

Direct Determination of Arsenic and Chromium in Seawater Samples Using On-Line Dilution and ICP-MS Analysis

María Carmen Barciela-Alonso, Marta Castrelo Otero, María Raquel Domínguez González, Elena Peña-Vázquez, Pilar Bermejo-Barrera*

Department of Analytical Chemistry, Nutrition and Bromatology,
Faculty of Chemistry. University of Santiago de Compostela
Avenida das Ciencias s/n, 15782 Santiago de Compostela. Spain

INTRODUCTION

Arsenic (As) and chromium (Cr) are toxic elements and widely distributed in the environment. They are present in seawater from natural and anthropogenic sources due to the different industrial applications in which these elements are used. Arsenic compounds, for instance, are used for the production of insecticides and herbicides, and as additives for animal feed and wood preservatives (1). Anthropogenic chromium discharges from industrial procedures such as plating and tanning, and from solutions for glassware cleaning and wood preservation (2, 3). Once these elements are released into the ocean, they are ingested by aquatic life and then become part of the food chain by polluting marine animals used for human consumption leading to health problems. With the aim to maintain safe quality aquatic ecosystems, the Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 established a framework for community action in the field of water policy (4). Similarly, the Spanish Law of 9/2010 of the Galician Waters (5) established quality objectives for the Galician estuaries as well as the allowable limits of emission for different elements in wastewater. As reported in the literature, the total As and Cr concentrations in clean coastal waters are between 1–3 $\mu\text{g L}^{-1}$ and 0.04–10.8 $\mu\text{g L}^{-1}$, respectively (6, 7).

*Corresponding author.
E-mail: pilar.bermejo@usc.es
Tel.: +34 881814266
Fax: +34 981 547 141

ABSTRACT

A method for total As and Cr determination in seawater samples has been developed. As and Cr were measured using the seaFAST2 automated sample introduction system coupled to an ICP-MS. The sampling system allows on-line sample dilution (10 times) before introduction into the ICP-MS.

Calibration was performed using the standard addition method, working in the concentration range of 0 to 50 $\mu\text{g L}^{-1}$ for As and 0 to 25 $\mu\text{g L}^{-1}$ for Cr. The method shows good sensitivity resulting in LODs and LOQs of 0.3 and 0.9 $\mu\text{g L}^{-1}$, respectively, for As and of 0.03 and 0.09, respectively, for Cr determination. The method was precise (RSD <2%) and accurate.

This method was applied to the determination of As and Cr in different seawater samples from the Galician coast of Spain. The concentrations found ranged from 0.3 to 3.1 $\mu\text{g L}^{-1}$ for As and from 0.03 to 0.1 $\mu\text{g L}^{-1}$ for Cr.

Various studies have reported on the As and Cr determination in seawater samples. The main problem with this type of analysis is the very low concentrations of these metals in the samples (on the order of ng L^{-1} to a few $\mu\text{g L}^{-1}$ levels). In addition, there is the problem of salinity of the samples, which can produce interferences in the analysis. Some of the methods used to overcome these limitations with preconcentration steps are the use of chelating resins (8–11), knotted reactors (12, 13), and co-precipitation with magnesium hydroxide (14, 15). Dif-

ferent detection systems have been used for their determination, including electrothermal atomic absorption spectrometry (ETAAS) (12, 13, 16), atomic fluorescence spectrometry (AFS) (7, 17), total reflection X-ray fluorescence spectrometry (18, 19), and inductively coupled plasma mass spectrometry (ICP-MS) (10, 11, 14, 15, 20–23). ICP-MS offers a number of advantages over other detection systems, such as sensitivity and the possibility of multielemental analysis.

The aim of this work was to develop a simple and fast method for the As and Cr determination in seawater samples obtained from the Galician coast (northwestern Spain) by ICP-MS using the seaFAST2 system for on-line sample preparation.

EXPERIMENTAL

Instrumentation

For this study, a model NexION® 300X inductively coupled plasma mass spectrometer (PerkinElmer, Shelton, CT, USA) was used, equipped with a collision cell. The instrumental operating parameters are listed in Table I. To minimize polyatomic interferences, He was used as the collision gas for As and Cr determination. The SeaFAST2 preconcentration system (Elemental Scientific, Inc., USA) was coupled to the ICP-MS for the automatic dilution of seawater samples (10 times) for total As and Cr determination (24). The system includes one peristaltic pump, three valves, two columns for cleanup of the carrier and buffer, and one column for preconcentration of the elements. The

peristaltic pump propels the reagents at 6 rpm with tubes of different internal diameters (1.14 mm for the carrier, 0.76 mm for the buffer, 0.13 and 0.38 mm for the eluent, and 1.3 mm for waste). The seaFAST2 system can operate in two different modes: the direct mode of analysis, which enables on-line dilution and addition of an internal standard, and the preconcentration mode. A schematic diagram of the seaFAST2 system is shown in Figure 1.

