



# 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

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## 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<sup>-1</sup> of NaCl. The detection limits in tandem MS (0.02–20 ng L<sup>-1</sup>) were marginally lower compared to full scan except for geosmin and trichloroanisole which go down to 0.1 and 0.02 ng L<sup>-1</sup>, 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<sup>-1</sup> 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<sup>-1</sup>.

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## 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<sup>-1</sup>) [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].

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Several authors have reported the presence of fragrances in surface waters, urban waste waters and river sediments [2,3,7,21–24]. Polycyclic musks occur at concentrations up to several  $\mu\text{g L}^{-1}$  while the nitroaromatic musks are present in the  $\text{ng L}^{-1}$  range. Earthy–musty odours have been found in surface and drinking waters in concentrations of a few  $\text{ng L}^{-1}$  [16,18,25,26].

The combined determination of earthy–musty compounds and fragrances in water would be highly convenient since it could replace the traditional and highly subjective organoleptic evaluation of water quality, besides avoiding risks for the operator. The available methods focus only in one of the groups [1,4,6–8,14,15,20,25], therefore joint determination would also significantly reduce the analysis time and costs.

Two approaches were used to improve the analytical capabilities of the proposed method based on solid-phase microextraction (SPME) coupled with gas chromatography–mass spectrometry (GC–MS): a recently developed polydimethylsiloxane–divinylbenzene (PDMS–DVB) SPME fibre on metal alloy core was evaluated as preconcentration media and a highly selective and sensitive detection by tandem mass spectrometry (MS/MS) was adopted. The metal alloy fibres are more mechanical resistant than the fused–silica making them last longer [27]. The PDMS–DVB adsorbent also has different thickness and diameter compared to the conventional fibres. Setkova et al. have investigated the reproducibility of different coatings on the metal alloy and conventional cores for the analysis of pump oil samples (benzene, 2-pentanone, 1-nitropropane, pyridine and toluene). The metal alloy fibres were generally more precise, the durability went beyond 200 extraction cycles without any significant loss in sensitivity but no comparison of the extraction efficiency and selectivity was given [27].

The developed method was optimised through an experimental design approach and multiresponse evaluation and then applied to the analysis of several water samples with the aim to screen odours and fragrances in as much as possible water sources (ground waters, surface waters, waste water and drinking waters).

## 2. Experimental

### 2.1. Chemicals and reagents

Isoborneol, 2-methylisoborneol, geosmin, 2,4,6-trichloroanisole, musk xylene and musk ketone standards were purchased from Sigma–Aldrich (Madrid, Spain). Galaxolide and tonalide were purchased from LGC Standards (Barcelona, Spain). Their chemical structure, molecular formula and important physico-chemical parameters for the SPME process are given in Table S1, as supplementary material. Individual stock standard solutions were prepared in methanol and stored at  $-18^\circ\text{C}$  protected from light. A mixture solution at  $1\text{ mg L}^{-1}$  was then obtained. Daily working solutions were prepared in ultra-pure Milli Q water (Millipore, Molsheim, France). Sodium chloride p.a. was used to adjust the ionic strength of aqueous standards and samples.

### 2.2. Solid-phase microextraction

Six SPME fibres on conventional fused silica core supplied by Supelco (Bellefonte, PA, USA) were tested:  $85\ \mu\text{m}$  polyacrylate (PA),  $100\ \mu\text{m}$  polydimethylsiloxane (PDMS),  $75\ \mu\text{m}$  carboxen/polydimethylsiloxane (CAR/PDMS),  $60\ \mu\text{m}$  polydimethylsiloxane/divinylbenzene (PDMS/DVB),  $65\ \mu\text{m}$  PDMS/DVB and  $50/30\ \mu\text{m}$  divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS). Two additional fibres on metal alloy core were compared for their analytical advantages:  $65\ \mu\text{m}$  PDMS/DVB and  $85\ \mu\text{m}$  CAR/PDMS. The fibres were conditioned in the GC injector

as recommended by the manufacturer. The samples (10 mL) were placed in headspace vials of 20 mL capacity. The extraction was carried out at a stirring rate of 250 rpm. The extraction time, temperature and ionic strength were optimised through a multi-factorial design to reach a compromise of extraction efficiency and practicality for both chemical families.

