



Recent approaches for the determination of synthetic musk fragrances in environmental samples



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ABSTRACT

We review the main analytical methods currently employed for the determination of synthetic musk fragrances in air, aqueous and solid samples, such as sewage sludge or sediments, and biological samples. The review covers instrumental aspects, and procedures for extraction and clean-up. We pay special attention to current trends, such as the replacement of conventional extraction techniques (e.g., liquid-liquid extraction and solid-phase extraction) by microextraction techniques (e.g., solid-phase microextraction and microextraction by packed sorbents) in order to obtain environment-friendly methodologies. We also discuss the applicability of comprehensive two-dimensional gas chromatography and mass spectrometry (MS) or high-resolution MS to enhance the separation of co-eluting compounds and to decrease the matrix effect. Further, we describe a number of degradation assays for the determination of the main transformation products of polycyclic musk fragrances.

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1. Introduction

Synthetic musk fragrances are a family of cyclic personal-care products (PCPs) widely used as additives in a broad range of daily products, such as cosmetics, flavorings, body oils, soaps, foods and drinks. These fragrances, which were synthesized to replace expensive natural musk fragrances, include a broad range of compounds that can be divided in four main groups according to their chemical structure: nitro, polycyclic, macrocyclic and alicyclic

musk fragrances [1,2]. Fig. 1 shows the structures of a representative synthetic musk fragrance from each group.

Nitro musk (NM) fragrances are two-fold or three-fold nitrate-benzene derivatives with additional alkyl, keto or methoxy groups. These musk fragrances were the first to be produced, but concerns about their toxicology soon arose because of the presence of a nitroaromatic compound in their structure. In this respect, European Directives 98/62/EEC [3] and 1223/2009/EEC [4], relating to cosmetics products, prohibit the use of musk ambrette (MA), musk moskene (MM) and tibetene (MT) in cosmetics and limits musk xylene (MX) and musk ketone (MK) content. Recently, the European Commission under the new chemical regulation REACH (Registration, Evaluation, Authorization and Restriction of Chemicals)

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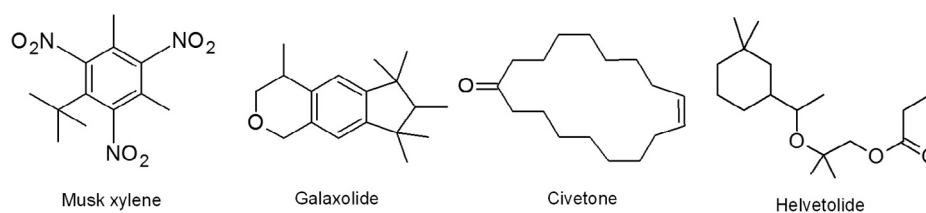


Fig. 1. Representative structures of four synthetic musk fragrances: musk xylene (nitro musk), galaxolide (polycyclic musk), civetone (macrocyclic musk) and helvetolide (alicyclic musk).

considered MX a very persistent, very bioaccumulative substance, so decided to ban it too [5]. This has led to a significant decrease in their use in recent decades due to their accumulation in environmental matrices and their potential carcinogenic effects [1]. Furthermore, NMs can be transformed in wastewater-treatment plants (WWTPs), or in biota, into amino metabolites [6], which display higher toxicity and higher hormone-disrupting potential [7,8].

Nowadays, polycyclic musk (PCM) fragrances are the most widely used. Compared with NMs, PCMs have better properties, such as a higher resistance to light and alkali [9]. The most representative PCMs are the commercially named galaxolide (HHCB) and tonalide (AHTN), which account for 95% of commercially-used PCMs [10]. For this reason, both compounds have been included on the EPA's high production list [11]. The use of AHTN in the cosmetic industry has been regulated through European Directive 2008/42/EC [12].

In contrast, macrocyclic musk (MCMs) fragrances, which are 15- or 17-membered ring systems that can be found in nature or synthesized, are not as widely used as PCMs because of the cost of their synthesis. However, they are becoming more generally available because of advances made in synthesis methods in recent years [13,14]. We expect that, over the next few years, the decreasing cost of synthesizing MCMs and their properties, such as stability with respect to light and alkalis, high fixation and quality odors and being easily degradable in the environment [15], will mean that they will replace PCMs on the market.

