue and irritation of mucous membranes. When exposure is extremely high, fluid retention can occur in the lungs, while bronchitis, pneumonia, asthma, nausea, chills, fever, sore throat, shortness of breath, conjunctivitis, vomiting, abdominal pain, diarrhoea and an enlarged liver are all symptoms [10].

Sensitive to this problem, governments of different countries have echoed the recommendations of the Environmental Protection Agency of the US (EPA) [11] and the World Health Organization (WHO) [12], which should ensure that the presence of these two elements in potable water to avoid harmful ingestion is below 10 µg/L. In Europe, the Directive 2000/60 EC [13] establishes quality criteria for these elements in water samples. The range of possible techniques for the determination of As and Se in waters is wide. It includes Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) [14,15], Graphite Furnace Atomic Absorption Spectroscopy (GF-AAS) [16,17], Hydride Generation Atomic Absorption Spectroscopy (HG-AAS) [18,19], UV-Vis Molecular Absorption Spectrophotometry [20,21], Ion Chromatography (IC) [22], Hydride Generation with cold trap of heptanes, Gas chromatography with multiple ion detector [23,24], Fluorimetry [25], Neutron Activation Analysis (NAA) [26,27], Anodic and Cathodic Stripping Voltammetry (ASV/CSV) [28] and Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) [29-31]. However, there exists an important necessity for analytical techniques to determine As and Se levels simultaneously and with high sensitivity.

Inductively Coupled Plasma Mass Spectroscopy is a relatively quick and versatile technique with very low limits of detection. The most significant disadvantage is the high cost of acquisition and maintenance of the equipment as well as the high level of training required in order to handle it. The 90-degree reflecting ICP-MS ion optics is a new optic system for routine sample analysis that delivers exceptional sensitivity.

The aim of this work is to develop a rapid routine ICP-MS method for the determination of As and Se in order to monitor the levels of these contaminants in the drinking water of the population. Also, the final method will be extended to the analysis in samples of groundwater, estuarine, sea water and sewage water.

## **2. Experimental**

## ***2.1 Reagents and standards***

High purity Argon gas of 99.999% (Praxair, Madrid, Spain) was used in this method to supply the plasma. Distilled water used in this method was provided from a combined Milli-Q Elix/Milli-Q Gradient system (Millipore Corporation, Bedford, MA, USA). Nitric acid 69% Hiperpur grade (Sharlab, Barcelona, Spain) utilised in this method was free from As and Se residues. Flush water was prepared by diluting Brijj 35 30% w/w aqueous solution (Sharlab, Barcelona, Spain) to 2%.

Tuning, internal standard solution and As and Se standards used in this method were prepared from stock standard solutions (Inorganic Ventures, Lakewood, NJ, USA).

## ***2.2 Apparatus***

Analyses were performed on an ICP-quadrupole-MS (ICP-QMS) Varian 810-MS equipped with a 90-degree reflecting ion optics system and a SPS-3 auto-sampler (Varian, Mulgrave, Victoria, Australia). The instrument was cooled by using a Kühlmobil 142 VD cooling system (Van der Heijden, Dörentrup, Germany). Data was acquired and processed using the ICP-MS Expert Software version 1.1 b49 from Varian.

The optimum performance of the experimental conditions for the ICP-MS was obtained from the parameters listed in Table 1.

The sample introduction system consists of a Micromist glass low-flow nebuliser, a peltier-cooled (4 °C) double pass glass spray chamber and a quartz torch. The spray chamber was cooled to reduce the vapour loading on the plasma, increasing the available energy for atomisation and ionisation of the elements of interest and to reduce the formation of solvent based interferences. Sample transport from the auto-sampler to the nebulizer was performed using a peristaltic pump.

In the ion optics system the ions are reflected and focused at 90° by a parabolic electrostatic field produced by an ion mirror. The Ion mirror had a hollow structure allowing photons and neutrals to pass through and reduce contamination of ion optics. The vacuum pump is mounted behind the ion mirror to remove unwanted particles and this creates a highly efficient vacuum.

## ***2.3 Sample pre-treatment procedure***

A Microwave digestion system Mars (CEM, Indian Trail, USA) was used when particulate matter was present in waste water. When the sample was clear (no particulate matter present or discoloured and turbidity <1 NTU) it was only necessary to acidify it with HNO<sub>3</sub> 4%. When unclear samples were analyzed (e.g. waste water), it was necessary to make a microwave-assisted digestion. Microwave pre-treatment used in this technique

consisted in adding 2 mL of HNO<sub>3</sub> 69% Hiperpur grade at 25 mL of sample and heating for 30 minutes at 200°C with the MW oven programmed at 300, 600 or 1200 Watts depending of the number of samples (<10, 10-30 or 30-45 samples respectively). After this, they were raised to 50 mL in plastic flasks and measured in the analytical instrument together clear samples.

