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Sorbent-packed needle microextraction trap for synthetic musks determination in wastewater samples

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ABSTRACT

A needle trap (NT) device filled with HF Bondesil-C18 as a sorbent material was evaluated for the dynamic headspace analysis of a family of nine synthetic musks compounds that include two nitro musks, six polycyclic musks (with galaxolide and tonalide as the most widespread used polycyclic musks) and the degradation product of galaxolide (galaxolidone) in wastewater samples. Different parameters affecting the adsorption capacity of the sorbent were studied (e.g. extraction mode, extraction temperature, salt concentration, preincubation time fill and ejection speed or fill volume). Furthermore, injection parameters used with the NT device (e.g. desorption mode, desorption temperature and time) were evaluated to optimize the desorption and transfer of the target compounds into the GC column. Method detection limits obtained with gas chromatography–tandem mass spectrometry (GC–MS/MS) detection were found in the low ng L^{-1} range, between 2.5 and 10 ng L^{-1}, depending on the target compounds. Moreover, under optimized conditions, the method gave good levels of intra-day and inter-day repeatabilities in wastewater samples with relative standard deviations ($n=5$, 100 ng L^{-1}) less than 11 and 17%, respectively. The developed method was satisfactorily applied to the analysis of aqueous samples obtained from three wastewater treatment plants. All the polycyclic musks studied were detected in influent samples with cashmeran, galaxolide and tonalide as the most representative compounds. The analysis of effluent wastewater showed a decrease in the concentrations of all of the polycyclic musk detected in influent samples and an increase in the concentration of galaxolidone until a maximum value of 820 ng L^{-1}.

1. Introduction

Sample preparation is the cornerstone of chemical analysis. Preconcentration is a crucial step when synthetic musk fragrances often occurring in concentrations as low as μg L^{-1} or ng L^{-1} are to be determined in environmental water samples. Some preconcentration techniques such as liquid–liquid extraction (LLE) [1–3], solid-phase extraction (SPE) [4–7], dispersive liquid–liquid extraction (DLLME) [8–10], solid phase microextraction (SPME) [11,12], single drop microextraction (SDME) [13,14], microextraction by packed sorbents (MEPs) [15,16] or dispersive microsolid-phase extraction (D-μ-SPE) [17] have been reported. Of all the extraction techniques mentioned, SPE is the most widely used in the environmental analytical field because it consumes minimal amount of organic solvents and a great diversity of sorbents is commercially available.

Nevertheless the development of economical and ecological small scale sample preparation techniques that are able to meet requirements such as enhanced sensitivity and selectivity, robustness and simple handling are desirable [18,19]. In this way, solvent-free extraction methods based on the partitioning of analytes between gaseous or liquid phase and stationary phase have become important and have been widely applied in research over the last decade, with SPME as one of the most successfully approaches [20,21].

Although Raschdorf [22] developed the first device based on a needle filled with Tenax sorbent in the 1970s, needle trap (NT) extraction devices have only recently become popular due to their combination of advantages of SPME (e.g. solvent-free, fast, sensitive and one-step sample preparation and injection method) and SPE (e.g. sensitivity of the method can be increased by increasing the sample volume) with robustness, easier handling during sampling and desorption, and the fact that they permit a high degree of automation and on-line coupling to GC instruments [23–26]. The literature found up to now can be divided in two categories depending on the NT device used: (a) internally coated needles [27–29] and (b) needles packed with commercially

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available sorbents [26,30–36] or chemically synthesized polymers [37,38]. Regardless of the kind of NT used, the extraction by NT has the advantages of being solvent-free and of having sampling and analysis times that are significantly shorter than most existing methods.

In this study, two different needles packed with 20 mm or 30 mm of HF Bondesil-C18 sorbent were evaluated in order to determine the optimal configuration to extract the synthetic musks fragrances present in wastewater samples prior to analysis by GC–MS/MS. The different parameters affecting the adsorption capacity of the NT as well as the desorption and transferring of the target compounds into the GC were also studied. Once the most appropriate experimental conditions were found, the NT methodology was compared in terms of method validation parameters with other microextraction techniques and was successfully applied for the analysis of synthetic musk fragrances in wastewater samples.

2. Experimental part

2.1. Chemical standards

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} solutions in acetonitrile from Sigma-Aldrich (Steinheim, Germany) and Riedel de Haën (Seelze, Germany), respectively. 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-1,1dimethyl-6-tert-butyllindane (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). International Flavors & Fragances Inc. (Barcelona, Spain) provided1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta-[*g*]-2-benzopyran-1-one (HHCB-lactone, galaxolidone) and the deuterated analogue ^{2}H15-Musk xylene (^{2}H15-MX, surrogate standard) was supplied as a 100 µg mL^{-1} solution in acetone by Symta (Madrid, Spain). Table 1 shows the boiling point and the octanol/water partition coefficient of each target compound.

