Dynamic reaction cell inductively couple plasma-mass spectrometry optimization for seawater analysis

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ABSTRACT

A direct method for dynamic reaction cell inductively coupled plasma- mass spectrometry (DRC-ICP-MS) trace mineral elements determination in seawater was optimized by Experimental Statistical Design. Five instrumental parameters, such as radiofrequency, sample, nebulizer and reaction gas flows, rejection parameter q and axial field voltage were studied. A Plackett-Burman design was used for screening the most important parameters and the most significant ones were optimized with a Central composite design. Fifteen elements and different isotopes for some of these were considered through the study. The optimization was achieved by using three different reaction gases (NH_3, CH_4 and O_2). The optimized method was used for the quantification of trace minerals in a certified seawater sample. The standard mode was adequate for the quantification of those elements that have a reduced number of interferences like [111]Cd and [238]U. However, the best results were obtained employing ICP-MS in NH_3-DRC mode which allowed the simultaneous determination of elements like [51]V, [55]Mn, [58]Ni, [68]Zn and [238]U, which can be determined in the reference sample with an accuracy error lower than 10% and [95]Mo determined with an accuracy error of 15%. The use of CH_4-DRC was restricted to quantify [111]Cd with an error of 16%. The use of O_2-DRC was suitable for determining [55]Mn, [66]Zn with errors lower than 3% and [51]V, when monitored it in oxide form [67]VO, with an accuracy error of 2%. O_2-DRC is the single DRC mode that allowed a satisfactory quantification of [75]As, with an error of 33% for a very low concentration, compared to other analysis mode in the direct analysis of seawater. Additionally Pb can be quantitatively recovered from spiked samples using NH_3 and O_2-DRC modes.

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1. Introduction

Trace mineral elements in oceans come from two kind of external sources: i) Natural sources as leaching of soil minerals, volcanic discharges, fires and ii) anthropogenic sources associated to pollution phenomena (urban waste waters, agricultural and industrial wastes, and combustion of fossil fuels) [1]

Trace elements are classified in two categories as essential and toxic ones depending on their biological functions. So, it is possible to distinguish between essential or bioactive elements which are necessaries for growth, normal physiological behaviour and life maintenance [2] and toxic elements without any metabolic function. Some of these elements are Ag, As, Au, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Se, U, V, Zn. In general at low concentration, Cr, Co, Cu, Mn, Mo, Se and Zn could act as essential elements for living beings, but some as As, Mo, Ni and V are essential only for some forms of life [3], and the optimal biological range is really narrow, and frequently their can cause pathologies [4]. So, all of them

can be considered as toxics at high concentration and can pass easily to the food chain through water plants and animals. Ag, Cd, Pb and U elements are directly toxic and Au is not considered an essential element but it might be involved in some bacterial activity [5].

The monitoring of mineral elements in seawater is important due to the effects of anthropogenic activities, in the marine wildlife particularly and in the food chain, in general. The environmental contamination by heavy metals is one of the most important matters for the human health, and for this reason, accurate and precise methodologies are required for their accurate determination.

Trace elements determination in a complex matrix, like seawater, is difficult due to their very low concentration on the samples and the matrix effects derived from the saline composition (3.5% w/v) which gets difficult the quantification of the trace elements. So, these special seawater characteristics make necessary the elimination of matrix interferences. Inductively coupled plasma mass spectrometry (ICP-MS) is an excellent tool for trace element analysis that can provide high sensitivity, precision, wide dynamic range and robustness. However, in spite the simplicity of mass atomic spectra, a lot of spectral interferences [6] can be present due to the overlap between molecular or atomic ions which have the same m/z ratio as the analyte. So, Table 1 are reflects

Table 1
The most frequent polyatomic interferences derived from seawater matrix.