Standard Solutions and Reagents

Ultrapure water of 18 MΩ·cm, obtained from a Milli-Q® water purification system (Millipore Corporation, Bedford, MA, USA), was used throughout the work.

A stock standard solution of As (1000 mg L⁻¹) was purchased from Fluka (Switzerland), while the stock standard solution of Cr (1000 mg L⁻¹) and Cr(NO₃)₃ in 0.5M HNO₃ was obtained from Scharlau (Barcelona, Spain). All standard solutions were prepared by dissolving the corresponding amount of salt in ultrapure water. Nitric acid of 69% Hiperpur-Plus was obtained from Sigma-Aldrich, USA. The internal standards used were Rh (1000 mg L⁻¹,

Fluka, Switzerland) and Y (1000 mg L⁻¹, Panreac, Spain) for the total As and Cr determination by ICP-MS.

To verify the accuracy of the method, the certified reference material NASS-4 Ocean Seawater (National Research Council Canada) was used.

Sample Preparation

Nine samples of surface seawater were collected from different areas along the Galician coast of north-western Spain. These are identified in Figure 2 and are listed as Vilanova de Arousa, Esteiro, Pontevedra, Marín, Cambados, Bouzas, Canido, Vilagarcía de Arousa and Portosin. The samples (1 L) were collected in pre-cleaned 2.5 L non-metallic free-flushing Niskin bottles. After collection, the samples were filtered (0.45 μm) and immediately stored in polyethylene bottles at -20 °C until analysis.

ICP-MS Determination of As and Cr

Total As and Cr determination was performed by ICP-MS. Both elements were quantified by means of the multielemental standard additions method ranging from 0–50 μg L⁻¹ and 0–25 μg L⁻¹ for As and Cr, respectively. Internal standards of ¹⁰³Rh and ⁸⁹Y were used to correct possible matrix effects and signal drift. A 10 μg L⁻¹ solution of the internal standards in 7.3% HNO₃ was mixed with the sample in the seaFAST2 system.

RESULTS AND DISCUSSION

Total As and Cr determination was performed using the seaFAST2 coupled to ICP-MS. The seaFAST2 is a completely automated introduction system for multi-mode determination of ultra-trace metals in undiluted seawater samples.

TABLE I
ICP-MS Instrumental Operating Conditions

Plasma gas flow	18 L min ⁻¹
Auxiliary gas flow	1.2 Lmin ⁻¹
Aerosol carrier	0.83 Lmin ⁻¹
Plasma power	1600 W
Monitored signal	⁷⁵ As, ⁵² Cr, ⁵³ Cr
Scan mode	Peak hopping
Dwell time	115 ms
Integration time	4600 ms
CCT-KED He	4 mL min ⁻¹
RPq	0.25
Sweeps/reading	20
Readings/replicate	2
Replicates	3

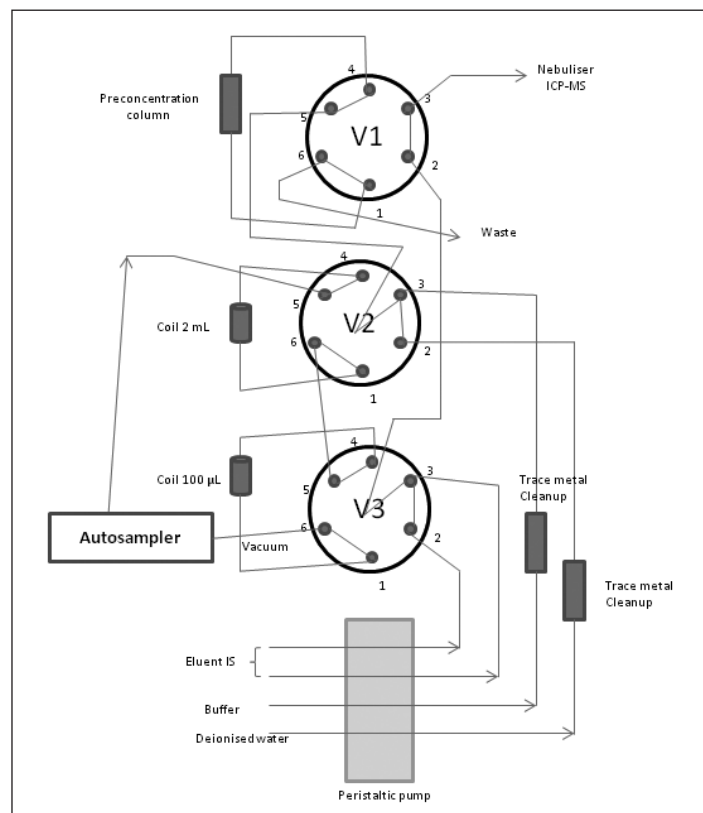


Fig. 1. Schematic diagram of seaFAST2 System.

