

Evaluation of commercial C18 cartridges for trace elements solid phase extraction from seawater followed by inductively coupled plasma-optical emission spectrometry determination

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Abstract

Possibilities of the use of commercial C18 cartridges to separate and preconcentrate trace elements from seawater have been evaluated. Trace elements (Al, Cd, Cu, Fe, Mn, Ni, Pb, Sn, V and Zn) were previously complexed with 8-hydroxyquinoline, 8-HQ (5×10^{-4} M as final concentration) at alkaline pH (8.0 ± 0.1) and then they were eluted with 2.5 ml of 2.0 M nitric acid. Metals eluted from cartridges were measured by inductively coupled plasma-optical emission spectrometry (ICP-OES). Variables affecting the metal-8-HQ complexation such as pH and 8-HQ concentration, and affecting the metal-8-HQ complexes solid phase adsorption and elution (load and elution flow rates and concentration and volume of eluting solution) were studied in order to find compromise operating conditions for the simultaneous metals complexation, adsorption and elution. After studies of contamination of commercial C18 cartridges for trace metals, high reagent blanks were reached for Ti so that they are useless for the determination of this element. In addition, commercial C18 cartridges can be used at least seven times without loss of adsorption properties. Working with a seawater sample volume of 100 ml and using an optimum nitric acid volume of 2.5 ml for elution, a preconcentration factor of 40 was achieved, factor high enough to determine trace elements in unpolluted surface seawater samples by ICP-OES. Analytical performances, such as limits of detection and quantification, repeatability of the overall procedure and accuracy, by analyzing saline (CASS-3 and SLEW-3) and non-saline (TM-24) certified reference materials, were finally assessed. © 2004 Elsevier B.V. All rights reserved.

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1. Introduction

Seawater analysis for heavy metals and other contaminants is increasing in contamination studies owing to the need to guarantee the good quality of seawater for different purposes. This is especially important for coastal or estuarine seawater because of the large number of industries dealing with seafood production which use the estuaries to keep, mainly, molluscs and seaweed. In fact, there is European Di-

rective relating to the quality of water to keep molluscs which limits the levels of several heavy metals such as Ag, As, Cd, Cr, Cu, Hg, Ni, Pb and Zn [1].

Since trace metal concentration levels in seawater are very low [2], sensitive analytical techniques as well as preconcentration methods must be used to assess background levels of trace elements. In addition, the saline composition of seawater can be an important drawback in seawater analysis because it is a source of high background signals [3] and, when using inductively coupled plasma-optical emission spectrometry (ICP-OES), a source of spectral [4] and matrix interferences [5]. To overcome these problems, different

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procedures such as liquid–liquid extraction, coprecipitation, electrodeposition and solid phase extraction, mainly using ionic exchange resins, have been developed. Among all these procedures, solid phase extraction techniques are quite popular since they offer a number of important advantages over other preconcentration methods. One of these benefits is that sorbent material can be packed into mini-columns or cartridges which provide sufficient exchanged/adsorption capacity for many applications [6,7].

The adsorption of non-polar species onto active carbon, silica gel or alumina is well established for non-polar and less polar organic analytes. However, a previous derivatisation stage is mandatory for inorganic species because only uncharged (non-polar) species can interact with the adsorbent material. Therefore, these methods involve a previous complexation of trace metals with an organic chelating reagent [8–12], which must form uncharged metal-complexes. 8-Hydroxyquinoline (8-HQ) forms uncharged chelates with at least 60 elements [13,14] and offers as advantage its lack of affinity for alkaline and alkaline earth metals. Some works dealing with the adsorption of metal-oxinates, such as the applications by Abbasse et al. [7,15] and Skinner and Salin [16], can be found in literature and all these procedures use high purity C18 adsorbent material laboratory-packed into columns.