Isotope	Interferences
^{51}V	$^{35}Cl^{16}O$, $^{40}Ar^{11}B$, $^{37}Cl^{14}N$
^{52}Cr	$^{35}Cl^{16}O^{1}H$, $^{40}Ar^{12}C$, $^{36}Ar^{16}O$, $^{37}Cl^{15}N$, $^{37}Cl^{14}N^{1}H$, $^{38}Ar^{14}N$, $^{35}Cl^{17}O$
^{55}Mn	$^{40}Ar^{14}N^{1}H$, $^{39}K^{16}O$, $^{37}Cl^{18}O$, $^{40}Ar^{15}N$, $^{37}Cl^{17}O^{1}H$, $^{23}Na^{32}S$, $^{23}Na^{16}O_2$
^{58}Ni	$^{23}Na^{35}Cl$, $^{40}Ar^{18}O$, $^{42}Ca^{16}O$
^{60}Ni	$^{44}Ca^{16}O$, $^{23}Na^{37}Cl$, $^{43}Ca^{16}O^{1}H$, $^{25}Mg^{35}Cl$
^{59}Co	$^{43}Ca^{16}O$, $^{42}Ca^{16}O^{1}H$, $^{24}Mg^{35}Cl$, $^{36}Ar^{23}Na$, $^{23}Na^{35}Cl^{1}H$
^{63}Cu	$^{40}Ar^{23}Na$, $^{40}Ca^{23}Na$
^{65}Cu	$^{40}Ar^{25}Mg$, $^{40}Ar^{24}Mg^{1}H$, $^{48}Ca^{16}O^{1}H$
^{64}Zn	$^{48}Ca^{16}O$, $^{40}Ar^{24}Mg$, $^{40}Ar^{23}Na^{1}H$
^{66}Zn	$^{40}Ar^{26}Mg$
^{68}Zn	$^{40}Ar^{14}N_2$
^{75}As	$^{40}Ar^{35}Cl$, $^{40}Ca^{35}Cl$
^{78}Se	$^{40}Ar^{38}Ar$, $^{38}Ar^{40}Ca$, $^{40}Ar^{37}Cl^{1}H$
^{80}Se	$^{40}Ar_2$, $^{40}Ar^{40}Ca$, $^{32}S^{16}O_3$, $^{79}Br^{1}H$
^{111}Cd	$^{79}Br^{32}S$

the polyatomic interferences produced mostly by the seawater components of seawater associated to the elements and isotopes commonly studied [7,8,9], being all of them with unitary positive charge.

They are available several techniques to balance, reduce or remove the aforementioned interferences as: i) the use of mathematical equations of correction, ii) the cold plasma technique or iii) the use of reaction/collision cells [6]. The mechanisms of interactions between polyatomic ions and gaseous molecules in DRC and collision cell have been widely studied [10]. In the reaction cell, interfering polyatomic ions, which could get into the cell in the ion beam together with the analyte ions interact with molecules of reaction gas, creating non-interfering reaction products at different mass values, being thus eliminated from the ion flow. The reaction selectivity is achieved through the choice of the reaction gas and electrical parameters of the quadrupole cell. In the collision cell, polyatomic ions collide with ions of inert gases and dissociate in ions or atoms less energetic than previous ones, being eliminated.

The reaction cell can use different gases as reaction gas. A very few research publications have described procedures of seawater analysis by using different gases in a direct way of analysis by employing direct reaction cell (DRC), collision cell or both [8,11,12,13]. Other authors used this technique in detection and quantification of elements after a sample pre-concentration procedures as co-precipitation with $Mg(OH)_2$ [14,15] or solid phase extraction [16]. However, the DRC mode needs an optimization of instrumental conditions as a function of samples to be analysed in order to avoid matrix interferences. In this work, we have evaluated the use of three different reaction gases (NH_3, CH_4 and O_2) for the determination of 15 elements and different isotopes.

For the optimization of an analytical method, it is necessary to sequentially or simultaneously adjust several factors in order to establish the best analysis conditions. This process can demand time, reagents and hard work if univariate strategies were used. Another drawback of the univariate optimization strategy is the lack of consideration of interactions between the different factors that may affect the results. So, it has been evidenced that univariate studies could provide false optimization results highly affected by the starting conditions of study.

