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Simultaneous speciation analysis of Sb(III), Sb(V) and $(CH_3)_3SbCl_2$ by high performance liquid chromatography-hydride generation-atomic fluorescence spectrometry detection (HPLC-HG-AFS): Application to antimony speciation in sea water

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Abstract

This paper presents an improvement for the simultaneous separation of Sb(V), Sb(III) and $(CH_3)_3SbCl_2$ species by high performance liquid chromatography (HPLC) and its detection by hydride generation-atomic fluorescence spectrometry (HG-AFS). The separation was performed on an anion exchange column PRP-X100 using a gradient elution program between EDTA/KHP (potasium hydrogen phtalate) as first mobile phase and phosphate solutions solution as the second one. The chromatographic separation and the HG-AFS parameters were optimized by experimental design. The best results were obtained by using an elution program with 20 mmol l^{-1} EDTA + 2 mmol l^{-1} KHP solution at pH 4.5, during 1.15 min, then change to 50 mmol l^{-1} $(NH_4)_2HPO_4$ solution at pH 8.3, switching back after 4.0 min to the first mobile phase, until 5 min, with a constant flow rate of 1.5 ml min^{-1}. Retention time of Sb(V), Sb(III) and trimethylantimony species were 1.22, 2.31 and 3.45 min and the detection limits were 0.13; 0.07 and 0.13 μg l^{-1}, respectively. Studies on the stability of this antimony species in sea water samples on the function of the elapsed time of storage in refrigerator at 4 °C was performed employing the optimized method. Results revealed that Sb(III) is easily oxidized within some hours to Sb(V) in sea water stored at 4 °C. However, when the sea water was immediately mixed with EDTA no oxidation of Sb(III) was observed up to 1 week of storage. The proposed methodology was then applied to the antimony speciation in sea water samples.
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1. Introduction

Antimony is a non-essential element in plants, animals and humans [1]. Occupational exposure to antimony compounds is known to cause adverse health effects in humans and animals [2,3].

In environmental samples beside the two inorganic antimony species, Sb(III) and Sb(V), methylated forms have been detected [4–8]. In sea water, methylantimony species represent about 10% of the total dissolved antimony [9–11].

Speciation of antimony is of great importance owing to the large differences regarding their toxic properties. Elemental antimony is more toxic than its salts, and generally, trivalent antimony compounds exert a toxicity that is 10 times higher than the pentavalent antimony species [1,12].

Most of the analytical techniques for the separation and detection of antimony species are based on the line coupling of high-performance liquid chromatography (HPLC)

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to element-specific detectors, such as a hydride generation-atomic absorption spectrometer (HG-AAS) [13–15], hydride generation-atomic fluorescence spectrometer (HG-AFS) [16–18], inductively coupled plasma-optical emission spectrometer (ICP-OES) [5] or to inductively coupled plasma-mass spectrometer (ICP-MS) [5,7,19–27]. Methodologies for speciation analysis of antimony have been reviewed by Smichowski et al. [28] and Nash et al. [29]. More recently, Krachler et al. [30] presented a review on the antimony speciation, focusing on hyphenated instrumental techniques, as well as the problems encountered. Antimony speciation methods based on anion exchange chromatography have led to the successful separation of aqueous Sb(III) and Sb(V) or Sb(V) and $(CH_3)_3SbCl_2$. In general, the elution of Sb(V) is easily achieved under different chromatographic conditions; while for Sb(III), long retention time, irreversible retention and severe peak tailing have been encountered. These problems have been partially solved by using complexing mobile phases, such as ethylenediamine-tetraacetic acid (EDTA) [15,21,26,27], EDTA mixed with potassium hydrogen phthalate (KHP) [21,22,27], tartrate [15,27,31] and citrate [22] buffer solutions. Furthermore, the elution of $(CH_3)_3SbCl_2$ is only achieved by using basic mobile phases, such as carbonate buffer, phosphate buffer, potassium hydroxide or tetramethylammonium hydroxide [8,19,27]. So far, only few analytical methodologies are reported regarding the simultaneous separation and on line determination of the two inorganic antimony species Sb(III), Sb(V) and the only trimethylated antimony standard $(CH_3)_3$ $SbCl_2$ or $(CH_3)_3$ $SbBr_2$ currently available to the scientific community [7,8,15–18,20]. Zheng et al. [8] showed that these three antimony species could be separated on an Asahipak HG-520 SEC column using 50 mmol l^{-1} of Tris buffer solution, pH 7.4. Sayago et al. [16] described firstly the separation of Sb(V) and Sb(III) and then, the optimization of the separation of Sb(V), Sb(III) and $(CH_3)_3SbBr_2$ on an anion exchange PRP-X100 column using HG-AFS as detection technique [17]. The separation was achieved by using a concentration gradient elution between 20 mmol l^{-1} potassium hydroxide, pH 11, and ammonium tartrate, with a concentration as high as 200 mmol l^{-1}, at pH 5 [17]. Under these experimental conditions, some chromatographic problems still remain, such as elution of $(CH_3)_3$ $SbBr_2$ in the void volume, insufficient peak resolution and severe peak tailing for Sb(III) [17]. Recently, Miravet et al. described a method for the speciation analysis of Sb(III), Sb(V) and $(CH_3)_3SbCl_2$ based on the same separation and detection techniques (HPLC-HG-AFS) [20]. The maximum efficiency and resolution were obtained using, as the mobile phase, a gradient elution between 250 mmol l^{-1}diamonium tartrate, pH 5.5 and 20 mmol l^{-1} KOH, pH 12. The analysis took about 7 min. The methodology was applied to antimony speciation in fresh waters [18]. From results presented in this paper, a non quantitative separation between trimethylantimony and Sb(III) species can be deduced, in spite of the high diamonium tartrate concentration and pH of the mobile phases employed.