## ***2.4 Determination of As and Se in water***

### ***2.4.1 Method of analysis***

The isotopes selected for As and Se were respectively <sup>75</sup>As and <sup>78</sup>Se. The stable isotope <sup>89</sup>Y was used as an internal standard to correct the matrix effect and drifts of sensitivity. The internal standard was added on-line in different tubes to the samples. The <sup>89</sup>Y internal Standard containing 5 µg/L of Yttrium was prepared by diluting a 1000 mg/L stock standard solution (Inorganic Ventures, Lakewood, NJ, USA).

The calibration curve (0.5, 1, 5, 20, 50, 250 µg/L) was prepared from the standard solution of As and Se. After the MW process had concluded, samples were introduced in test tubes in the SP3 auto-sampler to be measured by the instrument. The software supplied by the manufacturer interpolates the analytical signal in the calibration curve to obtain the concentration. When a MW process is used the result must be multiplied by a dilution factor.

A 10 µg/L standard of As and Se was measured as a quality control sample (QC) for each ten samples. In order to ensure the accuracy of the essay, this sample was prepared from a different provider (Panreac, Barcelona, Spain). A blank was measured after each QC sample to ensure that no contamination had. All results had to be under the limits of quantitations (LOQs). To ensure the precision of the instrument three replicates were taken and evaluated for the percentage of Relative Standard Deviation (RSD) that needed to be lower than the validation results.

### ***2.4.2 Validation of the analytical method***

The analytical method validation was designed according to these references: The Eurachem Guide [32], the harmonized guidelines for single-laboratory validation of methods of analysis [33], the practical guide to Analytical Method Validation [34], the ENAC G-CSQ-02 document [35] and the 2002/657/EC Commission Decision of 12 August 2002 [36]. Consequently, the validation parameters limits of detection (LOD) and quantitation (LOQ), working range, traceability, accuracy and precision were determined using this method for As and Se. These values were estimated with experiments that are summarized in Figure 1.

For the evaluation of the accuracy and traceability and the precision study of the complete procedure on the different matrices of water, two types of standard reference materials were used: A BCR-714 of influent wastewater (Community Reference Bureau, BCR, Brussels, Belgium) for complexes matrices and a NIST 1643e of groundwater (National Institute of Standards and technology, NIST, Gaithersburg, MD, USA) for simple matrices.

## **2.5 Proficiency study**

A proficiency testing was done in collaboration with other laboratories (Aquacheck proficiency test) [37]. The aim of this exercise is usually to ensure the accuracy of all participant laboratories. Ten laboratories were which they participated. The proficiency testing followed an operational plan and distribution schemes of samples based on waste waters and sludge samples where some parameters, such as nutrients, non-specific determinands, total phenol, cyanide, sulphate, ammonia, phosphate and nitrogen were analysed besides twelve metals.

The Z-Score was calculated with the formula:

$$Z = \frac{V_L - V_A}{\sigma}$$

Where:

$V_L$  = Result obtained with the method.

$V_A$  = Average of all participants that delivered acceptable results

$\sigma$  = Standard deviation of all participants that delivered acceptable results.

## **3. Results and discussion**

### **3.1. Interferences and instrument optimization**

The presence of chloride in samples of water is the main source of interferences for the As determination.  $^{35}\text{Cl}$  and  $^{40}\text{Ar}$  masses together constitute the poly-atomic spectral interference  $[^{40}\text{Ar}^{35}\text{Cl}]^+$  for determination of arsenic ( $^{75}\text{As}$ ). However, using the collision cell the effect was fully neutralized by the method.

In addition, there is no limit for the presence of chloride in the sample because if they are mostly in the sample, it must be diluted until the value of total dissolved solids is less than 0.2% by the intrinsic nature of the ICP-MS technique. Contents in total dissolved solids are calculated multiplying the value of electrical conductivity in  $\text{mS cm}^{-1}$  by the factor 0.64. When samples exceed 0.2% in solids they must to be diluted. Samples with

high concentrations of chloride and high value of conductivity they must to be diluted, consequently it reduces the grade of interference with Argon.