This system allows the on-line sample dilution (10 times) before its introduction into the ICP-MS. Sample dilution was performed using 7% HNO₃ Hiperpur-plus (69%) containing internal standards (10 µg L⁻¹ Rh and Y). For better results, the measurements were performed using the standard and KED mode (Kinetic Energy Discrimination) with He as the collision gas.

Calibration and Analyte Addition Graphs

First, experiments were performed to compare the slopes of the calibration and addition graphs. Calibration was performed using aqueous standards at As concentrations of 0, 5, 10, 20, 30, 40, and 50

µg L⁻¹ and at Cr concentrations of 0, 2, 5, 10, 15, 20, and 25 µg L⁻¹. The standard addition method was also used in the same range of concentrations using a pool of seawater samples. For Cr determination, the ⁵²Cr and ⁵³Cr isotopes were measured. Analysis was performed with (KED mode) and without (standard mode) He as the collision gas. When analysis were performed in the standard mode, better results were obtained for the ⁵²Cr isotope, most likely due to polyatomic interferences. In the presence of chloride, various interferences appear for ⁵³Cr such as, ³⁷Cl¹⁶O⁺, ³⁵Cl¹⁷O¹H⁺, ³⁵Cl¹⁸O⁺ (24). The use of He as the collision gas (KED mode) improved the results for both elements and for both isotopes

of Cr. Nevertheless, the sensitivity obtained using ⁵²Cr was higher than ⁵³Cr, thus ⁵²Cr was selected for the Cr determination.

The slopes as well as the correlation coefficients (r) obtained for the calibration and the standard addition graphs are shown in Table II. Both the calibration and the standard addition graphs show good linearity, with correlation coefficients higher than 0.995 for each element studied. The correction using internal standards did not improve the results. After statistical comparison of the slopes of the aqueous calibration and the standard addition graph by applying the Student's *t*-test (95% significant level) (25), statistical differences were observed for both elements. Taking these results into account, the standard addition method was selected to perform this study. The correction using internal standards was not necessary to perform the analysis.

TABLE II
Slopes and Correlation Coefficients Obtained for Calibration and Standard Addition Graphs

	Aqueous Calibration		Standard Addition Calibration	
	Slope	Correlation Coefficient	Slope	Correlation Coefficient
As	21.3	1.000	10.456	0.9995
Cr	216.8	0.999	123.58	0.9992

Sensitivity

The limit of detection and quantification was calculated according to LOD = (3SD)/m and LOQ = (10SD)/m, where SD is the standard deviation of 11 measurements of a blank and m is the slope of the addition graph. The LOD and LOQ values were 0.3 and 0.9 µg L⁻¹, respectively, for As determination and 29.3 and 97.1 ng L⁻¹, respectively, for Cr determination. A comparison of the LOD obtained for Cr in this study shows that it is lower than the values reported by Nicolai et al. (9) (66 ng L⁻¹) using ICP-MS, with on-line preconcentration and matrix elimination with a chelating resin, and also by Sánchez et al. (11) reporting 0.530 µg L⁻¹ for Cr using ICP-MS and on-line solid-phase chelation.

Precision and Accuracy

The precision of the method was evaluated by studying the repeatability (within-run precision). Within-run precision was calculated



Fig. 2. Sampling points on Galician coast in Spain.

by analyzing (10 times) a seawater sample with 1.2 and 0.7 $\mu\text{g L}^{-1}$ of As and Cr, respectively. The relative standard deviations obtained were 8% and 2% for As and Cr, respectively. The results are shown in Figure 3.

To study the accuracy of the method, certified reference material NASS-4 Ocean Seawater with certified As and Cr concentrations of $1.26\pm 0.09 \mu\text{g L}^{-1}$ and $0.115\pm 0.010 \mu\text{g L}^{-1}$, respectively,

was analyzed. The experimental As and Cr concentrations obtained were $1.28\pm 0.05 \mu\text{g L}^{-1}$ and $0.111\pm 0.018 \mu\text{g L}^{-1}$. These concentrations were compared with the certified concentrations using the Student's *t*-test (95% significance) (26). No statistical differences were observed between both concentrations; thus, the method is accurate for As and Cr determination.

Analytical recovery was assessed at four concentration levels. A sea-

water sample was spiked with 5, 20, 40 and 50 $\mu\text{g L}^{-1}$ of As and 2, 10, 20 and 25 $\mu\text{g L}^{-1}$ of Cr. The analytical recoveries obtained were $93\pm 4\%$ and $96\pm 4\%$ for As and Cr, respectively.

