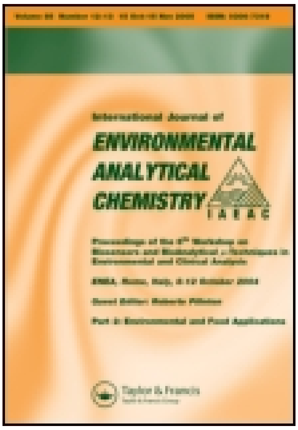

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/geac20

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

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To cite this article: Eusebio Álvarez Vázquez, Ramón Bouza Deaño, Miguel Ternero Rodríguez & Antonio J. Fernández Espinosa (2011): 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, International Journal of Environmental Analytical Chemistry, 91:5, 462-472

To link to this article: http://dx.doi.org/10.1080/03067310903045489

Intern. J. Environ. Anal. Chem.
Vol. 91, No. 5, 20 April 2011, 462–472

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

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(*Received 20 February 2009; final version received 14 May 2009*)

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 optimisation, where the torch alignment, flow of gases and ion optic adjustments were calibrated, the method was validated successfully. The parameters limits of detection, linearity, working range, sensitivity and the interferences, precision and accuracy were studied with three procedures for the method: measuring two SRMs (BCR-714 of influent wastewater and NIST 1643e of groundwater); 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 $\mu g\,L^{-1}$ 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 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 in recent 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 but 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 which occurred in Bangladesh [5,6], East Bengala [7] or Nepal [8].

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ISSN 0306–7319 print/ISSN 1029–0397 online

DOI: 10.1080/03067310903045489
http://www.informaworld.com

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].

In a response 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 $10\,\mu g\,L^{-1}$. In Europe, 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 catodic stripping voltammetry (ASV/CSV) [28] and inductively coupled plasma mass spectroscopy (ICP-MS) [29–31]. However, there exists an urgent necessity for analytical techniques to determine As and Se levels simultaneously and with high sensitivity. At the same time, the necessity is extended to techniques that remove or minimise the usual interferences for elements, specifically for As and Se, such as the spectral interferences, the formation of solvent based interferences and the poly-atomic spectral interferences of atomic masses.

ICP-MS 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 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, seawater 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, Bedford, MA, USA). Nitric acid 69% Suprapur 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).

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

		Ion optics (Volts)	
Flow parameters (L min^{-1})			
Plasma flow	17.5	First extraction lens	−2
Auxiliary flow	1.65	Second extraction lens	−155
Sheath gas	0.27	Third extraction lens	−210
Nebuliser flow	0.91	Corner lens	−218
		Mirror lens left	33
Torch alignment (mm)		Mirror lens right	21
Sampling depth	5	Mirror lens bottom	21
Other		Entrance lens	1
RF power (kW)	1.35	Fringe bias	−2.5
Pump rate	6	Entrance plate	−31
Stabilisation delay	60	Pole bias	0

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 parts near the torch, cones and the RF spire were cooled by using a Kühlmobil 142 VD cooling system (Van der Heijden, Dörentrup, Germany). Nebulisation chamber was cooled by Peltier effect, another recent improvement that also increases the sensitivity. 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 nebuliser was performed using a peristaltic pump.

The 90-degree reflecting ICP-MS ion optics is a new optic system for routine sample analysis that delivers exceptional sensitivity. 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 optics had a hollow structure that allows photons and neutrals passing through to reduce contamination to 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 wastewater. When the sample was clear (no particulate matter present or discoloured and turbidity <1 NTU) it was only necessary to acidify it with HNO_3 4%. When unclear samples were analysed (e.g. wastewater), it was necessary to make a microwave-assisted digestion. Microwave pre-treatment used in this technique consisted in adding 2 mL of HNO_3 69% Suprapur grade at 25 mL of sample and heating for 30 minutes at 200°C with the microwave 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 ^{75}As and ^{78}Se. The stable isotope ^{89}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 ^{89}Y internal standard containing $5\,\mu g\,L^{-1}$ of Yttrium was prepared by diluting a $1000\,mg\,L^{-1}$ stock standard solution (Inorganic Ventures, Lakewood, NJ, USA).

The calibration curve (0.5, 1, 5, 20, 50, $250\,\mu g\,L^{-1}$) was prepared from the standard solution of As and Se. After the microwave process had concluded, samples were introduced in test tubes in the SP3 auto-sampler to be measured by the instrument. When a microwave process is used the result must be multiplied by a dilution factor.

