Development of stir-bar sorptive extraction–thermal desorption–gas chromatography–mass spectrometry for the analysis of musks in vegetables and amended soils
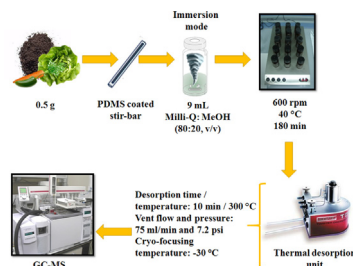
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HIGHLIGHTS

- Development of a new SBSE–TD–GC–MS method.
- PDMS coated stir-bar sorptive extraction of musks in vegetables and amended soil.
- Optimization of the extraction and thermal desorption conditions and parameters.
- Thorough evaluation of instrumental and matrix-matched calibration approaches.

GRAPHICAL ABSTRACT

ARTICLE INFO

ABSTRACT

The aim of this study was to develop a sensitive and environment-friendly method based on stir-bar sorptive extraction (SBSE) followed by thermal desorption–gas chromatography–mass spectrometry (TD–GC–MS) to determine 8 synthetic musks (musk ambrette, musk ketone, celestolide, tonalide, galaxolide, phantolide, traseolide, and cashmeran) in vegetables (lettuce, carrot, and pepper) and amended soil samples. In a first step sorptive extraction was studied both in the headspace (HSSE) and in the immerse mode (SBSE). The best results were obtained in the immersion mode which was further studied. The influence of the main factors: methanol (20%) and NaCl addition (0%), extraction temperature (40 °C) and time (180 min), extraction solvent volume (9 mL) and stirring rate (600 rpm) on the efficiency of SBSE was evaluated by means of experimental designs. In the case of TD, desorption time (10 min), desorption temperature (300 °C), cryo-focusing temperature (−30 °C), vent flow (75 mL/min) and vent pressure (7.2 psi) were studied using both a fractioned factorial design and a central composite design (CCD). The method was validated in terms of apparent recoveries (AR%), method detection limits (MDLs) and precision at two different concentration levels. Although quantification using instrumental calibration rendered odd results in most of the cases, satisfactory recoveries (74–126%) were obtained in the case of matrix-matched calibration approach for all of the analytes and matrices studied at the two concentration levels evaluated. MDLs in the range of 0.01–0.8 ng/g and 0.01–1.1 ng/g were obtained for vegetables and amended soil samples, respectively. RSD values within 1–23% were obtained for all the analytes and matrices. Finally, the method was applied to the determination of musks in vegetable and amended soil samples.

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1. Introduction

In recent years, some of the focus of the scientific community has shifted from priority to what are commonly called emerging pollutants [1]. Although some of these chemicals have been used for over

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a century, it is only within the last 20 years that their environmental impacts have been considered. As a result, there is little information available on occurrences and toxicological data, and few or no regulations or guidelines have been established so far. Examples of emerging contaminants include pharmaceuticals, personal care products (PCPs), detergents, flame retardants or disinfection by-products, among others. Within the PCPs, musk compounds are commonly used as fragrance additives in soaps, shampoos, detergents, lotions, and perfumes [2–5]. Synthetic musk fragrances have been described as a new group of bioaccumulative and persistent xenobiotics. Due to their bioaccumulative properties and health adverse reactions, which led to the prohibition of musk tibetene, musk moskene, and musk ambrette, their use declined in the 90s [4,6,7]. At the present, other two nitromusks, musk ketone, and musk xylene are still permitted but with restrictions [8,9]. On the other hand, there was a parallel increase in the use of polycyclic musks, a second group of synthetic musks which comprises several high volume use products, such as tonalide and galaxolide. Although these compounds are still largely used in personal care products and so on, research indicates that the musks fragrances are environmentally persistent, can accumulate in human bodies and they are suspected hormone disruptors [10]. Once used, these products are washed down the drain and ended up in wastewater treatment plants (WWTPs) [8,11,12]. Purification of wastewater produced in different human activities (i.e. household, industry, hospitals) usually takes place in WWTPs. After wastewater treatment, non-degraded compounds, together with their degradation products, are discharged by WWTP effluents into surface waters. Another potential route of introduction of pollutants and their metabolites into the environment is sewage sludge, since potentially harmful substances, such as organic contaminants, metals and pathogens can still be found in both effluent water and sewage sludge [13]. In this sense, sludge-amended soils can be considered a way for the introduction of the previously mentioned harmful substances into the food chain through the uptake of crops.

The introduction of organic contaminants by the food chain can be studied performing an uptake analysis by different crop plants. If any of the experiments on plant uptake or bioaccumulation of organic pollutants from crops should have any significance, the analysis should be performed using reliable analytical procedures.

Soxhlet extraction [14], accelerated solvent extraction (ASE) [15,16], microwave assisted extraction (MAE) [17] and sequential dispersion extraction [18] have been used in the literature for the analysis of musk in solid samples such as sludge or sediments. Since extraction techniques such as Soxhlet, ASE or MAE are not selective, further clean-up steps are usually necessary and, thus, intermediate evaporation steps are usually incorporated in order to reduce extract volumes. These extraction-evaporation–clean-up-evaporation sequences can introduce losses of analytes such as synthetic musks due to their semi-volatility.

