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On-line coupling of solid-phase extraction to gas chromatography–mass spectrometry to determine musk fragrances in wastewater

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ABSTRACT

An on-line coupling solid-phase extraction (SPE) has been developed for the first time to preconcentrate trace amounts of 17 musk fragrances extensively used in personal care products (6 polycyclic musks, 3 nitro musks, 7 macrocyclic musks and 1 polycyclic musk degradation product) from wastewater samples, prior to analysis by gas chromatography and mass spectrometry through an on-column interface. A 10 mm × 2 mm I.D. precolumn packed with Oasis HLB (60 μm) or C18 (60 μm) was compared for the optimization of the solid-phase extraction process. The parameters affecting the transfer of the analytes from the precolumn to the GC system (e.g. flow-rate, temperature and solvent vapor exit time) as well as SPE parameters (e.g. sample flow, sample volume, elution solvent, etc.) were optimized. An organic modifier such as methanol was added to the sample before the extraction process to avoid adsorption problems. The use of the MS detector under selected ion monitoring acquisition enabled the analytes to be quantified at low ng L^{-1} levels, preconcentrating only 10 mL of sample, and the limits of detection were between 1 and 30 ng L^{-1}. The method was applied for the determination of musk fragrances in wastewater samples from three urban wastewater treatment plants (WWTPs). The analysis of influent urban wastewater revealed that galaxolide, tonalide and ambrettolide were the most abundant musk compounds with concentrations ranging between 18 ng L^{-1} and 45,091 ng L^{-1}, 852 ng L^{-1} and 49,904 ng L^{-1} and 507 ng L^{-1} and 21,528 ng L^{-1} respectively. The remaining musks were present at lower concentrations and two of the macrocyclic musk studied (musk MC4 and civetone) were not detected. The analysis of effluent wastewater showed a decrease in the concentrations of all of the compounds present in influent samples, with the decrease being more significantly in the case of polycyclic and nitro musks than for macrocyclic musks. Only HHCB-lactone remained constant or increased its concentration.

1. Introduction

Among the extensive group of emerging compounds, musk fragrances such as polycyclic musks, nitro musks and macrocyclic musks, which are extensively used in soaps, cosmetics and other personal care products (PCPs) have gained increasing interest due to their presence in environmental waters [1,2]. A vast majority of these products are lipophilic compounds and, due to their use in many PCPs and the lack of effectiveness of procedures for their removal at wastewater treatment plants (WWTPs), they can enter aquatic environments. Therefore, the identification and quantification of these products is important. For this reason, many analytical methods based on gas chromatography (GC) mass spectrometry or tandem mass spectrometry have been developed in the last few years [3,4].

Due to the low concentrations at which musk fragrances are found in environmental water samples, some preconcentration techniques such as liquid–liquid extraction (LLE) [5–7], solid-phase extraction (SPE) [5,8–12], dispersive liquid–liquid extraction (DLLME) [13–15], solid phase microextraction (SPME) [16,17] single drop microextraction (SDME) [18,19] or microextraction by packed sorbents (MEPs) [20,21] have been reported. Of all the extraction techniques mentioned above, SPE is the most widely used in the environmental analytical field because it extracts and

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preconcentrates in a single step and a great diversity of sorbents is commercially available. Nevertheless, new microextraction techniques have recently been developed to solve some of the drawbacks of SPE and try to reduce or eliminate the use of organic solvents during the preconcentration steps, while also reducing the requirements of large volumes of sample to obtain more environmentally friendly analytical methods [22,23].

On-line SPE coupled to LC or GC appears to solve the disadvantages of off-line SPE, such as an increased chance of losses during sample handling and the requirement of large volume samples. Moreover, the automation of all the SPE procedure minimizes sample losses or contaminations during handling and improves the reproducibility of the analysis. Another advantage is the reduction of both sample volume and analysis time. In addition, it has also been applied for the determination of emerging organic compounds in environmental water samples [24–26]. However, on-line solid phase extraction coupling to GC requires the injection of relatively large volumes of organic solvents, while conventional GC injectors only permit microlitres. Therefore, the use of an injection technique is required, such as partially concurrent solvent evaporation (PCSE) using an on-column interface [27–35]. The aim of this study is the development of an automated method for determining musk fragrances in water samples using an on-line SPE-GC-MS system with an on-column interface. To the best of our knowledge, this on-line combination has never been used before to determine such a wide variety of musk fragrances that includes the most extensively used polycyclic musks, nitro musks and macrocyclic musks.

