



Optimisation of a headspace-solid-phase micro-extraction method for simultaneous determination of organometallic compounds of mercury, lead and tin in water by gas chromatography–tandem mass spectrometry

E. Beceiro-González^{a,*}, A. Guimaraes^b, M.F. Alpendurada^{b,c}

^a Department of Analytical Chemistry, University of A Coruña, Campus da Zapateira s/n, 15071 A Coruña, Spain

^b IAREN-Water Institute of the Northern Region, Rua Dr. Eduardo Torres, 229/4450-113 Matosinhos, Portugal

^c Laboratory of Hydrology, Faculty of Pharmacy, University of Porto, Rua Aníbal Cunha, 164/4050-047 Porto, Portugal

ARTICLE INFO

Article history:

Received 21 November 2008

Received in revised form 11 May 2009

Accepted 20 May 2009

Available online 29 May 2009

Keywords:

Speciation analysis

Solid-phase micro-extraction

Water analysis

GC–MS/MS

Lead

Mercury

Tin

ABSTRACT

In this work, a headspace-solid-phase micro-extraction (HS-SPME) combined with gas chromatography–mass spectrometry (GC–MS) method for multielemental speciation of organometallic compounds of mercury, lead and tin in water samples was upgraded by the introduction of tandem mass spectrometry (MS/MS) as detection technique. The analytical method is based on the ethylation with NaBH₄ and simultaneous headspace-solid-phase micro-extraction of the derivative compounds followed by GC–MS/MS analysis. The main experimental parameters influencing the extraction efficiency such as derivatisation time, extraction time and extraction temperature were optimized. The overall optimum extraction conditions were the following: a 50 μm/30 μm divinyl-benzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS) SPME fibre, 150 min derivatisation time, 15 min extraction time, sample agitation at 250 rpm and 40 °C extraction temperature. The analytical characteristics of the HS-SPME method combined with GC–MS and GC–MS/MS were evaluated. The combination of both techniques HS-SPME and GC–MS/MS allowed to attain lower limits of detection (4–33 ng l^{−1}) than those obtained by HS-SPME–GC–MS (17–45 ng l^{−1}). The proposed method presented good linear regression coefficients ($r^2 > 0.9970$) and repeatability (4.8–21.0%) for all the compounds under study. The accuracy of the method measured as the average percentage recovery of the compounds in spiked river water and seawater samples was higher than 80% for all the compounds studied, except for monobutyltin in the river water sample. A study of the uncertainty associated with the analytical results was also carried out.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

The toxicity, bioavailability and mobility of an element in the environment are critically dependent on the particular form in which this element occurs in the environment. Therefore, the study of different species of metals and organometallic compounds continues to be an important topic of analytical research. The most important and abundant organometallic species in the environment are organomercury, organotin and organolead compounds. The high toxicity of these compounds even at low concentration levels has demanded the development of accurate and sensitive analytical methods for their determination in environmental matrices. As an example, the Water Framework Directive (WFD, Directive 2000/60/EC) includes mercury and its compounds as well as butyltins in the list of 33 priority substances [1].

Mercury speciation studies are commonly dedicated to methylated (MeHg⁺) and Hg²⁺ species. Non-polar species such as elemental mercury (Hg⁰) and dimethylmercury (Me₂Hg) tend to be present in the atmosphere and when present in water systems are very easily volatilised during sampling, sample transport and storage because of their low water solubility [2]. MeHg⁺, the most toxic form of mercury, can accumulate in living organisms and damage their central nervous system [3]. This compound can originate from anthropogenic sources, although Hg (II) can also be biologically converted into the methylated form [4,5].

Organotin compounds have been extensively used as active ingredients of antifouling agents commonly applied to protect boats and ships. Thus, the major impact of contamination by these compounds can be found in harbours and marinas. The most toxic organotin species correspond to triorganotins, followed by di- and mono-organotin compounds. Additionally, it is important to note that tributyltin (TBT) is an endocrine disruptor, affecting marine organisms even at ng l^{−1} level [6]. Consequently, the determination of TBT and its metabolites in the aquatic environment is essential in order to assess the risks of an environmental pollution event.

* Corresponding author.

E-mail address: elisa@udc.es (E. Beceiro-González).