One of the aims of the current work is evaluating the possibilities of use of commercial C18 cartridges, commonly used for non-polar organic compounds pre-concentration and for clean-up purposes, for trace metals solid phase extraction. This evaluation has implied a study on the trace metals released from new commercial C18 cartridges, and the findings of a procedure to wash and prepare the cartridges for trace elements. In addition, the possibility of reusing the C18 cartridges was also considered in this study.

2. Experimental

2.1. Instrumentation

An Optima 3300 DV inductively coupled plasma-optical emission spectrometer (Perkin-Elmer, Norwalk, USA) equipped with an autosampler AS 91 (Perkin-Elmer) and a GemCone cross flow nebulizer type (Perkin-Elmer) and a cyclonic spray chamber (Perkin-Elmer) was used for all measurements. An 8-way Gilson peristaltic pump (Gilson, Villiers, France) equipped with 3.18 mm i.d. Tygon tubes (Gilson) was used to drive samples through the C18 chemically bonded silica gel (Sep-Pack Plus – 360 mg, Waters, Milford, MA, USA). A Class-100 clean fume hood (Telstar S.A., Terrassa, Spain) was used to perform all experiments in order to avoid contamination of samples and reagents.

2.2. Reagents

Ultra-pure water of resistivity 18 M Ω cm obtained from a Milli-Q purification device (Millipore Co., Bedford, MA,

USA). High purity nitric acid and hydrochloric acid were from Panreac (Barcelona, Spain). High purity ammonia and analytical grade methanol were purchased from Merck (Darmstadt, Germany). 8-Hydroxyquinoline solution (0.5 M) was prepared from analytical grade reagent (Merck) by dissolving in a 2.0 M hydrochloric acid solution. Ammonium acetate (0.01 M) was prepared from analytical grade reagent ammonium acetate (Merck) by dissolving in Milli-Q water. Multi-elemental standard solution containing As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, V, Ti and Zn at 100 $\mu\text{g ml}^{-1}$ was obtained from Perkin-Elmer. Single standard solutions of As, Cd, Cr, Ni, Pb, V, Sn and Zn (Merck), Al, Cu and Fe (Perkin-Elmer) and Mn (Panreac) at 1000 $\mu\text{g ml}^{-1}$ were also used. Coastal seawater (CASS-3) and estuarine seawater (SLEW-3) certified reference materials were obtained from the National Research Council of Canada. Lake water (TM-24) certified reference material was purchased by the National Water Research Institute of Canada.

All glass- and plastic-ware were rigorously cleaned and kept into 10% (m/m) nitric acid for at least 48 h. The material was then rinsed three times with Milli-Q water.

2.3. Seawater collection

Seawater samples were collected from the Ría de Muros-Noia estuary (north-west Spain) in pre-cleaned high density polyethylene bottles. After collection, seawater samples were acidified at pH lower than 2.0 by adding concentrated nitric acid in order to avoid metal adsorption onto the inner bottles walls. Acidified seawater samples were then filtered through a 0.45 μm polycarbonate membrane Nucleopore filter (Millipore).

2.4. C18 cartridge preparation

C18 sorbent packing material was firstly washed by passing 25 ml of 2.0 M nitric acid solution at a flow rate of 1.5 ml min $^{-1}$ in order to remove trace metals adsorbed in the packing material. Then, the C18 cartridges were rinsed by pumping 25 ml of Milli-Q water and they were activated by washing with 10 ml of methanol and rinsed with 10 ml of Milli-Q water. Finally, the activated silica into cartridges was conditioned by passing 10 ml of 0.01 M ammonium acetate (pH 7.0).

