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Determination of suspected fragrance allergens extended list by two-dimensional gas chromatography–mass spectrometry in ready-to-inject samples

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ABSTRACT

A new strategy was developed to elucidate and quantify 56 (69 analytes including isomers) suspected chemically defined fragrance allergens in perfumes that were recently targeted by the Scientific Committee on Consumer Safety (SCCS). Samples were analyzed with a two-dimensional gas chromatography–quadrupole mass spectrometry system (GC–GC–MS). Method performance was evaluated by the accuracy profile approach to determine uncertainties around the regulation limit of 10 mg/kg. This strategy was finally applied to 62 commercialized perfumes, analyzed in the routine workflow. Depending on the matrix, an acceptable result was obtained for 88–100% of the target analytes, which means that results were accurately defined under or above 10 mg/kg. This method saves considerable time for complete analysis and could be adopted for routine analysis due to its ruggedness and cost effectiveness.

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1. Introduction

The risk management of fragrance allergens is an important issue for the regulators and the cosmetic industry in Europe. The European regulation (EC) no. 1223/2009 on cosmetic products currently lists 26 potential fragrance allergens (24 chemically defined compounds) [1] for which information should be provided to consumers about their presence in cosmetic products, above 100 mg/kg in rinse-off products or 10 mg/kg in leave-on products.

The analytical method to quantify these compounds is based on gas chromatography–mass spectrometry (GC–MS) using two analytical columns of different polarity to limit the number of coelutions [2]. Because of this dual analysis and the complexity of fragrance matrices, data analysis is time consuming and requires trained users to accurately quantify coeluting compounds at the 10 mg/kg level. Recently, the Scientific Committee on Consumer Safety (SCCS) has issued an opinion which extends the number of substances that the consumer should be made aware of when they are present in cosmetic products. The list coming from this opinion talks about 84 substances, including 28 natural extracts and 56 chemically defined compounds [3].

From an analytical perspective, this represents a huge challenge, creating a need for both a specific analytical method and more efficient data treatment. To our knowledge, there is no method for the analysis of this extended list in perfumes currently in the literature. For the cosmetics list, previous studies have described methods to improve analytical specificity, favoring multi-dimensional gas chromatography due to the complexity of cosmetic matrices. High-resolution mass spectrometry (HRMS) is another alternative, but the cost of these instruments can be prohibitive.

Two multi-dimensional approaches have been described for cosmetic analysis, comprehensive gas chromatography (GC × GC) [4–8] and heart-cut gas chromatography (GC–GC) [9–11], both coupled to mass spectrometry (MS). These approaches have the advantage of improved separation capacity compared to classic GC–MS methods [2,5,12–15]. GC × GC is the most powerful system to improve separation capacity, providing a complete 2D sample analysis, but it can be difficult to set up and requires very specific data processing, which is not the case with GC–GC.

Heart-cut methods have traditionally been used to improve chromatographic separation in small numbers of complex elution windows [9,10], but a multiple heart-cut strategy (14 cuts) was developed to detect 24 allergens in fragrances, in which every

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target compound was analyzed in 2D [11]. However, this work did not present quantitative results, and the system required two GC ovens, which is relatively bulky.

The multiple heart-cut strategy was expanded in this work to quantify 56 suspected allergens from the SCCS extended list in complex fragrances. The innovative aspect of this research is the combination of multiple heart-cut chromatography with a low thermal Mass chromatography module (LTM) applied to quantification of extended list of allergens. The LTM technology produces independent and fast temperature gradients in the second dimension using space-saving equipment. With different isomers selected, 69 analytes were monitored, and the quantitative results were evaluated with the accuracy profile methodology [16–18]. This statistical approach has already been successfully applied in various areas [19–22]. It estimates the total error of an analytical measurement and compares it to an acceptance limit. Moreover, the graphical representation obtained at the end of the validation is a useful decision-making tool for the analyst.

2. Experimental

2.1. Reagents, standards and samples

The target solutes (Table 1) were supplied by Sigma–Aldrich (St-Quentin Fallavier, France), BLH-PIM (St. Vallier De Thiey, France), Charabot (Grasse, France), DRT (Dax, France), Firmenich (Geneva, Switzerland), Givaudan (Vernier, Switzerland), IES (Allauch, France), IFF (New York, USA), Indukern (Barcelona, Spain), Mane (Le bar sur loup, France), Moellhausen (Vimercate, Italy), Niel (Grasse, France), PCW (Mouans-Sartoux, France), Robertet (Grasse, France), SIPA (Grasse, France), Symrise (Holzminden, Germany), Synarome (Chartres, France), Takasago (Ota, Japan) and Ventos (Barcelona, Spain). The total set of analytes consisted of 59 fragrance materials to be weighted in standard solutions. It included the 24 allergens indicated in EC regulation 1223/2009 and the other suspected allergens recently listed by the SCCS. We decided to add two other compounds, isodamascone because it has a similar chemical structure than other damascones listed by the SCCS and 6-methylcoumarin which is a material that should be prohibited according to IFRA (international fragrance association). Some regulated compounds consisted of more than one isomer monitored (e.g., citral = neral + geranial; farnesol = three isomers; tetramethyl acetyloctahydronaphtalene (iso E) = three isomers; beta damascone = two isomers; ebanol = two isomers; hexamethylindanopyran = two isomers; santalol = two isomers and terpineol = two isomers). Finally, 69 analytes were monitored in the method.