A $10\,\mu g\,L^{-1}$ standard of As and Se was measured as a quality control sample (QC) for each 10 samples. Besides, a blank was evaluated after the calibration curve ends, to ensure that no contamination had, being the value lower than 75% of the quantitation limit. Additionally, three replicates were taken for samples 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 harmonised 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), working range, traceability, accuracy and precision were determined using this method for As and Se. These values were estimated with experiments that are summarised 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 (SRMs) were used: a BCR-714 of influent wastewater (Community Reference Bureau, BCR, Brussels, Belgium) for complexes matrices and an NIST 1643e of groundwater (National Institute of Standards and Technology, NIST, Gaithersburg, MD, USA) for simple matrices. An *F*-test was applied successfully to corroborate this spiking samples study for both elements.

2.5 *Proficiency study*

A proficiency testing was done in collaboration with nine other laboratories – $N = 10$ (Aquacheck proficiency test) [37]. The aim of this exercise is usually to ensure the accuracy of all participant laboratories. The proficiency testing followed an operational plan and distribution schemes of samples based on wastewaters and sludge samples where some

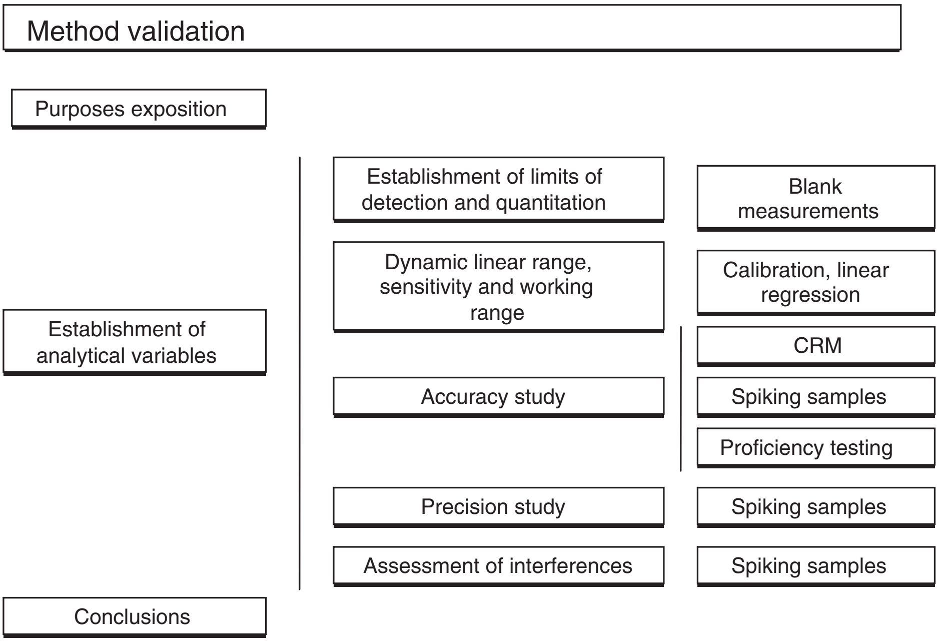

Figure 1. Scheme of the validation method.

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;
σ = standard deviation of all participants that delivered acceptable results.

3. Results and discussion

3.1 *Interferences and instrument optimisation*

The presence of chloride in samples of water is usually the main source of interference for As determinations. Both ^{35}Cl and ^{40}Ar masses constitute the poly-atomic spectral interference $[^{40}Ar^{35}Cl]^+$ for determination of arsenic (^{75}As). Using the Varian 810-MS, there is no limit for the presence of chloride in water samples because of two causes: First, the dilution done on samples of high salinity; second, the proper design of this model of Varian ICP-MS.

First, if there are high contents of chloride 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, so the dilution process minimises this interference with this model of ICP-MS. Due to the high salinity of marine waters, the dilution factor must to be so high that the

[Ar][Cl] interference result is almost annulled. Consequently, arsenic concentrations as well as chloride levels are diluted; nevertheless arsenic levels are higher than fresh waters and resulting arsenic concentration rests over the quantitation limit.

On the other hand, in matrices with appreciable levels of chloride but lower values of salinity any dilution was necessary in order to reach that total dissolved solids (TDS) be less than 0.2%. In this case the 90-degree reflecting ICP-MS ion optics system minimizes the interference due to the follows innovative specifications: First, the system design combines an extremely powerful ionic lens with a mass spectrometer that is configured 90 degrees with the cones (improving the signal-noise ratio), allowing together the important decrease of the quatitation limits of arsenic in presence of relatively high levels of chloride. Second, this quadrupole is circular, improving the resolution of masses, in front to a standard linear quadrupole, which cannot differentiate between the As^+ and the $ArCl^+$ masses. As^+ and $ArCl^+$ masses are similar but they are in fact different and the circular quadrupole improve this mass differentiation. Consequently, both dilution process and excellent design of this model of MS detector allowed eliminating the $[^{40}Ar^{35}Cl]^+$ interference.

