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Four-stage (low-)flow modulation comprehensive gas chromatography–quadrupole mass spectrometry for the determination of recently-highlighted cosmetic allergens

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ABSTRACT

The present research is based on the development and use of a flow-modulation (FM) comprehensive two-dimensional gas chromatography–quadrupole mass spectrometry (GC × GC–qMS) method for the determination of recently-highlighted (by the Scientific Committee on Consumer Safety) fragrance allergens (54) in cosmetics. FM GC × GC–qMS conditions were finely tuned to generate flow conditions (≈7 mL min^{-1}) compatible with the qMS system used. Six-point calibration curves, over the range 1, 5, 10, 20, 50, 100 mg L^{-1}, were constructed for the 54 target allergens, with satisfactory linearity observed in all cases. Absolute quantification was performed by using extracted ions; target analyte identification was performed through measurement of ion ratios (qualifier/quantifier), full-scan MS database matching and the use of linear retention indices. Additional analytical figures of merit subjected to measurement were intra-day repeatability, accuracy at the 25 and 5 mg L^{-1} levels, and limits of detection and quantification. The number of data points per peak, along with mass spectral skewing, was also subjected to evaluation. Finally, the FM GC × GC–qMS method was used not only for the quantification of target allergens in five commercial perfumes, but also for general qualitative profiling.

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1. Introduction

The first published comprehensive two-dimensional gas chromatography–mass spectrometry (GC × GC–MS) research appeared in 1999 [1]. A single quadrupole MS (qMS) was used for the qualitative analysis of a petrochemical sample and was, as recognized by the same authors, too "slow" to adequately reconstruct the narrow peaks exiting the second dimension. Since that first application, and obviously due to the importance of mass spectrometry, there has been a considerable expansion of GC × GC–MS.

The most commonly used mass analyzers in the GC × GC field have been (low-resolution) time-of-flight ones, with rapid-scanning single quadrupoles coming in second place [2]. It is noteworthy that the great majority of GC × GC–MS experiments have been performed with cryogenic modulators, which are effective but expensive transfer devices. Flow modulation (FM) is a low-cost interesting alternative to cryogenic systems [3], even though there has been no real expansion of the use of FM in the GC × GC–MS field, the main reason being the generation of high gas flows in such experiments (*e.g.*, 20–25 mL min^{-1}) [4–7]. However, in recent work based on the use of the FM model proposed by Seeley et al. [4], it was demonstrated that it is possible to use MS-compatible flows (*e.g.*, 6–8 mL min^{-1}) by extending the length of the re-injection period (*i.e.*, 400 ms) [8]. In additional work, it was found that the use of a long accumulation loop (*e.g.*, 50 cm) enabled a double accumulation/re-injection process, greatly improving post-modulation peak shape [9].

The above-reported FM GC × GC approach (with a qMS) is herein applied to the determination of fragrance allergens (skin sensitizers). The latter have been subjected to considerable attention in Europe: in 1999, the Scientific Committee on Cosmetic Products and Non-Food Products (SCCNFP) identified a set of 24 fragrance contact allergens, for which label information should be provided to consumers in relation to their presence in cosmetics [10]. The 24

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allergens (plus two extracts) are regulated by the European Directive 2003/15/EC setting a maximum residue limit for “leave-on” and “rinse-off” products of 0.001% (10 ppm) and 0.01% (100 ppm), respectively.

In 2012, the Scientific Committee on Consumer Safety (SCCS) not only confirmed the previously-regulated allergens, but extended the attention to additional substances which have been shown to be skin sensitizers [11]. Specifically, 82 compounds were classified as contact allergens, of which 54 were single chemicals and 28 were natural extracts. The SCCS also indicated that a general level of exposure of up to 0.8 $\mu g\,cm^{-2}$ (0.01% in cosmetic products) may be tolerated by the majority of consumers.

The determination of contact allergens is not new to the field of multidimensional GC (MDGC): for example, the 24 compounds indicated by the SCCNFP were subjected to cryogenic GC × GC–qMS analysis by Debonneville and Chaintreau [12], while in a recent research, classical MDGC–qMS was used for the analysis of the 54 compounds reported by the SCCS [13]. In the latter work, several heart-cuts were performed to cover the retention time windows of all the 54 target analytes.

The FM GC × GC–qMS method herein proposed is directed to the determination of the 54 compounds highlighted by the SCCS. Quantification was performed by using extracted ions, while identification was carried out through qualifier/quantifier ion ratios, MS database matching and the use of one-dimensional linear retention indices [14]. Following optimization, the method was evaluated in terms of linearity, intra-day repeatability, accuracy, and limits of detection/quantification. Finally, five commercial perfumes were subjected to both untargeted and targeted analysis.

2. Materials and methods

2.1. Samples and sample preparation

Fifty-three allergen standards were used (Table 1). A standard was not commercially-available (mixture of α- and β-santalol), thus it was isolated from sandalwood oil using a lab-constructed preparative MDGC system [15].

Two internal standards (IS), namely benzene-2-bromoethenyl (IS1) and 4,4′-dibromobiphenyl (IS2), were used at a concentration of 20 $mg\,L^{-1}$. Quantification was performed by using extracted ions (Table 1). Methanol (purity >99%) was used to form the calibration solutions (1, 5, 10, 20, 50, 100 $mg\,L^{-1}$). All standards and the solvent were supplied by Sigma–Aldrich/Supelco (Bellefonte, PA, USA).

