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Comprehensive two-dimensional gas chromatography in combination with rapid scanning quadrupole mass spectrometry in perfume analysis

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Abstract

Single column gas chromatography (GC) in combination with a flame ionization detector (FID) and/or a mass spectrometer is routinely employed in the determination of perfume profiles. The latter are to be considered medium to highly complex matrices and, as such, can only be partially separated even on long capillaries. Inevitably, several monodimensional peaks are the result of two or more overlapping components, often hindering reliable identification and quantitation. The present investigation is based on the use of a comprehensive GC (GC × GC) method, in vacuum outlet conditions, for the near to complete resolution of a complex perfume sample. A rapid scanning quadrupole mass spectrometry (qMS) system, employed for the assignment of GC × GC peaks, supplied high quality mass spectra. The validity of the three-dimensional (3D) GC × GC–qMS application was measured and compared to that of GC–qMS analysis on the same matrix. Peak identification, in all applications, was achieved through MS spectra library matching and the interactive use of linear retention indices (LRI).

Keywords: Comprehensive two-dimensional gas chromatography; Perfume analysis; GC × GC; Quadrupole mass spectrometry

1. Introduction

Perfumes have been applied to human skin for thousands of years and are, today, characterized by a global social and economical importance. Hence, the improvement and development of analytical techniques is considered of the upmost importance by the perfume industries. These complex matrices are characterized by a wide variety of natural and synthetic components belonging to several chemical classes [1]. It must be emphasized that, in the recent years, the risk of contact allergy, induced by perfumery ingredients, has been the object of scientific debate [2]. Under the current European legislation (7th Amendment of the Cosmetic Directive), the 26 most frequently recognized contact allergens (identified by the Scientific Committee on Cosmetics and Non-Food Products Intended for Consumers) must be labeled, by 11 September, 2004, on the final cosmetic product if specific quantities are exceeded.

Monodimensional gas chromatography (GC)-flame ionization detection (FID) and GC–MS are commonly employed in the analysis of major and minor (comprehending suspected allergens) perfume components. It must be added that the determination of trace-level components in fragrances is highly important as these can have a considerable olfactive and economical impact [1,3]. A series of single column GC methods have been described [4–6]. Unfortunately, the monodimensional approach often results inadequate in the analysis of the more complex perfume samples, with extensive co-elutions occurring both on apolar and polar stationary phases. The identification of unresolved compounds, when employing MS detection, can be achieved through the

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support of deconvolution techniques [7–10]. It is obvious, though, that especially in the case of severely overcrowded chromatograms, the attainment of an improved GC separation and, thus, of high quality analyte mass spectra is always desirable. Furthermore, deconvoluted profiles cannot be obtained for analytes that have very similar ionization patterns.

An enormous increase in resolving power, in respect to monodimensional GC, is the main characteristic of comprehensive GC. The principles of GC × GC have been described thoroughly in literature [11,12]. The unprecedented resolving power of this method as well as a greater detection sensitivity are ideal characteristics both for complex sample and trace-level analysis.

A GC × GC–FID technique, based on the use of an apolar–polar column set, was employed in the quantitation of five target allergens added to a complex perfume [13]. The quantitation of three out of five allergens was achieved, while nearly 500 peaks were counted on the contour plot.

The hyphenation of a MS detector to a comprehensive GC set-up provides a third analytical dimension. The employment of time-of-flight (TOF–MS) and quadrupole instrumentation has been reported. TOF–MS systems can easily achieve the required spectra acquisition rates (50–100 Hz) for reliable GC × GC peak assignment and quantitation [14–16]. Unfortunately, the high cost of such instrumentation is the main reason behind its limited laboratory diffusion.

The quadrupole mass spectrometry (qMS), on the contrary, has a relatively low cost and is widely employed in hyphenated GC [7]. It is characterized by high sensitivity but lacks the TOF–MS performance, in terms of detection capabilities. Although this aspect hinders the attainment of reliable GC × GC–qMS quantitative data, precious qualitative information can be obtained [17–20]. In Refs. [18,19], the use of a wider-bore secondary capillary, under the low qMS pressure conditions, enhanced the two-dimensional (2D) column efficiency. A further GC × GC–qMS research, performed in SIM mode and at a sampling rate of 30.7 Hz, described the quantitation of target allergens in fragrances [21]. In this case, the bidimensional chromatograms were greatly simplyfied and, hence, the detection of specific analytes was easier.

The innovative aspect of the present research is the degree of separation/identification, through the three-dimensional GC × GC–qMS application, of both harmless and potentially harmful perfume components. Furthermore, although a wide mass scan range was employed, the quadrupole mass spectrometer provided a high full scan data acquisition rate. The identification of just under 170 components was achieved through mass spectra matching with four different commercial libraries and the interactive use of LRI. Several contact allergens were also identified; peak assignment, in this case, was confirmed by the use of standard components.

