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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.

Keywords: Commercial C18 cartridges; Solid phase extraction; Trace metals; Unpolluted surface seawater; Inductively coupled plasma-optical emission spectrometry

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 Directive 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 MΩ 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 (Darmstad, 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 $\mu g\,ml^{-1}$ 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 $\mu g\,ml^{-1}$ 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