Prior to any further determinations of As and Se, the ICP-MS needed to be checked for optimum signal intensity and stability by measuring a 10 µg/L Be, Ba, Co, In, Ce, Pb and Th tuning solution. The aim of this check was to reach the conditions of Table 2.

In the instrument optimization previous to analysis there were several additional aspects that needed to be considered in the method development: first, the pump rate and the oxides formation: when the pump rate was high the sensitivity and oxide formation would increase; second, the sheath, nebulizer and auxiliary gas pressure parameters: a lower auxiliary flow gave a lower oxide ratio; for a heavier matrix more time was needed in the plasma than in the sheath; the nebulizer gas pressure had to be consistent with the type of matrix. Finally, the cones-torch distance needed to be aligned according to the matrix nature.

### ***3.2 Results of the validation parameters***

#### ***3.2.1 Limits of detection and quantitation (LOD/LOQ) of the method***

Limits of detection and quantitation were calculated from the standard deviation obtained from the measurements of seven blanks (distilled water) for three non-consecutive days. Limits of detection were 0.2 and 0.8 µg/L for As and Se respectively. Limits of quantitation were 0.6 and 2.5 µg/L for As and Se respectively.

LODs and LOQs were higher when a dilution factor was employed: So, the results were multiplied by the corresponding dilution factor. When it was necessary to make a MW, the dilution factor was 2. Samples of seawater used a dilution factor 10 due to their high salts concentration, over the maximum of total dissolved solids (0.2%).

#### ***3.2.2 Linearity and working range. Sensitivity***

The ICP-MS calibration curve was linear for both elements with correlation coefficients higher than 0.9999. The percentages of linearity obtained were 99.2 for As and 99.8% for Se. These results are according to the specification of the new ion optics system where good long term stability around 5 hours was achieved for elements with no sign of interface blockage or ion lens contamination. When the dilution factor was not considered, the As working range was 0.5-275.0 µg/L and 1.0-275.0 µg/L for Se.

The sensitivity obtained was more than 1 Gcps per mg/L (1000 million cps per mg/L). The Gigahertz sensitivity allows the flexibility to choose instrument conditions to suit the sample and the desired analyte concentration range.

### **3.2.3 Accuracy and traceability study**

For the traceability study the two standard reference materials BCR and NIST of waters were measured ten times for As and Se (Table 3). The *t*-test showed that no significance differences they were between experimental averages and certified values. Goods recovery values were obtained for both materials. The high recoveries were into the AOAC intervals.

Also, the accuracy of the method was evaluated by spiking three known quantities of As and Se standards seven times for three non consecutive days in four types of water: Groundwater and wastewater from the town of Burguillos (Seville, Spain); estuarine water from the Guadalquivir River (Seville, Spain); and seawater from the Mediterranean Sea (Almeria, Spain). Results are shown in Table 4. Goods values of recoveries were obtained for As and Se. All recovery values were according to the AOAC intervals, from 95.3 % for As in the wastewater matrix to 106.4 % for Se in the seawater matrix. The values of recoveries were better for the groundwater (100.6 % for As and 98.1 % for Se) and estuarine water (96.7 % for As and 103.8 % for Se) spiking than for the seawater (97.3 % for As and 106.4 % for Se) and wastewater (95.3 % for As and 97.2 % for Se) spiking. The lower recoveries were obtained for the low and medium levels of concentration in all matrices.

### **3.2.4 Precision study**

Precision was studied by measuring ten times the two certified reference materials BCR and NIST for As and Se (Table 3). Relative standard deviation values were lower for As and the NIST 1643e than for Se and the BCR 714 (0.26 % for As in NIST and 12.2 % for Se in BCR). In general low standard deviations were obtained except for Se in the BCR 714 reference where a poorer percentage of recovery was found in the traceability study.

Besides, precision was also assessed by spiking three different concentrations of As and Se standards seven times for three non consecutive days to each one of the four matrix studied above. Results are shown in Table 5. The *F*-test showed that no significance differences they were between experimental averages and theoretical values. In general, low values of relative standard deviation were obtained. The poorer values of precision were obtained for the sea water matrix (3.5% for As and 6.5% for Se). Groundwater, estuarine water and wastewater obtained lower values of RSD (2% for As and 4-5% for Se). Precision was always better for As (2.5% in RSD) than for Se (5.1% in RSD) in all matrices.

### **3.3. Proficiency testing study**



Additionally a proficiency study was done. Results are given respectively in Table 6. Values of recovery obtained by our method were agree with the AOAC intervals for As and Se reference values. The low values of Z-Score showed that for both elements good results were obtained ( $Z\text{-Score} < 2$ ). Results were better for Se than for As.