2. Experimental

2.1. Standards and reagents

Of the synthetic musk fragrances studied, the following polycyclic musk: 6,7-dihydro-1,1,2,3,3-pentamethyl-4(5H)-indanone (cashmeran, DPMI), 4-acetyl-1,1-dimethyl-6-tert-butylindane (celestolide, ADBI), 6-acetyl-1,1,2,3,3,5-hexamethylindane (phantolide, AHMI), 5-acetyl-1,1,2,6-tetramethyl-3-isopropylindane (traseolide, ATII), 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta-(*g*)-2-benzopyran (galaxolide, HHCB) and 7-acetyl-1,1,3,4,4,6-hexamethyl-1,2,3,4-tetrahydronaphthalene (tonalide, AHTN) were supplied by Promochem Iberia (Barcelona, Spain). 1,3,4,6,7,8-Hexahydro-4,6,6,7,8,8-hexamethylcyclopenta-(*g*)-2-benzopyran-1-one (galaxolidone, HHCB-lactone) were provided by International Flavors & Fragrances Inc. (Barcelona, Spain). The nitro musk fragrances 2,4,6-trinitro-1,3-dimethyl-5-tert-butylbenzene (musk xylene, MX) and 1,1,3,3,5-pentamethyl-4,6-dinitroindane (musk moskene, MM) were purchased as 100 ng μL^{-1} solutions in acetonitrile from Sigma–Aldrich (Steinheim, Germany) and Riedel de Häen (Seelze, Germany), respectively. The standard 4-aceto-3,5-dimethyl-2,6-dinitro-tertbutylbenzene (musk ketone, MK) was provided by Fluka (Buchs, Switzerland). The macrocyclic musk fragrances ethylenedodecanedioate (musk MC4), oxacyclohexadecan-2-one (exaltolide), cyclopentadecanone (exaltone) and oxacycloheptadec-8-en-2-one (ambrettolide) were purchased from Symta (Madrid, Spain). 9-Cycloheptadecen-1-one (civetone) was supplied by Sigma–Aldrich (Steinheim, Germany). Ethylenetridecanedioate (musk NN) as 10 ng μL^{-1} solution in cyclohexane, 3-methylcyclopentadecanone (muscone) as 100 ng μL^{-1} solution in cyclohexane and d15-musk xylene (labelled internal standard) as 100 ng μL^{-1} solution in acetone were also purchased from Symta (Madrid, Spain). Table 1 shows the main characteristics (formula name, CAS number, molar mass, boiling point and the octanol/water partition coefficient) of the target compounds [4,21,36,37].

Individual 1000 ng μL^{-1} standard solutions of all macrocyclic musks were prepared in cyclohexane with the exception of musk NN and muscone which were purchased already dissolved. Individual standard solutions of the polycyclic musks were prepared in acetone at concentrations of 4000 ng μL^{-1} and 1000 ng μL^{-1} for musk ketone and HHCB-lactone. A solution of 1 ng μL^{-1} in ethyl acetate was prepared weekly from the individual standard solutions and used to prepare diluted solutions and to spike water samples to the required concentrations.

Trace analysis grade cyclohexane, acetone and ethyl acetate were purchased from VWR (Llinars del Vallès, Barcelona, Spain). The methanol used as organic modifier in the on-line SPE was GC grade with purity > 99.9% (SDS, Peypin, France). The chromic mixture and HPLC grade isopropanol used for cleaning of the glassware were from Sigma Aldrich and VWR, respectively.

Ultrapure water was obtained using a Purelab ultra purification system (Veolia Water, Barcelona, Spain). Helium and nitrogen were supplied by Carburos Metálicos (Tarragona, Spain) with a quality of 99.999%.

2.2. Instrumentation

Chromatographic analysis were performed using a Hewlett-Packard HP 6890 Series gas chromatograph (Waldbronn, Germany) equipped with an on-column injector and an HP 5973 mass selective detector. In order to inject large volumes and perform the chromatographic separation, a 5 m × 530 μm I.D. retention gap from Micron Phenomenex (Torrance, California, USA), a 2 m × 250 μm I.D., 0.25 μm retaining precolumn and a 30 m × 250 μm I.D., 0.25 μm analytical column, both ZB-50 (50% phenyl/50% dimethylpolysiloxane) and from Phenomenex, were installed coupled to a solvent vent valve. The connection between the retention gap and the retaining precolumn was made with an ultimate union from Agilent Technologies (Palo Alto, USA) and a quartz press-fit splitter (Agilent Technologies, Palo Alto, USA) was chosen to conduct the excess of solvent injected to the solvent vent valve and the target analytes to the analytical column. Chromatographic data were recorded using a G1701DA MSD ChemStation, which was controlled by Windows (Microsoft).

For the solid-phase extraction, the precolumn (10 mm × 2 mm I.D.) was hand-packed with 20 mg of C18 (60 μm) or Oasis HLB (60 μm) sorbent from Scharlab (Barcelona, Spain) and Waters (Cerdanyola del Vallès, Barcelona, Spain), respectively. Three six-port Valco valves (Houston, USA) controlled by GC software were used in the SPE process. An HP 1100 pump was used to deliver the sample and the solvents needed to clean and activate the sorbent. The eluent was delivered with a syringe pump (Cole-Parmer, Illinois, USA). The analytes were transferred from the precolumn to the GC system via a 15 cm × 0.5 mm I.D. polyether ether ketone (PEEK) tubing connected to a syringe needle (point style 2). A 100 μm loop of PEEK tubing was used instead of the precolumn for direct injection. The scheme of the equipment described above to perform the on-line SPE-GC-MS method is shown in Fig. 1.

2.3. Sampling

Influent and effluent wastewater samples were collected between October 2012 and February 2013 at three urban wastewater treatment plants (WWTPs) located in Catalonia (NE Spain). The WWTPs receive urban sewages and some industrial discharges. All of the urban wastewater samples from WWTPs (A and B) were taken from the influent and effluent of the activate sludge biological treatment. However, WWTP C samples were taken from the influent and the effluent of the tertiary treatment based on reverse osmosis. Each sample was collected in