2.5. C18 cartridge solid phase extraction procedure

A volume of 0.1 ml of 0.5 M 8-HQ solution was added to 100 ml of acidified seawater samples, giving a final 8-HQ concentration of 5×10^{-4} M. Then, the pH was readjusted to 8.0 ± 0.1 by addition of a small volume (1–2 ml) of a 5.0 M ammonia solution. The seawater sample was then passed through a cleaned and conditioned C18 cartridge at a fixed flow rate of 6.0 ml min $^{-1}$ by using a peristaltic pump. The cartridges were then rinsed with 10 ml of 0.01 M ammonium acetate in order to remove the saline matrix, and the

adsorbed metal-complexes were eluted with 2.5 ml of 2.0 M nitric acid at a flow rate of 4.5 ml min^{-1} . A pre-concentration factor of 40 was achieved under these operating conditions.

2.6. ICP-OES measurements

Eluted trace elements were measured by ICP-OES (axial configuration, radiofrequency power of 1300 W and plasma, auxiliary and nebulizer gas flows of 15.0, 0.5 and 0.81 min^{-1} , respectively) without dilution. The standard addition method, covering analyte concentrations of 0, 0.04, 0.08 and 0.16 mg l^{-1} (Cd, Cu, Ni, Pb and V); 0, 0.2, 0.4 and 0.8 mg l^{-1} (Mn and Zn); 0, 0.4, 0.8 and 1.6 mg l^{-1} (Sn); 0, 1.0, 2.0 and 4.0 mg l^{-1} (Fe) and 0, 2.0, 4.0 and 8.0 mg l^{-1} (Al), taking into account a pre-concentration factor of 40, was used.

3. Results and discussion

In order to verify possible trace metal contamination of commercial C18 cartridges, five different aliquots (5 ml each one) of 2.0 M nitric acid solution were passed through the cartridges at a flow rate of 1.5 ml min^{-1} . The five sequential eluates, as well as 5 ml of a 2.0 M nitric acid solution (blank), were analysed by ICP-OES. Negligible concentrations in the five washing solutions were found for As, Cd, Cr, Cu, Mn, Ni and Pb. However, contamination was observed for Al, Fe, Ti, Sn and Zn, mainly after passing the first 5 ml nitric acid aliquot (Fig. 1). These metal concentrations were reduced moreover the volume of nitric acid solution was in-

creased and after passing 25 ml of the washing solution (the last 5 ml aliquot) the concentration of most of them were similar than those metal concentrations in 2.0 M nitric acid solution (blank). However, Ti concentrations found in the last washing solution was still extremely high, around $97 \text{ } \mu\text{g l}^{-1}$. Contamination of C18 cartridges by Ti must be probably due to the use of Ti-based devices for grinding and packing the adsorbent material. Further experiments, implying a more concentrated nitric acid solution as well as larger volumes of washing solution, were carried out in order to reduce the levels of Ti before using the cartridges for trace elements pre-concentration. All these experiments have resulted in high levels of Ti released from C18 cartridges. Therefore, Ti was not considered in further studies because of high Ti levels released from commercial C18 cartridges.

3.1. C18 cartridges solid phase extraction

Preliminary studies on the effect of the 8-HQ concentration on the formation of metal-8-HQ complexes have revealed that this variable is not significant. Therefore, an excess of 8-HQ concentration of $5 \times 10^{-4} \text{ M}$ to guarantee the formation of neutral metal-oxinates [14] was used for all experiments. This 8-HQ concentration is quite similar than those previously reported by other authors [7,16].

3.1.1. Effect of the pH on the metal-complexes formation

The efficiency of 8-HQ to react with metals and form uncharged metal-8-HQ complexes is largely dependent on pH. This is because 8-HQ is an ampholyte, forming oxinium (8-hydroxyquinolinium) ion by protonation of N in acid solutions and oxinate ion in basic solutions [13]. Most of the divalent and trivalent elements react with the oxinate form and the establishment of optimum pH values for the different elements is necessary.