#### **4. Conclusions**

The current research work was conducted in an optimized and validated routine method to determine As and Se levels in different types of water by Inductively Coupled Plasma Mass Spectrometry (ICP-MS). The validation method included various studies on the most important analytical properties such as measuring certified reference materials, spiking matrices and participating in a proficiency test. The results obtained by these different methods showed that the optimised method had an excellent accuracy and precision.

According to the complete results obtained during the process of optimization and validation it was concluded that the current method was suitable for the proposed use. Additionally, it met all the specifications called for in existing laws and recommendations and in the scientific literature and guidelines. Actually, the method is currently being satisfactorily applied in a routine laboratory with accreditation for about 35 samples per day.

Regarding the whole of results showed that the limits of detection and quantitation obtained were consistent with the requirements of the Directive 98/83/EC for drinking water which states that the detection limit of the method should be less than 10% of the value of the parametric analyte ( $10\ \mu\text{g/L}$  for As and Se). The precision values obtained in the spiking studies were in accordance with the criteria of Directive 98/83/EC and the criterion of Horwitz [38] to establish a maximum acceptable precision depending on the concentration.

Finally, the evaluation of the accuracy and traceability was done employing various methods. The accuracy study through the use of a certified reference material has led to excellent results, showing that the rates of recovery and accuracy levels were appropriate and the method was free of systematic errors. The accuracy was also evaluated through spiking studies at three different concentration levels, showing also excellent results. The percentages of recovery obtained were in accordance with the values tabulated by the AOAC [39]. The proficiency testing was the external validation, which achieved satisfactory and relevant results.

#### **References**

- [1] M. Dakeishi, M. Katsuyuki, P. Grandjean. *Environ Health*, **5**, 31 (2006).
- [2] U. Tinggi. *Essentiality and toxicity of Se and its status in Australia: a review*. Elsevier Science Ireland Ltd. (2002).
- [3] D.L. Macalady, D. Ahmann, J. Garbarino. Redox transformations, complexation and soil/sediment interactions of inorganic forms of As and Se in aquatic environments: effects of natural organic matter Tailings and Mine Waste '02. *Proceedings of the International Conference on Tailings and Mine Waste*. USA (2002).
- [4] A.A. Carbonell-Barrachina, F.M. Burló-Carbonell, J.J. Mataix-Beneyto. *Arsénico en el sistema suelo planta. Significado Ambiental*. Ed.: Universidad de Alicante (1995).
- [5] U.K. Chowdhury, B.K. Biswas, T.R. Chowdhury, G. Samanta, B.K. Mandal, G.C. Basu, C.R. Chanda, D. Lodh, K.C. Saha, S.K. Mukherjee, S. Roy, S. Kabir, Q. Quamruzzaman, D. Chakraborti *Curr Sci India* **73**, 48 (1997).
- [6] M. Tondel, M. Rahman, A. Magnuson. *Environ Health Persp* **107**, 727 (1999).
- [7] M.M. Rahman, U.K. Chowdhury, K. Paul, M.K. Sengupta, D. Lodh *B World Health Organ* **83**, 1 (2005).
- [8] S.R. Panthi, S. Sharma, A.K. Mishra. *Kathmandu Univ J Sci Engin Technol.* **2**, 1 (2006).
- [9] US-ATSDR. ToxFAQ™ for As. Agency For Toxic Substances & Disease Registry. Department of Health and Human Services. Buford Hwy NE, Atlanta, GA USA. <http://www.atsdr.cdc.gov/tfacts2.html> (2007).
- [10] US-ATSDR. ToxFAQ™ for Se. Agency For Toxic Substances & Disease Registry. Department of Health and Human Services. Buford Hwy NE, Atlanta, GA USA. <http://www.atsdr.cdc.gov/tfacts92.html> (2003).
- [11] US-EPA Environmental Protection Agency. National Primary Drinking Water Standards. Office of Water (4606M). EPA 816-F-03-016. <http://www.epa.gov/safewater/consumer/pdf/mcl.pdf> (2003).
- [12] WHO. Guidelines for drinking –water quality, third edition. [http://www.who.int/water\\_sanitation\\_health/dwq/gdwq3rev/en/](http://www.who.int/water_sanitation_health/dwq/gdwq3rev/en/) (2004).
- [13] Directive 2000/60/EC of the European parliament and of de council of 23 October 2000 establishing a framework for Community action in the field of water policy the European parliament and the council of the European Union.
- [14] US-EPA Environmental Protection Agency. Method 6010B. Inductively coupled plasma. Atomic Emission spectrometry. Revision 2 (1996).

