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Influence of pre-treatment process on matrix effect for the determination of musk fragrances in fish and mussel

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ABSTRACT

Musk compounds are widely used as fragrances in personal care products. On account of their widespread use and their low biodegradation, they can be found in environmental samples. In our study two extraction methodologies were compared and different clean-up strategies were also studied in order to develop a reliable analytical method, with minimum matrix effect and good detection limits, to determine synthetic musk fragrances- six polycyclic musks, three nitro musks and the degradation product of one polycyclic musk- in fish and mussel samples. The first extraction technique involves a QuEChERS extraction, a consolidate extraction methodology in the field of food analysis of growing interest over recent years, followed by a dispersive solid-phase extraction (dSPE) as clean-up strategy. The second extraction technique consists of a conventional pressurised liquid extraction (PLE) with dichloromethane and an in-cell clean-up to decrease the matrix effect and remove the undesired components*present in PLE extracts. Large volume injection (LVI) followed by gas chromatography-ion trap-tandem mass spectrometry (GC-IT-MS/MS) was chosen as the separation and detection technique. Validation parameters, such as method detection limits and method quantification limits were found at ng g^{-1} levels for both fish and mussel matrices. Good levels of intra-day and inter-day repeatabilities were obtained analysing fish and mussel samples spiked at 50 ng g^{-1} (d.w.) ($n=5$, RSDs < 17%). The developed PLE/GC-IT-MS/MS method was successfully applied to determine the target musk fragrances present in fish and mussel samples from the local market in Tarragona and fish samples from the Ebro River. The results showed the presence of galaxolide ($2.97\text{--}18.04 \text{ ng g}^{-1}$ (d.w.)) and tonalide ($1.17\text{--}8.42 \text{ ng g}^{-1}$ (d.w.)) in all the samples analysed, while the remaining polycyclic musks such as cashmeran, celestolide and phantolide, were only detected in some of the fish samples analysed. None of the samples analysed contained detectable traces of the nitro musks studied.

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1. Introduction

Musk compounds are a family of cyclic personal care products (PCPs), that include polycyclic musks, nitro musks and macrocyclic musks, widely used as fragrances in consumer products such as cosmetics, toiletries, detergents, soaps, body oils, toothpaste and also as flavours in foods and drinks: in short, they are used in a broad range of everyday products. They belong to the so-called emerging organic compounds (EOCs), which have been of increasing interest, to scientists in recent years [1–8].

Discussions on the toxicology of nitro musks soon arose because of the presence of a nitro aromatic compound in their structure. In this respect, the European Directive 98/62/EEC [9] relating to cosmetic products prohibits the use of musk ambrette,

musk moskene and tibetene in cosmetics and limits musk xylene and musk ketone content. Furthermore, nitro musks can be transformed in wastewater treatment plants (WWTPs) - as well as in biota - into amino metabolites [10], and these transformation products can be even more problematic than the parent compounds [11,12]. This has led to a significant decrease in their use, while polycyclic musk production has increased significantly. Polycyclic musks are the musk fragrances that dominate the global market today, and two of them, galaxolide and tonalide, have been included on the EPA's high production list [13]. The use of tonalide in the cosmetic industry has in fact been regulated through European directive 2008/42/EC [14]. Macrocyclic musks, which smell more intensive than polycyclic musk and so less mass is needed to achieve the same performance in perfumery, are not as widely used as polycyclic musks because of the cost of their synthesis. Nevertheless, they are becoming more generally available because of advances made in synthesis methods over the last few years [2,15,16]. It is expected that over the next few years the

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decrease in the price of synthesising macrocyclic musks and their environmentally friendly properties will mean that they will replace polycyclic musk in the market.

On account of their widespread use, musk compounds can be considered ubiquitous throughout the world, and due to their lipophilic characteristics and slow biodegradation, they can be found in surface water [17–19], sewage [20,21], sediments [22] and fish species living in contaminated rivers and estuaries [23–25].

A wide range of analytical methods have been developed to determine musk fragrances in fish tissue. These methods have used a varied assortment of extraction techniques (Soxhlet, microwave assisted extraction (MAE), focused ultrasound-solid liquid extraction (FUSLE), and pressurised liquid extraction (PLE) usually followed by a clean-up step (silica gel, florisil and/or gel permeation chromatography (GPC)) prior to analysis with GC–MS or GC–MS/MS [23,26–29]. In this article, a new extraction methodology of growing interest in the field of food analysis over recent years [30–32] – QuEChERS (quick, easy, cheap, effective, rugged and safe) – was tested and compared in terms of validation parameters with PLE. Special effort was on the reduction of matrix effect.

The QuEChERS methodology was first developed by Anastasiades et al. [33] for the extraction of pesticides from food matrices and involves two basic steps. At first QuEChERS methods use a single step buffered acetonitrile extraction and simultaneously salt out water from the aqueous sample using anhydrous magnesium sulphate to induce liquid-liquid partitioning. Subsequently, a clean-up step using a dispersive solid-phase extraction (dSPE) is often conducted to clean up the mixture, removing any undesired sample components. The main advantages of this extraction methodology are its speed, ease of implementation (instrumentation is not required), minimal solvent requirement and low cost when compared with instrumental extraction techniques.

The aim of this investigation was therefore to develop a rapid, sensitive and accurate analytical method based on GC-IT-MS/MS for determining ten synthetic musk fragrances in fish and mussels. PLE or QuEChERS as extraction procedures were compared and different clean-up strategies as in-cell clean-up sorbent for PLE or dSPE for QuEChERS were assayed to minimise the matrix effect. To the best of our knowledge, this is the first time that QuEChERS has been used to extract musk fragrances present in fish samples.