2. Experimental

2.1. Standard components

C8–C36 hydrocarbons in *n*-hexane solutions (0.1 μg/mL) were purchased from Supelco (Milan, Italy).

Amyl cinnamaldehyde, anisyl alcohol, benzyl alcohol, benzyl cinnamate, methyl 2-octynoate, citral, cinnamaldehyde, benzyl benzoate, benzyl salicylate, cinnamyl alcohol, amylcinnamyl alcohol, coumarin, eugenol, isoeugenol, farnesol, citronellol, geraniol, hydroxycitronellal, hexylcinnamaldehyde, limonene, α-isomethylionone, lilial, linalool, estragole, *cis*-dihydrocarvone and neo-dihydrocarveol were purchased from Sigma–Aldrich (Milan, Italy). Lyral and γ-terpineol were purchased from IFF (Milan, Italy).

2.2. Sample and sample preparation

The perfume was purchased in a local perfumery and stored at 4 °C. The sample was not diluted prior to monodimensional and comprehensive GC analysis.

2.3. GC–qMS and GC × GC–qMS analyses

GC–qMS and GC × GC–qMS analyses were carried out on a Shimadzu GCMS-QP2010 gas chromatograph mass spectrometer (Shimadzu, Milan, Italy) equipped with commercial mass spectral libraries. The GC was equipped with a LMCS Everest longitudinally modulated cryogenic system (LMCS; Chromatography Concepts, Doncaster, Australia), with a mechanical stepper motor drive for movement of the cryotrap (not activated in GC–qMS applications). A modulation period of 0.125 Hz was applied in all GC × GC analyses and initiated by the GC solution programmed external events that via the electronic controller starts also the motor operation. CO_2 is supplied to the trap, and its expansion cools the trap that is thermostatically regulated at about 0 °C. A small internal flow of nitrogen gas (about 10 mL/min) prevents ice formation inside the trap. An increase in the CO_2 tank pressure was achieved through compression of the carbon dioxide with nitrogen. The introduction into the cylinder of this lighter gas enabled an increase in the CO_2 pressure of about 100 atm. The pressurization of the cylinder with nitrogen was achieved by the seller with the normal pressurization system using the CO_2 cylinder instead of an empty one, and by providing the cylinder with a security valve calibrated at 220 atm (1 atm = 101325 Pa). A tube insert placed inside the gas cylinder allowed the exit flow of the sole CO_2 from the bottom of the cylinder. The two-stage regulator connected to the cylinder was modified in order to deliver a 150 atm CO_2 flow to the LMCS system. Data were collected by the GCMS Solution software (Shimadzu, Milan, Italy) and by using its export function; the ASCII data were converted into a matrix with rows corresponding to a 8 s duration, and data columns covering all successive second dimension 8 s chromatograms using the Comprehensive Chromatography Con-

verter 1.0 software (Avantech, Angri, Salerno, Italy). Contour representation of the two-dimensional chromatograms was achieved through the same software. The column set for GC–qMS and GC × GC–qMS analysis consisted of two columns, which were serially connected by a zero-dead-volume press-fit (Mega, Legnano, Italy). In this study, we used the following columns: the conventional first dimension was a BPX-5 (5% diphenyl + 95% dimethyl polysiloxane) column 30 m × 0.25 mm i.d. × 0.25 μm film thickness (SGE Italy, Milan, Italy) and the secondary fast column was a Supelcowax-10 (polyethylene glycol) 1 m × 0.25 mm i.d., 0.25 μm film thickness (Supelco Italy, Milan, Italy). The operational conditions were: temperature programmed conditions from 50 to 230 °C at 1.5 °C/min, to 260 °C (3 min) at 15 °C/min. The GCMS-QP2010 was equipped with a split/splitless injector (250 °C); injection volume: 1 μL, in the split mode (ratio 10:1). Carrier gas: He delivered at constant pressure: 119.2 kPa; linear velocity: 50 cm/s. Interface temperature 250 °C; MS ionization mode: electron ionization; detector voltage: 0.9 kV; acquisition mass range 40–400 u; scan speed 10000 u/s; acquisition mode: full scan; scan interval: 0.05 s (20 Hz); solvent delay: 5 min.