Application of the Method

The developed method was applied for As and Cr determination in nine seawater samples from the Galician Coast. Surface seawater samples (1 L) were collected in pre-cleaned 2.5 L non-metallic free-flushing Niskin bottles. After collection, the seawater samples were filtered (0.45 μm) and immediately stored in a polyethylene bottle at $-20 \text{ }^\circ\text{C}$ until analysis.

Samples were analyzed in triplicate using the method described above. As and Cr were determined using the standard addition method, using a pool of seawater samples, in the concentration ranges from 0–50 $\mu\text{g L}^{-1}$ and 0–25 $\mu\text{g L}^{-1}$, respectively. The results obtained are shown in Table III. As can be seen, the As and Cr concentrations were not detected in the sample collected in Pontevedra. The As concentrations varied from 1.1 to 3.1 $\mu\text{g L}^{-1}$ and the highest concentration was found in Vilagarcía de Arousa, followed by Vilanova de Arousa and Esteiro. Cr was only detected in three of the samples analyzed (Cambados, Esteiro, and Vilagarcía de Arousa) with concentrations ranging from 0.04 to 0.1 $\mu\text{g L}^{-1}$. In general, the As and Cr concentrations obtained in the samples analyzed in this study are within the levels reported in the literature for seawater (26–28) and are lower than the limits established by the Spanish Law of 9/20/10 of Galician Waters.

CONCLUSION

A simple, precise (RSD <2%), sensitive, and accurate method for total As and Cr determination using the SeaFAST2 automated sample

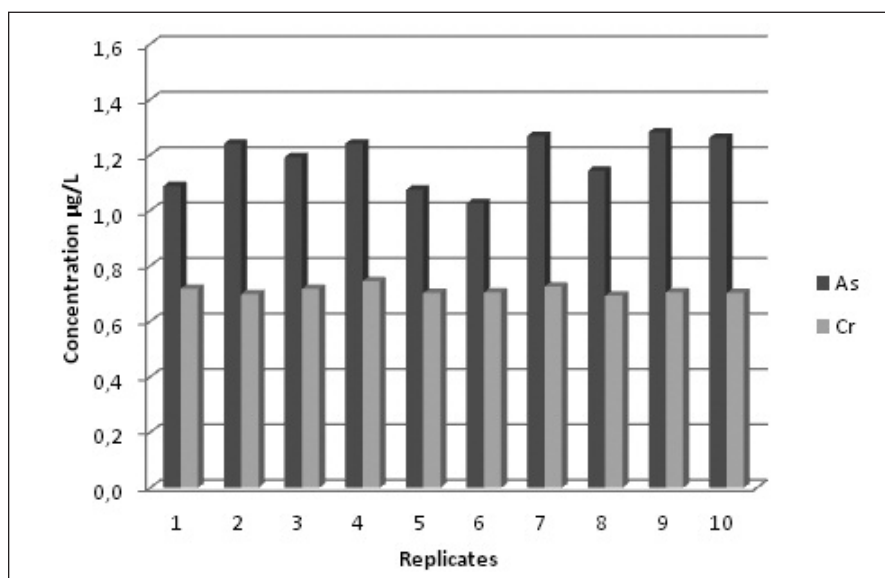


Fig. 3. Study of repeatability of the method for As and Cr determination in a seawater samples.

TABLE III
Concentration ($\mu\text{g L}^{-1}$) of Total As and Cr and Arsenic Species in Different Seawater Samples

Sampling Point	No.	As ($\mu\text{g L}^{-1}$)	Cr ($\mu\text{g L}^{-1}$)
Bouzas	1	1.8 ± 0.03	<LOD
Cambados	2	2.5 ± 0.2	0.04 ± 0.0001
Canido	3	1.1 ± 0.2	<LOD
Esteiro	4	2.9 ± 0.06	0.08 ± 0.03
Marín	5	1.5 ± 0.04	<LOD
Pontevedra	6	<LOD	<LOD
Portosín	7	1.8 ± 0.07	<LOD
Vilagarcía de Arousa	8	3.1 ± 0.07	0.1 ± 0.02
Vilanova de Arousa	9	2.4 ± 0.05	<LOD
LOD		0.3	0.03

introduction system coupled with ICP-MS was developed. The seaFAST2 system allows on-line sample dilution (10 times) before introduction into the ICP-MS. This system minimizes the risk of sample contamination and reduces the time needed for sample preparation. Because of the influence of the sample matrix, calibration using the standard addition method was used for the determination of both elements. The use of internal standards (Y and Rh) did not improve the analytical performance.

The proposed method was successfully applied to the determination of As and Cr in nine seawater samples from the Galician coast and obtaining concentrations lower than 3.1 and 0.1 $\mu\text{g L}^{-1}$ for As and Cr, respectively. These values are lower than the limits as established by the Spanish Law of 9/20/10 of Galician Waters.

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