- [15] Standard Method 3120 B. Inductively Coupled Plasma (ICP) Method. Standard Methods for the examination of water and wastewater. 19<sup>th</sup> Edition. American Public Health Association (1995).
- [16] US-EPA Environmental Protection Agency. Method 200.9. Determination of trace elements by stabilized temperature Graphite furnace atomic absorption. Revision 2.2, Methods for the determination of Metals in environmental samples – Supplement I, EPA7600/R-94-111 (1994).
- [17] Standard Method 3113 B. Electrothermal Atomic absorption Spectrometric Method. Standard Methods for the examination of water and wastewater. 19<sup>th</sup> Edition. American Public Health Association (1995).
- [18] Standard Method 3114 B. Manual Hydride Generation/ Atomic Absorption Spectrometric Method, Standard Methods for the examination of water and wastewater. 19<sup>th</sup> Edition. American Public Health Association (1995).
- [19] US-EPA Environment Protection Agency. Method 7740. Method for analysis of aqueous Se samples by GHAA (1997).
- [20] Standard Method 3500 B. As. Colorimetric Method, Standard Methods for the examination of water and wastewater 19<sup>th</sup> Edition. American Public Health Association (1995).
- [21] Standard Method 3500 C. Se. Colorimetric Method. Standard Methods for the examination of water and wastewater 19<sup>th</sup> Edition. American Public Health Association (1995).
- [22] E.C.V. Butler. *J Chromatogr* **450**, 353 (1988).
- [23] S.H. Vien, R.C. Fry. *Anal. Chem.* **60**, 465 (1988).
- [24] Y. Odanaka, N. Tsuchiya, O. Matano, S. Goto *Anal Chem.* **55**, 939 (1983).
- [25] P. Anjali, R.J. Nikhil, K.S. Tapan, B. Manas, P. Tarasankar. *Anal Comm* **33**, 315 (1996).
- [26] R.S. Braman, D.L. Johnson, C.C. Foreback. *Anal Chem.* **49**, 621 (1977).
- [27] I. Drabaek, V. Carlsen, L. Just. *J Radioanal Nucl Ch* **103**, 249 (1986).
- [28] K. McLaughlin, D. Boyd, C. Hua, M.R. Smyth. *Electroanalysis* **4**, 689 (2005).
- [29] US-EPA Environmental Protection Agency. Method 6020A. Inductively coupled plasma. Mass spectrometry. Revision 1 (1998).

- [30] US-EPA Environmental Protection Agency. Method 200.8. Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma Mass Spectrometry. Revision 5.4 (1994).
- [31] ISO 17294\_2. Water quality. Application of inductively coupled plasma mass spectrometry. Part 2. Determination of 62 elements (2003).
- [32] Eurachem Guide. The fitness for purpose of analytical methods. A laboratory guide to method validation and related topics. LGC. <http://www.eurachem.org/guides/valid.pdf> (1998).
- [33] M. Thompson, S.L.R. Ellison, R. Wood. *Pure Appl. Chem.* **74**, 835 (2002).
- [34] J.M. Green. A practical guide to Analytical Method Validation. *Analytical Chemistry*, **68**, 305 A 309 A (1996).
- [35] ENAC G-CSQ-02. Guía para los laboratorios que realizan validaciones de métodos de análisis químicos. Entidad Nacional de Acreditación. Spain (1996).
- [36] 2002/657/EC: Commission Decision of 12 August 2002 implementing Council Directive 96/23/EC concerning the performance of analytical methods and the interpretation of results. Doc. No. C(2002) 3044 (2002).
- [37] Aquacheck. Issue No 2006-7/1. Aquacheck distribution No. 307 (2006).
- [38] W. Horwitz, *Anal. Chem.*, **54**, 67 (1994).
- [39] AOAC Peer verified methods program. Manual on Policies and procedures (1993).

Table 1. Values assigned to ICP-MS parameters in the method.