To study the effect of pH on the efficiency of metal-8-HQ complexes formation, different aliquots of 100 ml from an acidified seawater sample were spiked with $3 \text{ } \mu\text{g l}^{-1}$ of each metal. Trace metals were complexed with 8-HQ and the pH was readjusted by adding small volumes of 5.0 M ammonia solution to obtain pH values within the 7.5–9.5 range. Each pH value was tested three times. Solutions were passed through the pre-conditioned commercial C18 cartridges at a fixed load flow rate of 1.5 ml min^{-1} by using a peristaltic pump. The cartridges were then rinsed with 10 ml of 0.01 M ammonium acetate in order to remove the saline matrix, and the adsorbed metal-8-HQ were eluted with 5.0 ml of 2.0 M nitric acid at an elution flow rate of 0.6 ml min^{-1} . Trace metal concentrations for each experiment at each pH value after analyzing the spiked seawater samples using metal standards in 2.0 M nitric acid for calibration are plotted in Fig. 2.

It can be seen that most of the studied metals are largely formed/retained at pH 8.0. Elements such as Cu, Ni, Fe, Sn and Pb appear not being dependent on the pH value, while As, Cd and Mn are efficiently complexed and retained at pHs within 8.0–9.5 range, decreasing at pHs lower than 8.0.

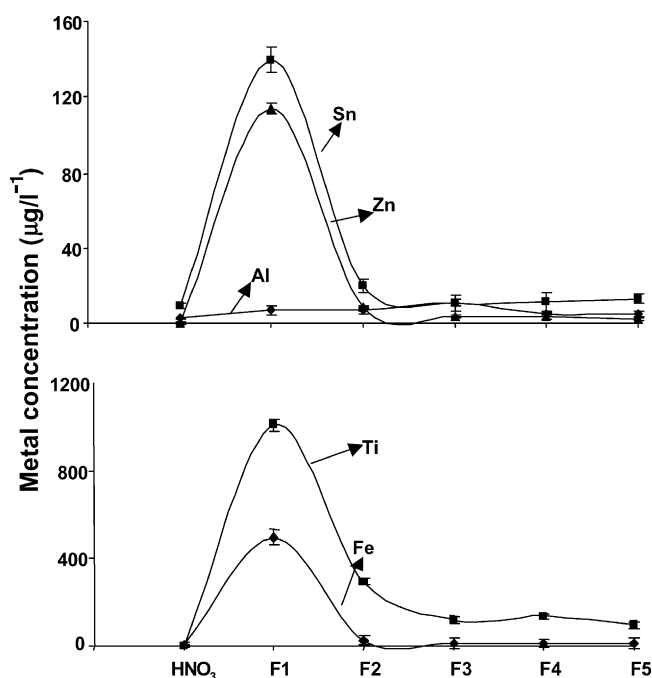


Fig. 1. Concentrations of selected metals in 2.0 M nitric acid washing solutions after passing through commercial Sep-Pack Plus C18 cartridges.

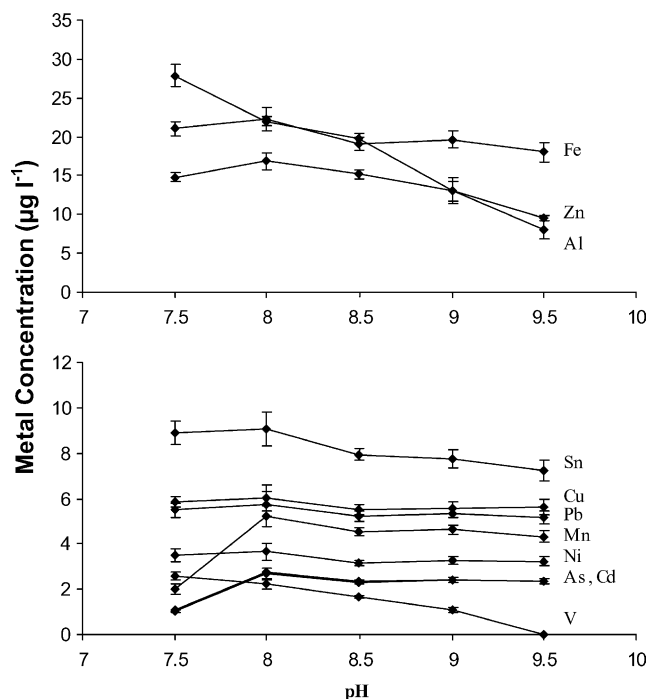


Fig. 2. Effect of the pH on the metal complexation with 8-HQ.