Besides, traditional extraction procedures, some of which have been mentioned above, are still used even though they are time-consuming, labor-intensive, complicated, and expensive and they produce considerable quantities of waste. Within this scenario in the last years new microextraction techniques have been developed in order to improve sample pretreatments. Introduced in 1999 for analyte pre-concentration from aqueous samples, stir-bar sorptive extraction (SBSE) device consists of a magnetic stir-bar, a coating of extraction phase on the outside, and a thin glass layer between the two [19,20]. For the extraction, the bar is allowed to stir the sample solution to speed up the partitioning of the analytes between the matrix and the coating. Once the extraction process is finished, the stir-bar is usually thermally desorbed. As far as we know, even some studies have demonstrated the feasibility of SBSE for the extraction of alcohols, aldehydes, ketones, acids, and terpenes, [21], esters [22], phenols, and lactones [23] from food and soil samples [24], SBSE has not yet been applied in the analysis of musks from vegetables or soil.

Thus, the main objective of this work is the development of a new preconcentration method based on sorptive microextraction using PDMS coated stir-bars for the analysis of musks compounds in vegetables and amended-soil minimizing the consumption of sample, solvents, and time in order to study not only the presence of target analytes in amended-soil but also the potential uptake of musks by different crops (lettuce, peppers, and carrots).

2. Experimental

2.1. Cleaning procedure

All the glassware was cleaned with abundant water and soaked into clean acetone (LabScan, HPLC grade, 99.8%) for at least 45 min. No detergent was used during the cleaning of the amber vials in order to avoid possible interferences produced by the detergent residues. Afterwards, the material was rinsed with Elix water (Millipore, Bedford, MA, USA) and Milli Q water (<0.057 S/cm, Milli Q model 185, Millipore, MA, USA). The glassware was dried in an oven at 100 °C for an hour and, finally, at 400 °C for 3 h for further clean-up of the glassware.

2.2. Reagents and materials

The studied polycyclic musks 6,7-dihydro-1,1,2,3,3-pentamethyl-4(5H)-indanone (Cashmeran, DPMI, 89.5%), 4-acetyl-1,1-dimethyl-6-tert-butylindane (Celestolide, ADBI, 99.8%), 6-acetyl-1,1,2,3,3,5-hexamethylindane (Phantolide, AHMI, 93.1%), 5-acetyl-1,1,2,6-tetramethyl-3-iso-propylindane (Traseolide, ATII, 83.2%), 1,3,4,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta-(γ)-2-benzopyran (Galaxolide, HHCB, 53.5%), and 7-acetyl-1,1,3,4,4,6-hexamethyl-1,2,3,4-tetrahydronaphthalene (Tonalide, AHTN, 97.9%) were purchased from LGC Standards GmbH (Augsburg, Germany). The studied nitro musk fragrances 1-tert-butyl-2-methoxy-4-methyl-3,5-dinitrobenzene (Musk Ambrette, MA, 99%) and 4-aceto-3,5-dimethyl-2,6-dinitrotertbutylbenzene (Musk Ketone, MK, 98%) were obtained from Dr. Ehrenstorfer GmbH (Augsburg, Germany). The mass-labeled surrogate standard musk xylene [^{2}H$_{15}$]-MX was purchased from Dr. Ehrenstorfer GmbH at 100 mg/L in acetone. Stock solutions for each compound were dissolved in isopropanol in order to prepare 100 mg/L dilutions.

The CAS number of each chemical, together with the structure, boiling points, and the octanol water partition coefficient (log K_{ow}) values, are shown in Table 1.

Ethyl acetate (HPLC grade, 99.8%), methanol (HPLC grade, 99.9%), isopropanol (HPLC grade, 99.8%) dichloromethane (HPLC grade, 99.8%), and acetone (HPLC grade, 99.8%) were obtained from Labscan (Dublin, Ireland), and acetonitrile (HPLC, 99.9%) from Sigma–Aldrich (Steinheim, Germany).

The PDMS stir-bars employed (so called twisters supplied by Gerstel, Mülheim an der Ruhr, Germany) were 20 mm × 0.5 mm (long x film thickness) size. Prior to use, in the case of liquid desorption of the stir-bars, a chemical cleaning step was firstly performed in an acetonitrile: methanol (1:1, v/v) mixture under ultrasound energy during 30 min before the use of the twisters. Finally, the stir-bars were conditioned in a thermal condition unit at 280 °C for 2 h under a nitrogen atmosphere. In the case of thermal desorption of the stir-bars no condition was required.

Agitation was carried out using a 15 position magnetic stirrer (Ika Werke, Staufen, Germany).

The vegetables (carrot, pepper, and lettuce) were bought in a local supermarket. The different soils (soil 2.1 and soil