Various aspects were considered in optimising the instrument. Contents in total dissolved solids are calculated multiplying the value of electrical conductivity in $\mathrm{mS\,cm^{-1}}$ by the factor 0.64. When samples exceed 0.2% in solids they must be diluted, consequently, this 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 $10\,\mu g\,L^{-1}$ 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 optimisation 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 increased; second, the sheath, nebuliser 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 nebuliser 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 (LOD) of the method*

Limits of detection 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 $0.8\,\mu g\,L^{-1}$ for As and Se, respectively.

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

Signal	Requested value
^{9}Be	$>5\times10^{6}$ c/s/mg L^{-1}
^{115}In	$>5\times10^{7}$ c/s/mg L^{-1}
^{208}Pb	$>2\times10^{7}$ c/s/mg L^{-1}
Ratio CeO/Ce	<3%
Ratio Ba^{++}/Ba^{+}	<3%

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 microwave, the dilution factor was 2. Samples of seawater used a dilution factor 10 due to their high salt 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 percentages of linearity of 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 $\mu g\,L^{-1}$ and the SE working range was 1.0–275.0 $\mu g\,L^{-1}$.

The sensitivity obtained was more than 1 Gcps per mg L^{-1} (1000 million cps per mg L^{-1}). The Gigahertz sensitivity grants 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 10 times for As and Se (Table 3). Good 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. Good 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

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 ($\mu g\,L^{-1}$)	60.45	11.97	18.3	9.8
Expanded uncertainty	0.72	0.14	1.6	1.2
Experimental mean ($\mu g\,L^{-1}$)	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

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 10 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 matrices studied above. Results are shown in Table 5. The *F*-test showed that there were no significance differences between experimental averages and theoretical values. In general, low values of RSD were obtained. The poorer values of precision were obtained for the seawater 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 in Table 6. Values of recovery obtained by our method were in agreement 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*-Score <2). Results were better for Se than for As.

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 ($2\,\mu g\,L^{-1}$)	96.1	97.6	108.5	78.4	97.1	98.1
Medium level ($10\,\mu g\,L^{-1}$)	96.8	98.9	105.4	95.4	100.2	102.8
High level ($50\,\mu g\,L^{-1}$)	99.0	97.0	105.9	103.8	102.8	104.2
Estuarine water						
Low level ($2\,\mu g\,L^{-1}$)	91.2	93.1	92.3	92.1	120.8	96.1
Medium level ($10\,\mu g\,L^{-1}$)	96.8	96.1	101.2	105.9	102.7	104.2
High level ($50\,\mu g\,L^{-1}$)	100.1	96.4	103.4	101.0	103.6	107.8
Wastewater						
Low level ($2\,\mu g\,L^{-1}$)	92.3	102.0	95.3	91.4	95.2	95.8
Medium level ($10\,\mu g\,L^{-1}$)	92.4	91.8	92.1	96.4	97.8	102.6
High level ($50\,\mu g\,L^{-1}$)	93.7	94.9	103.2	95.3	100.8	99.4
Seawater						
Low level ($20\,\mu g\,L^{-1}$)	89.2	102.6		91.2	129.8	
Medium level ($100\,\mu g\,L^{-1}$)	103.4	99.3		100.8	114.3	
High level ($250\,\mu g\,L^{-1}$)	100.3	89.1		98.3	103.8	

4. Conclusions

The current research work was conducted in an optimised and validated routine method to determine As and Se levels in different types of water by 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 optimisation 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

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^{-1})	3	4	4	10	5	4
Medium level (10 μg L^{-1})	1	1	2	3	4	3
High level (50 μg L^{-1})	1	1	1	2	1	2
Estuarine water						
Low level (2 μg L^{-1})	4	3	5	11	12	4
Medium level (10 μg L^{-1})	2	2	2	9	5	1
High level (50 μg L^{-1})	1	1	1	2	0	1
Wastewater						
Low level (2 μg L^{-1})	4	3	5	9	8	11
Medium level (10 μg L^{-1})	1	2	1	5	4	3
High level (50 μg L^{-1})	1	1	1	2	2	1
Seawater						
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	

Table 6. Results obtained in the Aquacheck proficiency testing.

	As	Se
Reference value (μg L^{-1})	13.4	42.4
Value of our method (μg L^{-1})	14.7	44.1
% Recovery	109.7	104.0
AOAC interval	65–115	65–115
Average of all participants (μg L^{-1}), $N = 10$	13.2	43.2
Standard deviation	2.31	2.25
Z-Score	0.65	0.40

satisfactorily applied in a routine laboratory with accreditation for about 35 samples per day.

The whole results showed that the limits of detection obtained were consistent with the requirements of 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 ($10\,\mu g\,L^{-1}$ 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.

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