However, V and Al are not complexed and/or retained at high pH values, and a decrease on the formation/adsorption efficiency is observed for pH higher than 7.5. This result can be expected for V, because the most stable species is VO^{2+} , which is only complexed by 8-HQ in acid medium (pH 7.0 or lower than 7). At alkaline pH, VO^{2+} is oxidised to VO_4^{3-} , species which is not complexed by the oxinate form of 8-HQ [7]. Finally, Zn offers a particular trend, showing decreases on the solid phase extraction efficiency when using pH higher and lower than 8.0. Therefore and in order to fix compromise conditions for all elements tested, a pH of 8.0 was chosen, pH that results adequate for most of the elements studied, except for Al and V, for which a pH close to 7 would be the best.

3.1.2. Effect of volume and concentration of nitric acid for elution

Elution conditions were carefully studied. Since uncharged metal-8-HQ complexes are adsorbed onto the adsorbent packing material in C18 cartridges, elution of metals must imply the metal-8-HQ destruction, obtaining divalent and trivalent charged metals which do not interact with the adsorbent. This is easily reached using an acid [7,15] as eluting solution or using methanol [16]. Therefore, different nitric acid solutions were tested in order to elute metals. Two variables affecting metals elution were studied: the nitric acid concentration and the nitric acid volume. This last variable should adopt the lowest value so that a large pre-concentration factor could be assessed. Therefore, two nitric acid solutions at 2.0 and 4.0 M were simultaneously studied for eluting volumes between 2.5 and 6.0 ml (pre-concentration factors within the 40.0–16.7 range). The eluting volume of 2.5 ml

was the lowest volume studied because the ICP-OES used requires at least 2.0 ml to perform the measurements. It must be also noticed that there are many systems that can work with smaller volumes, hence higher pre-concentration factor may be possible.

Under optimum values for pH, metal-8-HQ retained on the C18 cartridge were eluted at a fixed flow rate of 0.6 ml min^{-1} using different nitric acid volumes and nitric acid concentrations. Results have shown that efficient metals elution are reached under all nitric acid volumes when using 2.0 M nitric acid as eluting solution. Similar results have been obtained when using 4.0 M nitric acid. Therefore, the lowest nitric acid concentration (2.0 M) and the lowest nitric acid volume (2.5 ml) were chosen, implying a pre-concentration factor of 40.

3.1.3. Effect of the load flow rate on the metal-complexes solid phase extraction

Load flow rate through the C18 cartridges should be fast enough to perform the solid phase extraction in a short time, but it should be slow enough to allow the interaction between the metal-complexes and the adsorbent packing material in the cartridges.

To study this variable, different aliquots of 100 ml from an acidified seawater sample spiked with $3 \mu\text{g l}^{-1}$ of each metal were 8-HQ complexed at a pH 8.0 and the solutions were loaded on the C18 cartridges at different flow rates, from 1.5 to 9.0 ml min^{-1} . After sample load, the cartridges were rinsed with 0.01 M ammonium acetate solution (10 ml) and the retained metal-8-HQ were eluted with 2.5 ml of a 2.0 M nitric acid at a flow rate of 0.6 ml min^{-1} . Results have shown that 8-HQ can be retained when pumping solutions at flow rates within the 1.5 and 6.0 ml min^{-1} . Larger load flow rates than 6.0 ml min^{-1} has led to uncompleted adsorption for some elements, such as Mn. Therefore, a sample load flow rate of 6.0 ml min^{-1} was selected. This rate is high enough to load the sample in a moderate short time and so that metal-8-HQ can interact with the adsorbent material.

