



New developments in the analysis of fragrances and earthy–musty compounds in water by solid-phase microextraction (metal alloy fibre) coupled with gas chromatography–(tandem) mass spectrometry

S. Machado^a, C. Gonçalves^{a,b}, E. Cunha^b, A. Guimarães^a, M.F. Alpendurada^{a,b,*}

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

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

ARTICLE INFO

Article history:

Received 4 November 2010

Received in revised form 3 March 2011

Accepted 8 March 2011

Available online 16 March 2011

Keywords:

Fragrances

Earthy–musty

Water

Metal alloy

SPME

Odour and taste

Galaxolide

Musk xylene

ABSTRACT

Fragrances are widespread aquatic contaminants due to their presence in many personal care products used daily in developed countries. Levels of galaxolide and tonalide are commonly found in surface waters, urban wastewaters and river sediments. On the other hand, earthy–musty compounds confer bad odour to drinking water at levels that challenge the analytical capabilities. The combined determination of earthy–musty compounds and fragrances in water would be a breakthrough to make the traditional organoleptic evaluation of the water quality stricter and safer for the analyst. Two approaches were attempted to improve the analytical capabilities: analyte pre-concentration with a newly developed PDMS–DVB solid-phase microextraction fibre on metal alloy core and sensitive detection by tandem mass spectrometry (MS/MS). The optimization of SPME parameters was carried out using a central composite design and desirability functions. The final optimum extraction conditions were: headspace extraction at 70 °C during 40 min adding 200 g L^{−1} of NaCl. The detection limits in tandem MS (0.02–20 ng L^{−1}) were marginally lower compared to full scan except for geosmin and trichloroanisole which go down to 0.1 and 0.02 ng L^{−1}, respectively.

The analysis of different water matrices revealed that fragrances and earthy–musty compounds were absent from ground- and drinking waters. Surface waters of river Leça contained levels of galaxolide around 250 ng L^{−1} in the 4 terminal sampling stations, which are downstream of WWTPs and polluted tributaries. Geosmine was ubiquitously distributed in natural waters similarly in rivers Leça and Douro at concentrations <7 ng L^{−1}.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Fragrances are synthetic chemicals widely employed in developed countries to improve the olfactory properties of many personal care products (soaps, detergents, deodorants, perfumes and creams) [1–3]. There are two main groups of synthetic fragrances: polycyclic musks (the most consumed being galaxolide (GAL) and tonalide (TON)) and nitroaromatic musks (mainly musk xylene (MX) and musk ketone (MK)) [1]. Especially the polycyclic musks are used in huge quantities so their residues may easily reach the water compartments via domestic wastewaters [4,5]. Typically, these substances are very lipophilic and hardly degraded in the aquatic environment [1,6–8]. Nevertheless, the simple feature of being continuously discharged into the aquatic media explains their environmental significance and supports their inclusion in the group of emerging pollutants. The use of some

fragrances was prohibited due to their potential to bioaccumulate in the fat tissue of wildlife and their endocrine disruptive activity [9,10]. Neurotoxicity has also been reported [2]. The Oslo and Paris Commission (OSPAR) has included musk xylene in the list of priority substances [2,11,12]. In the preparatory stage of the Directive “Environmental Quality Standards in the field of Water Policy” the European Union has evaluated four fragrances as candidate priority substances [9]; however the final version (Directive 2008/105/EC) only includes musk xylene in Annex III [13].

On the other hand, earthy–musty compounds bestow bad odour to drinking water at excessively low levels (at sub- or a few ng L^{−1}) [14–16]. Additionally, they are difficult to remove by conventional chemical drinking water treatment [17,18]. The most important earthy–musty compounds are: geosmin (GSM), isoborneol (IB) and 2-methylisoborneol (MIB) produced by Actinomycetes bacteria, fungi and algae; and 2,4,6-trichloroanisole (TCA) formed by biomethylation of trichlorophenol [14,15,19]. Some evidences indicate that GSM and MIB can lead to mutagenicity and hepatotoxicity [20].

* Corresponding author.

E-mail address: mfalpendurada@iaren.pt (M.F. Alpendurada).