Otherwise, they are methodologies that use mathematical and statistical tools that enable the design of experimental strategies and treatment and interpretation of data to optimize several variables simultaneously, with a reduced number of experiences. Experimental Statistical Design permits this improving the speed and accuracy of optimization methods as compared with the univariate sequential methods. It also permits to estimate the statistical relevance and significance of factors that can affects the process and to evaluate the interaction between the factors. In our knowledge, the use of statistical design processes has been reduced to the evaluation of three parameters in multiple collector inductively coupled plasma- mass spectrometry

(MC-ICP-MS) for Gd determination in spent nuclear fuel [17], four parameters in ICP-OES determination of Se and As determination in estuarine sediments [18] and three parameters for Li, Na, K, Al, Fe, Mn and Zn determination in human serum [19]. In this study, we have used Experimental Statistical Design to optimize the instrumental conditions of DRC-ICP-MS for fifteen trace elements direct determination in seawater, with different isotopes, also comparing the efficiency of the use of different reaction gases.

2. Experimental

2.1. Reagents and standards

ICP multielement standard solution containing 26 elements at a concentration level of 100 mg/L was purchased from Scharlab (Barcelona, Spain). ICP Uranium standard of 10 g/L Fisher Chemical from Fisher Scientific (Madrid, Spain). Atomic absorption spectrometry AAS gold standard of 1000 mg/L from Panreac (Barcelona, Spain) prepared from $HAuCl_4·4H_2O$ in HCl 1.2% (v/v). Silver nitrate for analysis from Merck (Madrid, Spain). AAS rhodium standard solution Specpure of 1000 mg/L Alfa Aesar from VWR International Eurolab (Barcelona, Spain) was employed as internal standard.

Artificial seawater was prepared employing 99.999% (w/w) sodium chloride Trace Select, 99.9995% (w/w) potassium chloride Trace Select, 99.999% (w/w) sodium fluoride Trace metal basis and 99,999% (w/w) boric acid Trace metal basis from Sigma-Aldrich (Madrid, Spain). 99.998% (w/w) sodium hydrogen carbonate Puratronic, 99.9955% (w/w) sodium sulfate anhydre Puratronic, 99,999% (w/w) potassium bromide Puratronic, 99.999% (w/w) magnesium chloride hexahydrate Puratronic and 99.9965% (w/w) calcium chloride monohydrate Puratronic from Alfa Aesar. Ultrapure ammonia, methane or oxygen from Carburos Metálicos (Cornellà de Llobregat, Spain) were used as the reaction gas to be introduced in the dynamic reaction cell (DRC).

All solutions were prepared with high-purity deionized water, with a resistivity higher than 18.2 MΩ, obtained using a MilliQ-plus unit from Millipore (Bedford, MA, USA) and 69% (v/v) nitric acid trace metal analysis from Scharlab, was used for sample dilution.

For ICP-MS daily performance checking, a solution containing 1 μg/L Ba, Be, Ce, Co, In, Mg and U in 0.5% (v/v) HNO_3 was used.

2.2. Sample preparation

The high saline content of seawater samples causes several physical problems in their direct analysis like gradual deposition of salts in nebulizer, torch, cones and even in the lenses which result in a signal drift and a continued need to clean the system.

A simple mode to reduce the aforementioned problems is to dilute the samples. Different dilution factors were assayed and finally chosen a dilution factor of 1/10 that presents an adequate reproducibility corresponding to a relative standard deviation of <5%.

Because of the particular characteristics of elements considered, samples were prepared in acid media to assure their stability and to avoid their adsorption in both, bottles and system tubes. The use of nitric acid in several proportion was evaluated and finally a fixed a 0.5%v/v concentration was selected to prepare the samples. This proportion assures an adequate clean of system, eliminates the memory effects and minimizes the contribution to background.

Samples were diluted 1/10 with 0.5% nitric acid prior to their analysis; triplicate samples were diluted and analysed for all experiments. As an internal standard, 10 μg/L of Rh was added to all standard and sample solutions. These solutions were then introduced into the ICP-MS system.

Five liters of artificial seawater were prepared with high purity alkaline and alkaline heart salts and at levels described by Lyman and Fleming [20], excluding $SrCl_2$ to avoid the formation of precipitates with sulphates present in the sample. Once the salts were dissolved, solutions were acidified with 5 mL of 69% HNO_3.