Alicyclic musk (ACMs) fragrances, which are considered the fourth generation of synthetic musk fragrances and are known as the linear musks (e.g., helvetolide, Fig. 1), are still used in PCPs to a very limited degree [16]. However, due to their biodegradable properties and low cost of manufacture compared to MCMs, ACMs are considered to be the future of synthetic musk fragrances.

On account of their widespread use, PCMs and NMs can be found everywhere in the world and, due to their lipophilic characteristics and slow biodegradation, they can accumulate in sediments [17], sludge [17,18], surface water [19,20] and fish species living in contaminated rivers and estuaries [21,22].

2. Instrumental analysis

2.1. Chromatographic approaches

Gas chromatography (GC) is a versatile technique suitable for the determination of thermally-stable volatile and semi-volatile organic compounds, and is the preferred technique for determining synthetic musk fragrances, because these compounds have high thermal stability and lipophilicity [1]. One of the main advantages of GC is that it is compatible with sample-preparation techniques that require subsequent liquid desorption or thermal desorption of the analytes, so it can be used in combination with a wide range of sample-preparation techniques. In addition, all common injectors, including split/splitless (SSL), on-column (OC) and programmed temperature vaporizer (PTV), have successfully been applied for determining synthetic musk fragrances in environmental samples [17,23,24]. The most commonly-used injection system is SSL, which allows the

injection of 1–4 μL . However, the use of large-volume injection (LVI) through OC and PTV injectors is one of the strategies currently used to improve sensitivity. Nonetheless, due to the large volumes that can be injected in OC and PTV injectors (50 μL or more), they are recommended only when clean samples are used. Otherwise, the chromatographic system can easily become polluted and give unreliable results [1].

The separation of the synthetic musk fragrances is normally performed in low-polar 5% phenyl/95% dimethylpolysiloxane GC columns (e.g., DB-5MS, HP-5MS) [17,21,25,26]. However, as the separation of HHCB enantiomers/diastereoisomers is impossible with these columns (see Fig. 2a), a mid-polarity 50% phenyl/50% dimethylpolysiloxane column, such as ZB-50, has successfully been used for this purpose (see Fig. 2b) [27–29]. The columns used are usually 30 m in length, with a 0.25-mm internal diameter and 0.25- μm film thickness, and the separation is performed in 20–45 min. Furthermore, as shown in Fig. 2c, the enantiomers/diastereoisomers of the PCMs and their metabolites can be separated by enantioselective GC using a heptakis-(2,3-di-*O*-methyl-6-*O*-*t*-butyldimethyl-silyl)- β -cyclodextrin (25 m \times 0.25 mm ID, 0.2–0.3- μm film thickness) [10,30–33] column. In this case, the separation of the PCMs was extended up to 130 min.

However, the complexity of environmental matrices can cause several problems with identification and quantification of target musk fragrances. The chromatographic peaks of the synthetic musk fragrances can sometimes co-elute with matrix components, so their separation by one-dimensional GC is very difficult. To overcome this difficulty, GCxGC has been applied [34–36]. For example, Gómez *et al.* [36] developed a method based on GCxGC to determine a group of priority emerging organic contaminants in wastewater and river water, including 15 polycyclic aromatic hydrocarbons (PAHs), 27 pesticides and 13 PCPs; six of them were synthetic musk fragrances. Excellent results were obtained for separation efficiency and compound identification. Also, reliable confirmation of analyte identity was possible at low concentration levels (ng L^{-1}), even for typically troublesome compounds, such as PAHs [36]. As demonstrated by Herrera-López *et al.* [34] and Bester [31], both GCxGC and GC can be used for the study of HHCB and AHTN degradation products generated in degradation processes.

2.2. Detection

Although a flame-ionization detector (FID) or electron-capture detector (ECD) has been used for the determination of NMs [37], MS is the most commonly-used detection technique for determining synthetic musk fragrances. In GC analysis, the full-scan mode of MS is employed in screening or as an untargeted approach to overcome the restrictions encountered with target analysis, though the reduction in acquisition speed, poor response and interferences limit the suitability of such approach.

Whereas selective ion monitoring (SIM) and tandem MS (MS/MS) limit the number of compounds that can be analyzed due to the need to select ions (SIM) or transitions (MS/MS) and, consequently, they are usually applied to achieve high sensitivity for

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