3. Results and discussion

In preliminary GC × GC–qMS applications on the perfume sample, a series of stationary phase combinations were tested. Most comprehensive GC investigations reported in literature are based on the use of a primary apolar and a secondary polar column, as this type of combination provides a true orthogonal separation. It must be emphasized that total orthogonality is not always the most suitable choice and other column sets can be more rewarding [22]. In the present research, though, the classical apolar–polar coupling proved to be the most suitable option. In fact, the polar–apolar (polyethylene glycol–5% diphenyl + 95% dimethylpolysiloxane) or polar–slightly polar (polyethylene glycol–20% diphenyl + 80% dimethylpolysiloxane) set-ups presented a series of advantages and, mainly, disadvantages. While bidimensional peaks were generally better shaped in comparison to the orthogonal set, the secondary column lacked selectivity towards several of the medium to highly polar one-dimensional co-eluting compounds. Furthermore, the stronger retention of the more polar volatiles on the primary column increased the overall analysis time (120 min). The apolar–polar set-up, while generating a certain number of excessively retained and, thus, broadened peaks, provided a more complete separation of the perfume components in a shorter analytical time (95 min). It must be noted, though, that many polar perfume components, characterized by high capacity factors on the polyethylene glycol stationary phase, were retained far longer than the 8 s modulation period in the second dimension. Attempts were thus made to decrease the excessive retention observed on the secondary polar column.

The benefits, in terms of speed and column efficiency, of increasing column internal diameters in vacuum outlet conditions are well-known ([23] and references therein) and have been exploited in comprehensive GC [18,19]. The employment of a 0.25 mm i.d. secondary capillary enabled increases that regarded analysis speed and the optimum average gas linear velocity (both as a consequence of the higher diffusion coefficient of the solute in the mobile phase). The higher solute volatility and a relatively high helium velocity had beneficial effects on analyte wrap-around/broadening. Moreover, the increase in sample capacity enabled the injection of greater sample amounts and the detection of several trace-amount components. The latter, in fact, were not detected in preliminary applications on the initial column set (primary 30 m × 0.25 mm i.d. and secondary 1 m × 0.1 mm i.d.). It is obvious, that the employment of a second oven would enable the application of higher second dimension temperatures thus reducing analyte wrap-around. This particular option will be tested in future research.

3.1. GC–qMS perfume analysis

The commercial perfume matrix was initially analysed on the apolar–polar column set without cryogenic modulation. The single axis total ion current (TIC) GC–qMS chromatogram relative to this application is reported in Fig. 1. The entirely or partially resolved peaks, with a signal-to-noise ratio of at least three, are 186. Peak assignment was carried out through mass spectra probability matching with the following four commercial libraries: Wiley 229, NIST 147 (Shimadzu Europe, Duisburg, Germany), SHIM 1607 [24] and SZ TERP [25] (only spectra similarities of 90% and over were considered) and the interactive use of LRI (when reference values were available). The search procedure, similar to one already described [26], is as follows: the LRI relative to an unknown peak is calculated prior to assignment. During spectra library matching, dedicated software (see Section 2) automatically deletes library hits with lower than 90% probability (filter 1) and with a LRI, in respect to the calculated unknown peak value, outside an acceptable retention index window (filter 2). The latter, chosen by the analyst, is typically +/− 5 units for a single apolar column analysis. In this case, linear retention indices were calculated for a 31 m column (30 m apolar plus 1 m polar). The values obtained were matched with data reported in literature for the primary 30 m column [24]. It must be added, that the influence of a 1 m polar capillary, in terms of retention, is negligible for the less polar analytes, while the more polar components, on the contrary, have intense interactions and are strongly retained. Hence, a large retention index window of 50 units (−5/+45) was applied by the authors, thus reducing the effectiveness of the LRI filter. It must be added, that the retention window was chosen on the basis of knowledge acquired through the development of a flavour and fragrance laboratory-constructed MS library. Pure mass spectra, in fact, are derived from GC × GC–qMS applications using mainly the same column combination as