This paper presents, based on a similar chromatographic approach, an improvement of the simultaneous separation of Sb(III), Sb(V) and $(CH_3)_3SbCl_2$ on an exchange PRP-X100 column using mobile phases of lower concentration and pH and subsequent post column sensitive detection by hydride generation atomic fluorescence spectrometry (HPLC-HG-AFS). Atomic fluorescence spectrometry (AFS) can be a good alternative to inductively coupled mass spectrometry (ICP-MS) detector, with the advantage of a lower cost of investment and handling. The separation of the antimony species by using a gradient elution between EDTA + KHP (potassium hydrogen phthalate) and different phosphate solutions was investigated. The separation conditions were optimized by experimental design, in order to achieve good efficiency and resolution within a short analysis time. The optimized methodology was then applied to study the stability of these antimony species in sea water samples, matrix where the antimony speciation has been few studied, probably due to the high chloride concentration which leads to detection interferences, especially using ICP-MS detection. The methodology was applied to antimony speciation in sea water samples collected from Valparaíso bay.

2. Experimental

2.1. Chemicals and reagents

For the preparation of all solutions, high purity water (18 MΩ) from a Nanopure system (Barnstead, Dubuque, IA, USA) or a Milli-Q (Millipore, Bedford, MA, USA) system was used. Chemicals were of analytical-reagent grade or higher purity. Glass and plastic wares were cleaned by soaking for 1 day in 10% (v/v) nitric acid (analytical grade) and were rinsed several times with high purity water before use.

Antimony (III) standard was obtained as potassium antimonyl tartrate $K(SbO)C_4H_4O_6H_2O$ (Aldrich, 99.95% purity); a standard solution of 100 mg l^{-1} Sb(III) was prepared daily by dissolving this compound in water. A stock solution of Sb(V) was prepared by dissolving solid potassium hexahydroxo-antimonate $KSb(OH)_6$ (Aldrich, 99.95% purity) in water. Trimethylantimony dichloride $(CH_3)_3SbCl_2$ was purchased from Aldrich (96% purity). Stock standard solutions were prepared in water to give 100 mg Sb l^{-1}. All standard solutions were stored in polyethylene bottles at 4 °C. Working antimony solutions were prepared daily by an appropriate dilution in the mobile phase (20 mmol l^{-1} EDTA + 2 mmol l^{-1} KHP).

The mobile phases were freshly prepared as follows: the mixture of 20 mmol l^{-1} EDTA + 2 mmol l^{-1} potassium hydrogen phthalate (KHP, Merck) was prepared by dissolving di-sodium dihydrogen ethylene diamine tetraacetate salt dihydrate (Na_2 EDTA·$2H_2O$, Merck) and potassium hydrogen phthalate in high purity water. Different mixtures of diammonium hydrogen phosphate and ammonium di-hydrogen phosphate ($(NH_4)_2HPO_4$ + $(NH_4)H_2PO_4$) were

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