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

Ultrapure water was obtained using an ultrapure water purification system from Veolia waters (Sant Cugat del Vallés, Barcelona, Spain). Helium gas with a purity of 99.999% was used for the chromatographic analysis (Carburos Metálicos, Tarragona, Spain).

2.2. Sampling

Influent and effluent wastewater samples were collected from three urban wastewater treatment plants (WWTPs) located in Tarragona (WWTP A), Reus (WWTP B) and Vila-seca/Salou (WWTP C) between October and December 2013. The WWTPs receive urban sewage and industrial discharges from a population of about 130,000 inhabitants. The three WWTPs use activated sludge for biological treatment and the WWTP C also employs a tertiary treatment based on reverse osmosis (RO). All samples were collected by using pre-cleaned amber glass bottles and were filtered using a 1.2 µm glass fibre filter (Fisherbrand, Loughborough, UK) and a 0.22 µm nylon filter (Scharlab, Barcelona, Spain). Samples were analysed within three days of their collection (stored at 4 °C in the fridge).

Table 1
Boiling point, log K_{ow}, retention times (t_R) and parent and products ions of the target compounds.

No.	Compound	Boiling point (°C)	Log K_{ow}[a]	t_R (min)	Parent ion (m/z)	Product ions (m/z)[b]
1	Cashmeran (DPMI)	286.1	5.9	8.33	191	107, **135**, 173
2	Celestolide (ADBI)	309	5.4	10.24	229	131, **173**, 187
3	Phantolide (AHMI)	336.6	5.9	10.98	229	131, 145, **187**
4	Traseolide (ATII)	350	6.3	12.02	215	131, 171, **173**
5	Galaxolide (HHCB)	326	5.9	12.31	243	171, **213**
6	Tonalide (AHTN)	356.8	6.3	12.36	243	**145**, 159, 187
7	Musk xylene (MX)	392.3	3.8	13.24	282	**265**, 266, 281
8	Musk moskene (MM)	351.1	5.2	13.35	263	187, 201, **211**
9	Galaxolidone (HHCB-lactone)	*	*	16.93	257	183, 201, **239**
10	^{2}H15-musk xylene (^{2}H15-MX)[c]	*	*	13.10	294	170, **276**, 295

* Information not found in the bibliography.
[a] Log K_{OW} values predicted from SRC-K_{OW}Win software.
[b] Quantification ions (m/z) are shown in bold type.
[c] Surrogate standard (SS).

2.3. Preparation of the needle trap

Hamilton (Bonaduz, Switzerland) 22 gauge stainless steel (metal hub) needles (O.D.=0.718 mm, I.D.=0.413 mm and 51 mm length) with point style 5 (Fig. 1) were filled with HF Bondesil-C18 sorbent (120 µm) from Agilent Technologies (Palo Alto, USA). Stainless steel wire (AISI 316L, GoodFellow, Huntingdon, UK) of 100 µm diameter was used to prepare spiral plugs to hold sorbent particles inside the needles. First, a small piece of spiral plug (five turns, ~1.5 mm) was fixed in the tip of the needle to prevent sorbent particles from being fixed in the side hole of the needle. Then, 20 mm or 30 mm of C18 sorbent particles were positioned inside the needle. Finally, another spiral plug was carefully introduced in the upper position of the needle until it reached the end of the sorbent layer to fix the sorbent particles. Using this needle configuration, needle traps were conditioned in the GC injector at 230 °C for 30 min to eliminate any contaminations from the manufacturing process or shipping. Each needle was stored inside a closed vial until analysis.

2.4. Needle trap extraction

A CombiPAL autosampler (CTC Analytics, Zwigen, Switzerland) equipped with a single Magnet Mixer, a 100 µL Hamilton syringe and controlled by the Cyclo Composer Macro Editor 1.4 Software was used for the fully automated needle trap (NT) micorextraction. The general microextraction procedure was as follows: 10 mL of sample or standard solution was introduced into a 20 mL HS glass vial and immediately sealed with a Teflon septum. When the temperature of the heat/stir accessory reached 60 °C, the vial was automatically transported there and the headspace was allow to equilibrate with the sample at the extraction temperature for 15 min. The needle with 30 mm of HF Bondesil-C18 sorbent was inserted in the vial to perform the HS dynamic extraction. 500 µL of headspace vapours