Flow parameters (L/min)		Ion Optics (Volts)	
Plasma Flow	17.5	First Extraction Lens	-2
Auxiliary Flow	1.65	Second Extraction Lens	-155
Sheath Gas	0.27	Third Extraction Lens	-210
Nebulizer Flow	0.91	Corner Lens	-218
		Mirror Lens Left	33
		Mirror Lens Right	21
		Mirror Lens Bottom	21
		Entrance Lens	1
		Fringe Bias	-2.5
		Entrance Plate	-31
		Pole Bias	0
Torch Alignment (mm)			
Sampling Depth	5		
Other			
RF Power (kW)	1.35		
Pump Rate	6		
Stabilization Delay	60		

Table 2. Requested values of a tuning solution in the previous check of the ICP-MS.

Signal	Requested value
<sup>9</sup> Be	> 5 x 10 <sup>6</sup> c/s/mg/L
<sup>115</sup> In	> 5 x 10 <sup>7</sup> c/s/mg/L
<sup>208</sup> Pb	> 2 x 10 <sup>7</sup> c/s/mg/L
Ratio CeO/Ce	< 3%
Ratio Ba <sup>++</sup> /Ba <sup>+</sup>	< 3%
Background at mass 5	< 5 %

Table 3. Results obtained for the replicates of the two CRMs\*.

	NIST 1643e		BCR 714	
	As	Se	As	Se
N	10	10	10	10
Certified value (µg/L)	60.45	11.97	18.3	9.8
Expanded uncertainty	0.72	0.14	1.6	1.2
Experimental mean (µg/L)	60.37	11.83	18.5	10.2
SD	0.16	0.23	0.4	1.2
% RSD	0.26	1.94	2.2	12.2
% Recovery	99.88	98.93	101.09	104.08
AOAC interval	90-107	90-107	90-107	80-110

\*A t-test<sup>1</sup> was applied successfully to corroborate this SRM study for both elements.

Table 4. Percentages of recovery obtained in the spiking experiment of samples.

		% Recovery obtained (7 replicates per day)					
		Arsenic			Selenium		
		Day 1	Day 2	Day 3	Day 1	Day 2	Day 3
Groundwater	Low level (2 µg/L)	96.1	97.6	108.5	78.4	97.1	98.1
	Medium level (10 µg/L)	96.8	98.9	105.4	95.4	100.2	102.8
	High level (50 µg/L)	99.0	97.0	105.9	103.8	102.8	104.2
Estuarine water	Low level (2 µg/L)	91.2	93.1	92.3	92.1	120.8	96.1
	Medium level (10 µg/L)	96.8	96.1	101.2	105.9	102.7	104.2
	High level (50 µg/L)	100.1	96.4	103.4	101.0	103.6	107.8
Wastewater	Low level (2 µg/L)	92.3	102.0	95.3	91.4	95.2	95.8
	Medium level (10 µg/L)	92.4	91.8	92.1	96.4	97.8	102.6
	High level (50 µg/L)	93.7	94.9	103.2	95.3	100.8	99.4
Sea water	Low level (20 µg/L)	89.2	102.6		91.2	129.8	
	Medium level (100 µg/L)	103.4	99.3		100.8	114.3	
	High level (250 µg/L)	100.3	89.1		98.3	103.8	



Table 5. Percentages of RSD obtained in the spiking experiment\*.

		% RSD obtained (7 replicates per day)					
		Arsenic			Selenium		
		Day 1	Day 2	Day 3	Day 1	Day 2	Day 3
Groundwater	Low level (2 µg/L)	3	4	4	10	5	4
	Medium level (10 µg/L)	1	1	2	3	4	3
	High level (50 µg/L)	1	1	1	2	1	2
Estuarine water	Low level (2 µg/L)	4	3	5	11	12	4
	Medium level (10 µg/L)	2	2	2	9	5	1
	High level (50 µg/L)	1	1	1	2	0	1
Wastewater	Low level (2 µg/L)	4	3	5	9	8	11
	Medium level (10 µg/L)	1	2	1	5	4	3
	High level (50 µg/L)	1	1	1	2	2	1
Sea water	Low level (20 µg/L)	5	6		12	12	
	Medium level (100 µg/L)	4	3		5	4	
	High level (250 µg/L)	2	1		3	3	

*\*An F-test was applied successfully to corroborate this spiking samples study for both elements.*

Table 6. Results obtained in the Aquacheck proficiency testing <sup>1</sup>.

	As	Se
Reference value (µg/L)	13.4	42.4
Value of our method (µg/L)	14.7	44.1
% recovery	109.7	104.0
AOAC interval	65-115	65-115
Average of all participants (µg/L), N = 10	13.2	43.2
Standard deviation	2.31	2.25
Z-Score	0.65	0.40

Figure 1. Scheme of the validation method.