3.1.4. Effect of the elution flow rate

The effect of elution flow rate was finally studied. After fixing all variables at optimum values (pH 8.0, load flow rate 6.0 ml min^{-1} and 2.5 ml of 2.0 M nitric acid for elution) metal-8-HQ retained were eluted at flow rates from 0.6 to 4.5 ml min^{-1} . Results showed that metals are efficiently eluted from cartridges at all elution flow rates studied and an elution flow rate of 4.5 min^{-1} was selected.

3.1.5. Study of the number of solid phase extraction performed with conventional C18 cartridges

Commercial C18 cartridges, although sold as single use cartridges, were tested in order to know the number of sequential solid phase extraction that can be performed without losses on metal-8-HQ adsorption and/or metals elution. This experiment was carried out with three different cartridges which were used several times for a period of 2 months.

Different seawater samples spiked with variable concentrations of metals were determined and the analytical recoveries for each element obtained. Results have shown that some elements such as Cu, Fe, Pb, Sn and Zn are not efficiently retained/eluted after seven uses, and analytical recovery is poor when using the same C18 cartridges more than seven times. In addition, it has been found that for some elements, even being efficiently retained after seven uses, the repeatability got worse when using the cartridges more than seven times. Therefore, conventional C18 cartridges can be used at least seven times without losing of efficiency of the adsorbent packing material adsorption properties.

3.2. Analytical performance

Although solid phase extraction implies metals separation from the seawater matrix, a comparison between calibration matched with 2.0 M nitric acid and standard addition was established for each element in order to study possible matrix effect. The standard addition technique was obtained after spiking different 100 ml aliquots from the same acidified seawater sample by triplicate with different metal concentrations (up to $4.0 \mu\text{g l}^{-1}$ for As, Cd, Cu, Ni, Pb and V, $20 \mu\text{g l}^{-1}$ for Mn and Zn, $40 \mu\text{g l}^{-1}$ for Sn, $100 \mu\text{g l}^{-1}$ for Fe and $200 \mu\text{g l}^{-1}$ for Al). After solid phase extraction, the eluates were measured by ICP-OES (Section 2.6) and 2.0 M nitric acid calibrations and standard addition graphs were obtained. The standard deviation and the mean for the slopes of two standard addition graphs and six external 2.0 M nitric acid calibrations were statistically compared by using the Cochran's C and Bartlett's tests at 95.0% to compare variances, and the ANOVA test to compare means. It can be said that slopes for external 2.0 M nitric acid calibration and standard addition graphs are statistically different for all cases, except for V. Therefore, although a large volume of ammonium acetate solution was used to remove possible salts on C18 cartridges just before metals elution, a certain matrix effect was observed when determining all elements, being necessary the establishment of a standard addition graph to perform seawater analysis.

The limit of detection, given by $\text{LOD} = 3(\text{S.D.}/m)$, where S.D. is the standard deviation of eleven measurements of a reagent blank, and m the slope of the standard addition graph, were calculated. After a pre-concentration factor of 40, LODs of 1.28, 0.04, 0.04, 0.02, 0.19, 0.001, 0.03, 0.03, 0.07, 0.06 and $1.13 \mu\text{g l}^{-1}$, were reached for Al, As, Cd, Cu, Fe, Mn, Ni, Pb, Sn, V and Zn, respectively. Such LODs are low enough to determine trace metals levels in unpolluted seawater samples.

The repeatability of the over-all procedure (solid phase extraction and ICP-OES determination) was assessed by analyzing three times a same seawater sample. The average percent relative standard deviations (R.S.D.s) were 3.5, 0.7, 3.7, 6.3, 4.7, 5.3, 0.2, 5.2, 5.4, 7.5 and 3.5% for Al, As, Cd, Cu, Fe, Mn, Ni, Pb, Sn, V and Zn, respectively. Since these results it can be concluded that the procedure offer good repeatability for all elements (R.S.D.s lower than 10%).

