



The survey of analytical methods for sample preparation and analysis of fragrances in cosmetics and personal care products



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ABSTRACT

Fragrances most widely utilize in cosmetics and personal care products. These are known as allergens and emerging organic contaminants that induce the adverse effects on human health. In addition, dealers are tempted to adulterate the products by adding lower cost materials. It is therefore essential to detect fragrances in raw materials, cosmetics, and personal care products. The aim of this review is a survey of the main sample preparation and analysis methods proposed in previously published works dealing with the detection of fragrances in cosmetics and personal care products. Different sample preparation methods were utilized according to the matrix complexity e.g. dilution for the simple matrix, and headspace, direct, and tandem methods for the complex matrix. Also, different methods have been used for the analysis of fragrances in cosmetics and personal care products, investigated in four parts: chromatography, spectroscopy, mass spectrometry and electronic nose methods.

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1. Introduction

Fragrances as a compilation of art and science are organic compounds with pleasant or sweet odors produced by perfumers and chemists. Nowadays, fragrances are utilized in every aspect of our daily lives such as perfumes and deodorants, aftershave products, creamy shampoos and conditioners, laundry products, cleaning products and so on. Currently, more than 3000 chemical substances either natural fragrance materials or synthetic fragrance chemicals are responsible for odorous properties of scented products, while a mixture of 20 to over 200 among them constructs the fragrance compounds [1]. As can be seen in Fig. 1, fragrances are classified from different points of view like their sources, their provided note, and their chemical structures [2]. Natural fragrances are divided into two major classes, aroma and musk compounds. Plants are the largest source of aroma compounds or essential oils that may be derived from various parts of a plant, whereas the original musk components of fragrances were extracted from animal sources [2]. Other natural sources like Lichens and Seaweeds are used too. Because synthetic aromatics can reduce perfume costs and can be obtained without problems related to poor crop quality

or lack of supply, they are often used as an alternative source of compounds that are not easily obtained from natural sources or not found in nature. Also, new chemicals can be synthesized, and thus new scents are developed that are not found naturally [2].

The most famous international companies in fragrance field are Givaudan (Swiss), IFF (American), Firmenich (Swiss), Symrise (German), Quest International (Anglo-Dutch), and Takasago (Japanese) that own 57% of the total market [3]. The global market for flavors and fragrances was valued at \$26.0 billion in 2015 which is expected to increase to \$37.0 billion in 2021 [4]. The quota of cosmetics from fragrance industry is 80% [1]. Cosmetics and personal care products (PCPs) are classified from different aspect of view, for example based on their tendency to be removed after application or to stay in prolonged contact, there are two classes (a) 'rinse-off product' and (b) 'leave-on product', respectively. Based on another classification, different types of cosmetics are: hair cosmetics; washing products; skin lotions, creams and packs; make-up products; face and toilet powders; lip colors; nail make-up; perfumes; bath preparations; cosmetic oils; face cleansing products; sunscreens; soaps; and oral care products [2]. Fragrances are found in almost all forms of these products to create good scents.

Fragrance materials as allergens can induce allergic contact dermatitis that may be present in natural essential oils or obtained by synthetic ways [5]. Oxidized derivatives are responsible for the allergenic activity, such as peroxides, as in the case of limonene and

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Fig. 1. Classification of fragrances from different points of view: (a) their sources, (b) their provided note, and (c) their chemical structures.

linalool [6]. Although more than 3000 chemical substances are used in fragrance compounds, the Scientific Committee on Consumer Safety (SCCS) identified that 82 substances among them could be classified as established contact allergens in humans, 54 single chemicals and 28 natural extracts. The chemical structures of allergenic fragrances were depicted in Fig. 2. Preservatives, perfumes, and deodorants are the most frequent sources of sensitization to fragrance ingredients in women, while aftershave products and deodorants are most often responsible for men's sensitization [1]. As a result, the regulation foresees that any allergen, present more than 100 mg kg^{-1} in rinse-off and of 10 mg kg^{-1} in leave-on formulations, must be reported on the label of the product [7]. Moreover, due to the adverse effects of fragrances on human health and their potential bioaccumulation (such as genotoxicity, which could even lead to mutagenic or carcinogenic effects, or estrogenicity because of their endocrine disruption activity), they are clearly an emerging health and environmental concern [8]. Meanwhile, because of the high prices of essential oils, dealers are tempted to adulterate the products by adding lower cost materials but still asking the same high price for the mixture. The techniques used in adulteration can be altering from the crude to the very sophisticated that are revealed by some of the quality control (QC) methods used routinely in industry [3].

According to the mentioned above reasons, in order to the assessment of allergenic properties, environmental contamination and adulteration of fragrances in raw materials, cosmetics, and personal care products, use of analytical techniques seems inevitable. From 1963 until July 2017, 402 reviews have been published about flavors and fragrances from various aspects such as fragrance ingredients, synthesis, production, impurities, safety, toxicity, allergenic properties, legislation, encapsulation, photochemistry, which subject classification of these reviews is demonstrated in Fig. 3a. To our knowledge, only 11 of them were about analytical methods, among them solely four reviews were about analysis of fragrances, flavors in perfume mixtures by atmospheric-pressure chemical ionization tandem triple quadrupole mass spectrometry (1984) [9], analysis, occurrence, kinetics, and toxicology of musk xylene in cosmetics and other matrices (1998) [10], extraction methods of 26 fragrance allergens from essential oils, cosmetics, indoor air and environmental water samples (2013) [11], and quantification of flavors and fragrances by mass spectrometry (2016) [12]. The aim of this review is a comprehensive survey of the used methods for sample preparation and analysis of fragrances in cosmetics and PCPs for the first time that the number of their publication per years was shown in Fig. 3b. First, the conventional methods in each type of sample

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