2. Experimental part

2.1. Reagents and standards

The six polycyclic musks studied were supplied by Promochem Iberia (Barcelona, Spain) and were the following: 6,7-dihydro-1,1,2,3,3-pentamethyl-4(5H)-indanone (DPMI, cashmeran), 4-acetyl-1,1-dimethyl-6-*tert*-butylindane (ADBI, celestolide), 6-acetyl-1,1,2,3,3,5-hexamethylindane (AHMI, phantolide), 5-acetyl-1,1,2,6-tetramethyl-3-isopropylindane (ATII, traseolide), 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta-(g)-2-benzopyran (HHCB, galaxolide) and 7-acetyl-1,1,3,4,4,6-hexamethyl-1,2,3,4-tetrahydronaphthalene (AHTN, tonalide). The nitro musk fragrances 2,4,6-trinitro-1,3-dimethyl-5-*tert*-butylbenzene (MX, musk xylene) and 1,1,3,3,5-pentamethyl-4,6-dinitroindane (MM, musk moskene) were purchased as 100 µg mL⁻¹ individual solutions in acetonitrile from Sigma–Aldrich (Steinheim, Germany) and Riedel de Haën (Seelze, Germany), respectively. The standard 4-aceto-3,5-dimethyl-2,6-dinitro-*tert*-butylbenzene (MK, musk ketone) was provided by Fluka (Buchs, Switzerland). International Flavors & Fragrances Inc. (Barcelona, Spain) supplied 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta-[g]-2-benzopyran-1-one (HHCB-lactone, galaxolidone) while the internal standard ²H15-musk xylene (²H15-MX) came as

a 100 µg mL⁻¹ solution in acetone from Symta (Madrid, Spain). Suppl. Table 1 shows the main characteristics (formula name, molecular structure, CAS number, molar mass and boiling point) of the target compounds [1,34,35].

Individual standard solutions of the synthetic musk fragrances were prepared in acetone at concentrations of 4000 µg mL⁻¹ for polycyclic musks and 1000 µg mL⁻¹ for musk ketone and HHCB-lactone. A working mixture solution of 100 µg mL⁻¹ was prepared in ethyl acetate except for MX, MM and ²H15-MX which were supplied directly at a concentration of 100 µg mL⁻¹ in acetonitrile and used as received. Acetone and ethyl acetate were GC grade with purity >99.9% from Prolabo (VWR, Llinars del Vallès, Barcelona, Spain).

The extraction solvents dichloromethane, methanol, and hexane were GC grade (of >99.9% purity) from Prolabo, while acetonitrile was HPLC grade from Prolabo. Ultrapure water was obtained using an ultrapure water purification system from Veolia Water (Sant Cugat del Vallés, Barcelona, Spain). Helium gas with a purity of 99.999% was used for the chromatographic analysis (Carbueros Metálicos, Tarragona, Spain).

2.2. Sampling and sample pre-treatment

Red mullet (*Mullus surmuletus*) and mussels (*Mytilus galloprovincialis*) were selected for method development, optimisation and validation. The method was successfully applied to determine musk fragrances in gilt head bream (*Sparus aurata*), turbot (*Psetta maxima*), red mullet (*Mullus surmuletus*) and mussels (*Mytilus galloprovincialis*), which had been purchased locally (Tarragona market) and mostly caught or collected in the Mediterranean Sea between May and December 2013. Perch (*Perca fluviatilis*), sheatfish (*Silurus glanis*) and carp (*Cyprinus carpio*) samples, which had been caught in the wild (between May and November 2013) and collected from the Ebro River, were also analysed.

After collection, the samples were immediately preserved in a refrigerated box. Lateral fillets were then dissected from the fish, homogenised and stored in a freezer until analysis. Frozen samples were lyophilised using the freeze-drying system (Labconco, Kansas City, MO, USA), crushed using a mortar and pestle and sieved through a 125 µm screen to homogenise the diameter of the particles.

2.3. Sample extraction

2.3.1. Quick, easy, cheap, effective, rugged and safe (QuEChERS)

A total of 0.5 g (d.w.) of freeze-dried sample was weighed into 50 mL centrifuge tubes from Scharlab (Barcelona, Spain), 10 mL of ultrapure water was added to the tube, and the tube was shaken vigorously for 1 min. Then, 10 mL of acetonitrile was added, followed by an extraction salt packet (Scharlab) for the European Committee for Standardization (CEN) extraction method [36], which contains 4 g of magnesium sulphate, 1 g of sodium chloride, 0.5 g of sodium citrate dibasic sesquihydrate and 1 g of sodium citrate dihydrate. The mixture was then vortexed (3 min) and centrifuged for 5 min at 7000 rpm (Hettich Universal 32 R, Tuttingen, Germany). The supernatant (acetonitrile layer) was removed and transferred to a 15 mL centrifuge tube containing 1 g of florisil (Sigma–Aldrich) for the dSPE clean-up. The tube was vortexed for 3 min and centrifuged again at 7000 rpm for 5 min and the supernatant was evaporated under a gentle stream of nitrogen to a final volume of ≈1 mL. The internal standard (IS, 50 ng g⁻¹) was added to the extract before it was reconstituted to 2 mL with ethyl acetate. Extracts were filtered with a 0.22 µm PTFE syringe filter and analysed by GC-IT-MS/MS.

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