Table 1

Percent analytical recoveries ($n = 6$) of the method

	Percent analytical recoveries		
	Low ^a	Medium ^b	High ^c
Al	87.3 ± 3.0	92.0 ± 1.3	101.2 ± 1.7
As	102.3 ± 1.5	101.6 ± 0.2	100.1 ± 0.1
Cd	103.3 ± 0.8	101.7 ± 0.4	100.3 ± 0.1
Cu	107.6 ± 1.7	101.9 ± 3.2	100.9 ± 0.5
Fe	95.1 ± 2.3	98.7 ± 1.9	99.7 ± 0.3
Mn	104.9 ± 4.0	102.1 ± 0.9	100.3 ± 0.3
Ni	106.3 ± 1.3	104.7 ± 2.7	100.8 ± 0.8
Pb	98.3 ± 1.8	99.0 ± 5.2	99.9 ± 0.1
Sn	92.2 ± 0.3	92.5 ± 5.3	99.8 ± 0.3
V	70.7 ± 5.2	97.9 ± 0.6	87.7 ± 6.6
Zn	108.2 ± 0.4	102.7 ± 3.4	100.2 ± 0.7

^a $1 \mu\text{g l}^{-1}$ for As, Cd, Cu, Ni, Pb and V; $5 \mu\text{g l}^{-1}$ for Mn and Zn; $10 \mu\text{g l}^{-1}$ for Sn; $25 \mu\text{g l}^{-1}$ for Fe and $50 \mu\text{g l}^{-1}$ for Al.

^b $2 \mu\text{g l}^{-1}$ for As, Cd, Cu, Ni, Pb and V; $10 \mu\text{g l}^{-1}$ for Mn and Zn; $20 \mu\text{g l}^{-1}$ for Sn; $50 \mu\text{g l}^{-1}$ for Fe and $100 \mu\text{g l}^{-1}$ for Al.

^c $4 \mu\text{g l}^{-1}$ for As, Cd, Cu, Ni, Pb and V; $20 \mu\text{g l}^{-1}$ for Mn and Zn; $40 \mu\text{g l}^{-1}$ for Sn; $100 \mu\text{g l}^{-1}$ for Fe and $200 \mu\text{g l}^{-1}$ for Al.

The accuracy of the method was verified by studying the analytical recovery and by analyzing different saline water certified reference materials (CASS-3 and SLEW-3) and a non-saline water certified reference material (TM-24). Analytical recovery was assessed for three concentration levels, after spiking two different seawater samples with analyte concentrations of 1.0, 2.0 and $4.0 \mu\text{g l}^{-1}$ for As, Cd, Cu, Ni, Pb and V; 5, 10 and $20 \mu\text{g l}^{-1}$ for Mn and Zn; 10, 20 and $40 \mu\text{g l}^{-1}$ for Sn; 25, 50 and $100 \mu\text{g l}^{-1}$ for Fe and 50, 100 and $200 \mu\text{g l}^{-1}$ for Al. The concentration levels tried are representative of clean surface seawaters. Each concentration level in each seawater samples was tried three times, thus, analytical recoveries listed in Table 1 are the mean of six independent measurements. From Table 1 it can be concluded that good analytical recovery (within the 90–110% range) are reached for all elements at all concentration levels, except for V at the lowest concentration level. This could be attributed to a less efficient solid phase extraction for V for which a more acidic pH (lower than 8.0) would be desirable.