Preparation of standards and ISTDs solutions was based on the standardized method of the 24 allergens [2]. Allergen standards were mixed in two different stock solutions at approximately 5 g/L in 2-fluorotoluene (Merck, Darmstadt, Germany) to limit acetal formation: one containing the carbonyl compounds and the other containing non-carbonyl compounds. An internal standard solution of 1,4-dibromobenzene (VWR, Fontenay-sous-Bois, France) and 4,4′-dibromobiphenyl (Merck, Darmstadt, Germany) was prepared at 10 g/L in the same solvent. 2-Fluorotoluene was also used for intermediate dilution mixing both standard solutions of allergens (500 mg/L) and the final solution of ISTDs (100 mg/L). Then, a final dilution of standard allergens (50 mg/L) was made by dilution in ethanol (96.2% purity) supplied by Dislaub (Buchères, France) before preparing the calibration solutions (1–40 mg/L). Calibration solutions were made by an addition of different volumes of the final standard allergens solution and a fixed volume of the final ISTDs solution (100 μL) completed with ethanol to 1 mL. For the perfumes, a sampling of 900 μL, weighted, was done with a 100 μL ISTDs final solution addition.

For validation, an “allergen-free” perfume was prepared (matrix A) with non-allergen raw materials frequently used in commercial perfumes (Supplemental Table S1), diluted in ethanol at 10% (w/w). The GC analysis of this homemade matrix was representative of a common fragrance with approximately 300 chromatographic peaks detected (ingredients + isomers + impurities). A commercialized perfume was also used as a second validation matrix (matrix B).

2.2. Instrumentation and analytical conditions

The GC–GC–FID–MS system was composed of an Agilent GC 7890A gas chromatograph equipped with an Agilent 7693 autosampler, a split/splitless injector, an Agilent LTM II series, a microfluidic heart-cut system (Deans switch) from Agilent, and an FID detector. It was coupled to an Agilent inert MSD 5975C with a triple axis detector (Palo Alto, USA). The first dimension separation was carried out on a VF1-MS capillary column (40 m × 0.15 mm i.d. × 0.150 μm film thickness, Agilent). The second dimension separation was performed on an LTM DB17-MS capillary column (20 m × 0.18 mm i.d. × 0.180 μm film thickness, Agilent). This system is illustrated in Fig. 1.

A strategy based on two injections of the same sample with two specific methods (M1 and M2) was developed. In such configuration, analytes were split between the two methods, conditions are described below. All parameters relative to the first dimension separation were the same for both methods: 1 μL split injection (15:1 ratio) at 250 °C with helium as the carrier gas at a 73 psi constant inlet head pressure. The GC oven temperature was programed from 100 °C to 240 °C at 10 °C/min and a final ramp to 300 °C at 25 °C/min (held 34 min). In both methods, the first GC column was connected to the Deans switch, where a constant helium pressure of 45 psi was applied to guide samples either to the FID (260 °C; H_2 flow: 45 mL/min; air flow: 450 mL/min) or to the second dimension through specific cut programs (Fig. 2).

Two specific 2D temperature programs were optimized for each method: M1 was set from 30 °C (held 7.5 min) to 200 °C (held 0.2 min) at 300 °C/min, to 30 °C (held 16.17 min) at 300 °C/min, to 100 °C at 65 °C/min, to 180 °C at 5 °C/min, and a final ramp to 280 °C (held 5 min) at 30 °C/min. M2 method was programmed from 30 °C (held 25 min) to 100 °C at 65 °C/min, to 180 °C at 5 °C/min, and a final ramp to 280 °C (held 5 min) at 30 °C/min.

The transfer line temperature to the mass spectrometer was set at 300 °C, ion source was heated at 230 °C and the MS was operated in SIM/scan mode, scanning between 40 and 300 amu. Selected ions for the SIM programs are shown in Table 1.

2.3. Validation protocol

Quantitative results were evaluated using the accuracy profile method [16–18] (see Supplementary data, Fig. S1, for more). It is a useful tool that aids the analyst in determining whether method performance is compliant with requirements. It is based on an evaluation of the trueness and intermediate precision. The acceptance limit (red lines in Supplemental Fig. S1) is a threshold value, fixed by users in relation to the method objectives, and the tolerance limit (green lines in Supplemental Fig. S1) is an interval assumed to contain a known part of the results that will be generated by the method [16–18]. This interval is called β and was fixed at 90% in our study. It was admitted that resulting tolerance limits should be within the acceptance limit set at ±35%.

Five calibration levels (1, 5, 10, 20 and 40 mg/L), four levels of spiked matrix (5, 10, 15 and 30 mg/L) and a non-spiked level were injected in triplicate. Operation was repeated during three

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