### 2.3. Gas chromatography–mass spectrometry analysis

Chromatographic analyses were carried out in a Varian CP 3800 (Walnut Creek, CA, USA) gas chromatograph equipped with a fused–silica capillary column coated with 5% diphenylmethylsiloxane, VF-5 MS ( $30\text{ m} \times 0.25\text{ mm I.D.}$ ,  $0.25\ \mu\text{m}$  film thickness) from Varian. High-purity helium (99.9999%) at a constant flow rate of  $1\text{ mL min}^{-1}$  was used as the carrier gas and also as the collision gas at the ion trap chamber. Samples were analysed using the following oven temperature programme: initial temperature  $60^\circ\text{C}$ , increased by  $40^\circ\text{C min}^{-1}$  to  $100^\circ\text{C}$  (held for 1 min), increased by  $15^\circ\text{C min}^{-1}$  to  $200^\circ\text{C}$ , increased by  $1^\circ\text{C min}^{-1}$  to  $205^\circ\text{C}$  and finally increased by  $40^\circ\text{C min}^{-1}$  to  $260^\circ\text{C}$ . The analytes were desorbed from the fibre at an injector temperature of  $250^\circ\text{C}$  for 2 min in splitless mode followed by 3 min in split mode. Compounds were detected by a 4000 GC–MS ion trap mass spectrometer from Varian Instruments (Walnut Creek, CA, USA) operated in full scan and MS/MS modes. The trap and transfer line temperatures were set at 180 and  $280^\circ\text{C}$ , respectively. The emission current of the ionisation filament was set at  $50\ \mu\text{A}$ . The electron multiplier voltage was 1400 V. The GC–MS system was mounted with a CombiPal autosampler (CTC–Analytics, AG, Switzerland) that allowed controlling all SPME variables.

### 2.4. Multifactorial design

A multifactorial experimental design – central composite design (CCD) – was employed with multiple objectives: to evaluate the main variables that affect the extraction of earthy–musty odours and fragrances; to disclose interactions between variables; to determine the optimum extraction conditions; and to evaluate the robustness of the method in the vicinity of that optimum. The CCD was established for the following variables: extraction time, temperature and ionic strength at 5 levels for each factor ( $-\alpha$ ,  $-1$ ,  $0$ ,  $+1$ ,  $+\alpha$ , with  $\alpha = 1.6818$ ). The experimental conditions evaluated were: 10, 22.16, 40, 57.8 and 70 min of extraction time; 30, 42.4, 60, 77.8 and  $90^\circ\text{C}$  for temperature and 0, 40.54, 100, 159.46 and  $200\text{ g L}^{-1}$  of NaCl concentration for ionic strength. The border values were chosen taking into account previous studies in the literature. The CCD was run with genuine duplicates for each experiment. The experiments were divided in 3 blocks with 2 central points in each block, in a total of 34 experiments. For optimizing the response of multiple dependent variables (8 compounds) we have used a desirability function considering a linear and “the highest the best” desirability factor. A quadratic model for fitting desirability surfaces/contours was employed. The data was previously normalized to the maximum of each compound along the experimental series (by variable). The experimental design was produced and analysed using the programme Statistica 6.0 (Statsoft, Tulsa, USA).

## 3. Results and discussion

### 3.1. Detailed optimisation of the chromatographic separation and detection

The initial experiments were performed with the aim to obtain full resolution of the analytes. Chromatographic separation and quantification of galaxolide and tonalide is particularly challenging since the two compounds have the same molecular weight (Mr 258.403) and some common important fragment ions ( $m/z$

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