CASS-3, SLEW-3 and TM-24 certified reference materials were analyzed by triplicate for most of the elements. Determinations were performed by using the standard addition technique. Results, listed in Table 2, reveal good agreement between found concentrations and certified values for most of the elements in the three certified reference materials. However, Cd, Pb and Zn have not been determined in CASS-3 and SLEW-3 because certified concentrations of these elements in these materials are lower than the LODs of the method for these elements. In addition, V concentration found is not within the V certified concentration range due to a pH of 8.0 is not the optimum to form V-8-HQ complexes (see Fig. 2). Finally and although As levels in the three certified reference materials are quite higher than the LOD of the method for this element, As in the three certified reference materials was not determined. Arsenic is present mainly as HAsO_4^{2-} (As(V))

Table 2

Analysis of certified reference materials ($n = 3$)

	SLEW-3		CASS-3		TM-24	
	Certified ($\mu\text{g l}^{-1}$)	Found ($\mu\text{g l}^{-1}$)	Certified ($\mu\text{g l}^{-1}$)	Found ($\mu\text{g l}^{-1}$)	Certified ($\mu\text{g l}^{-1}$)	Found ($\mu\text{g l}^{-1}$)
Al	–	–	–	–	22 \pm 19	28 \pm 1
As	1.36 \pm 0.09	^a	1.09 \pm 0.07	^a	2.7 \pm 1.0	^a
Cd	0.048 \pm 0.004	<LOD	0.030 \pm 0.005	<LOD	12.5 \pm 3.5	14.6 \pm 1.0
Cu	1.55 \pm 0.12	1.96 \pm 0.12	0.517 \pm 0.062	0.648 \pm 0.060	8.0 \pm 4.1	9.0 \pm 0.3
Fe	0.568 \pm 0.059	0.520 \pm 0.002	1.26 \pm 0.17	1.09 \pm 0.12	5.4 \pm 2.3	5.4 \pm 0.5
Mn	1.61 \pm 0.22	1.62 \pm 0.19	2.51 \pm 0.36	2.78 \pm 0.38	3.1 \pm 1.4	2.9 \pm 0.1
Ni	1.23 \pm 0.07	1.35 \pm 0.13	0.386 \pm 0.062	0.353 \pm 0.033	3.5 \pm 3.0	3.7 \pm 0.1
Pb	0.0090 \pm 0.0014	<LOD	0.012 \pm 0.004	<LOD	7.3 \pm 2.6	9.7 \pm 0.2
V	2.57 \pm 0.31	1.96 \pm 0.16	–	–	6.7 \pm 2.0	4.0 \pm 1.0
Zn	0.201 \pm 0.037	<LOD	1.24 \pm 0.25	<LOD	13.6 \pm 4.8	20.8 \pm 0.4

^a Not determined.

in seawater [2] but 8-HQ only reacts with As(III) species. Therefore, good analytical recovery is reached when spiking with As(III), as shown in Table 1, but lack of accuracy has been obtained after analyzing certified reference materials, in which As occurs as As(V).

4. Conclusions

The use of commercial Sep-Pack Plus C18 silica cartridges, commonly used for non-polar organic analytes, can be used to pre-concentrate trace elements from seawater after 8-HQ complexation. A previous washing step, involving the use of 25 ml of 2.0 M nitric acid, is required to avoid contamination from the silica adsorbent packing material. After this wash treatment, contamination problems are significant for Ti and this element cannot be pre-concentrated because of high reagent blanks. In addition, although C18 cartridges are sold as single use cartridges, they can be reused at least seven times without losing of analytical performances. Compromise conditions for different variables affecting the metal-8-HQ formation and the adsorption on and elution from the adsorbent silica allow the simultaneous solid phase extraction of Al, Cd, Cu, Fe, Mn, Ni, Pb, Sn, V and Zn from seawater. The optimized solid phase extraction is fast and it offers a high sample treatment rate (simultaneous solid phase extraction of eight samples can be carried out using an 8-way peristaltic pump in 30 min). In addition, the sample volume required is low when comparing to other proposed methods [7,16], which imply a fast sampling and advantages when storing samples. This fact combined with the adequate

sensitivity by ICP-OES of new generation allows the application of this method to routine multi-element analysis of seawater.

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