The five commercial perfumes (P1–P5) were purchased in a local store.

2.2. FM GC × GC–qMS analyses

All FM GC × GC–qMS applications were performed on a system consisting of two independent GC2010 gas chromatographs (GC1 and GC2), and a QP-2010 Ultra qMS (Shimadzu, Kyoto, Japan). The two GC ovens were linked through a heated transfer line (310 °C). The primary GC was equipped with an AOC-20i auto-injector and a split-splitless injector (310 °C).

The first dimension (D1) column (situated in GC1), an SLB-5ms [silphenylene polymer virtually equivalent in polarity to poly(5% diphenyl/95% methyl siloxane)] 20 m × 0.18 mm ID × 0.18 μm d_f (Sigma–Aldrich/Supelco), was connected to the modulator, after passing through the heated transfer line. An SLB-35 [equivalent in polarity to poly(35% diphenyl/65% methyl siloxane)] 5 m × 0.25 mm ID × 0.25 μm d_f capillary (Sigma–Aldrich/Supelco), was used as second dimension (D2) column.

The following GC conditions were used: injected volume: 1 μL; split ratio: 10:1; GC1 temperature program: 45–228 °C at 3 °C min^{-1}; GC2 temperature program: 50–233 °C at 3 °C min^{-1}; initial (45 °C) and final (228 °C) inlet pressures (He): 130.8 and 216.2 kPa; initial (50 °C) and final (233 °C) auxiliary pressures (He): 65.2 and 143.2 kPa.

Flow modulation was performed following the model proposed by Seeley [4]. Briefly, the modulator was constructed by using two MXT Y-unions (Restek Corporation, Bellefonte, PA, USA) and a 2-way solenoid valve (located outside the GC), connected to an auxiliary pressure source. The output ports of the solenoid valve were connected to the unions by using two metal branches. One of the Y-unions was linked to the primary-column outlet, while the other directed the flow to the second dimension. A fused silica accumulation loop measuring 40 cm × 0.53 mm ID (Sigma–Aldrich/Supelco) bridged the two Y-unions. A scheme of the modulator is available as supplementary material (Fig. S1).

Modulation period was 5400 ms, with a 500 ms flushing pulse.

Quadrupole MS conditions: ionization mode: electron ionization (70 eV). Interface and ion source temperatures: 250 °C and 200 °C, respectively. Mass range: 40–360 m/z; scan frequency: 25 Hz. Mass spectral matching was carried out by using the FFNSC 3.0 database (Shimadzu).

Data were acquired using the GCMSsolution software (Shimadzu). Bidimensional chromatograms were generated by using the ChromSquare software v. 2.0 (Shimadzu).

3. Results and discussion

3.1. Optimized FM GC × GC–qMS operational conditions

FM GC × GC method optimization can be a rather complicated task, and is here described treating the first and second column, along with the FM, in an independent manner. GC1 temperature program was 45–228 °C at 3 °C/min, while a small positive offset of 5 °C was used in GC2. The different oven temperatures slightly reduced retention of many polar allergens on D2, reducing wrap-around. General information on gas flows and average linear velocities (ALVs) are summarized in Table 2. The initial and final D1 (apolar, 20 m × 0.18 mm ID) ALVs were approx. 16 $cm\,s^{-1}$ (0.46 mL min^{-1}) and 13 $cm\,s^{-1}$ (0.33 mL min^{-1}), respectively. The use of low, non-ideal D1 gas ALV conditions is related to the necessity to avoid breakthrough during the FM accumulation step (4900 ms).

The initial and final D2 (medium polar, 5 m × 0.25 mm ID) ALVs were about 235 $cm\,s^{-1}$ (7.0 mL min^{-1}) and 250 $cm\,s^{-1}$ (7.0 mL min^{-1}), respectively. It is noteworthy that the (constant) D2 gas flow was well within the pumping capacity of the qMS system (15 mL min^{-1}). The initial and final FM accumulation ALVs were approx. 2.2 $cm\,s^{-1}$ (0.46 mL min^{-1}) and 1.7 $cm\,s^{-1}$ (0.33 mL min^{-1}), respectively. Considering such ALV values, and the duration of the accumulation step, the initial and final lengths of the accumulated chromatography band should be ≈11 and 8 cm, respectively. The initial and final FM re-injection ALVs were approx. 34.8 $cm\,s^{-1}$ (7.0 mL min^{-1}) and 37.1 $cm\,s^{-1}$ (7.0 mL min^{-1}), respectively. Again, considering such ALV values and the duration of the re-injection step (500 ms), the intra-loop chromatography band should be pushed ≈17.5 and 18.5 cm, at the beginning and end of the analysis, respectively. As aforementioned, the use of a long loop enables a four-stage FM process [9]: at the beginning of the analysis (50 °C), and after the first accumulation process, the analyte band would reach an intra-loop distance of approx. 11 cm; the first re-injection step would push the band another 17.5 cm, with the front end reaching a distance of about 28.5 cm; after the second accumulation step, the band should reach a distance within the loop of about 39.5 cm, and then be entirely released from the loop with the second re-injection step. Efficient four-stage modulation was observed at the end of the analysis, as can be derived by

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