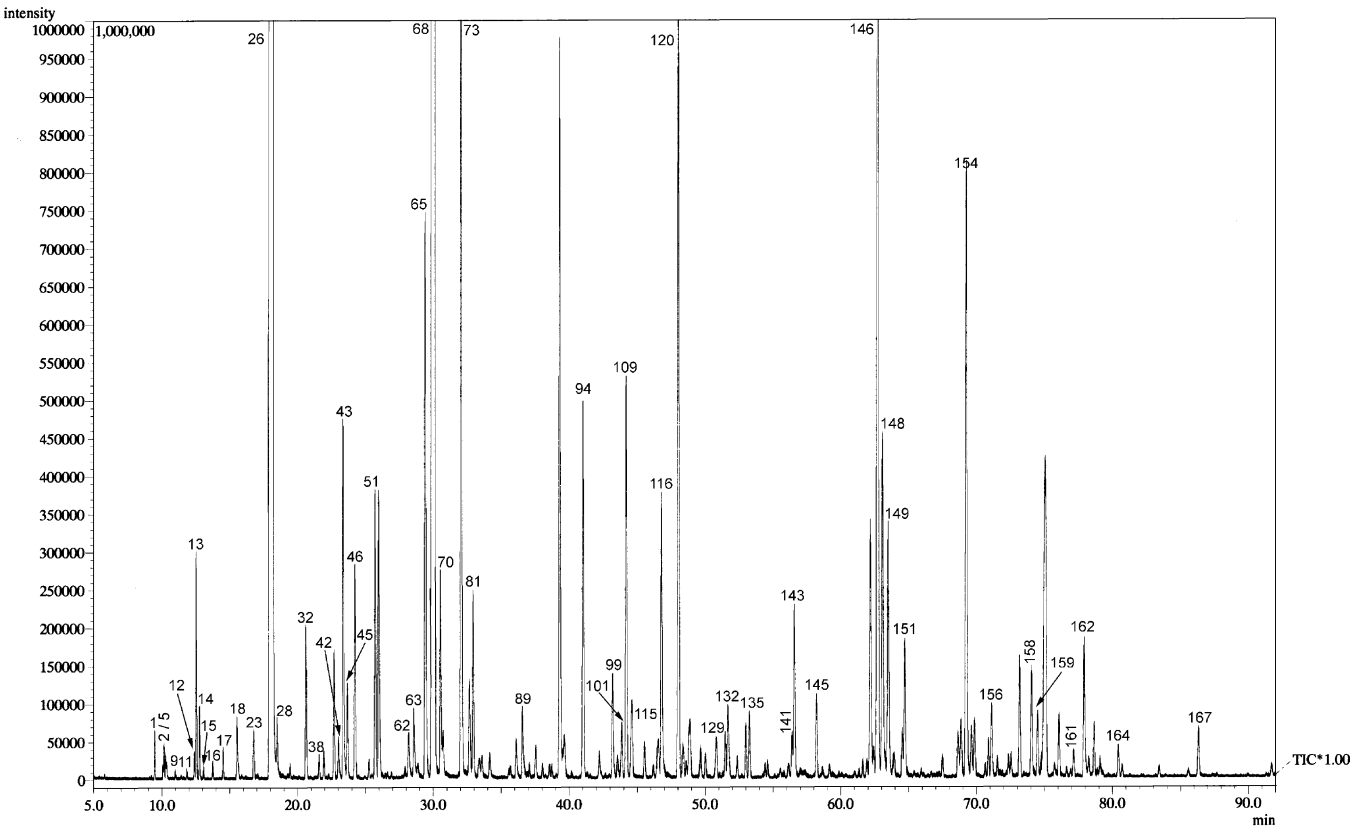

Fig. 1. GC–qMS TIC chromatogram relative to a perfume sample and achieved on the twin column set without cryogenic modulation (complete peak identification can be obtained via e-mail through request to the corresponding author).

Table 1
GC–qMS (13 components) and GC × GC–qMS (19 components) peak identification

Peak	Compound	Ref.	1D LRI	1D Hits	Best (%)	2D LRI	2D Hits	Best (%)
13	**Limonene**	1029	1029	3	96	1028	4	96
26	**Linalool**	1097	1111	3	97	1111	3	98
52	Estragole	1196	–	–	–	1208	4	98
53	*cis*-Dihydrocarvone	1193	–	–	–	1208	3	96
54	γ-Terpineol	1199	–	–	–	1210	2	94
55	Neo-dihydrocarveol	1194	–	–	–	1210	3	94
63	**Citronellol**	1226	1238	3	95	1239	2	98
65	**Neral (component of citral)**	1238	1248	3	96	1249	3	96
70	**Geraniol**	1253	1261	3	97	1263	3	98
73	**Geranial (component of citral)**	1267	1279	3	96	1280	3	96
82	**Hydroxycitronellal**	1288	1304	3	92	1309	3	97
89	**(*E*)-Cinnamyl alcohol**	–	1333	3	94	1360	3	96
92	***Eugenol***	1359	–	–	–	1375	2	96
116	**Coumarin**	1434	1457	3	96	1473	3	96
117	***α-Isomethyl ionone***	–	–	–	–	1473	2	95
135	**Lilial**	1529	1535	1	91	1536	2	94
154	**2-Hexyl-(*E*)-cinnamaldehyde**	1750	1754	2	96	1755	4	97
156	**Benzyl benzoate**	1760	1780	3	95	1789	4	95
162	**Benzyl salicylate**	1866	1881	3	94	1892	4	95

Abbreviations: ref.: reference LRI; 1D and 2D hits: number of 1D and 2D library matches; best: most probable library match. Compounds in bold: allergens identified in both monodimensional and bidimensional applications. Compounds in bold italics: allergens identified only in the bidimensional application.

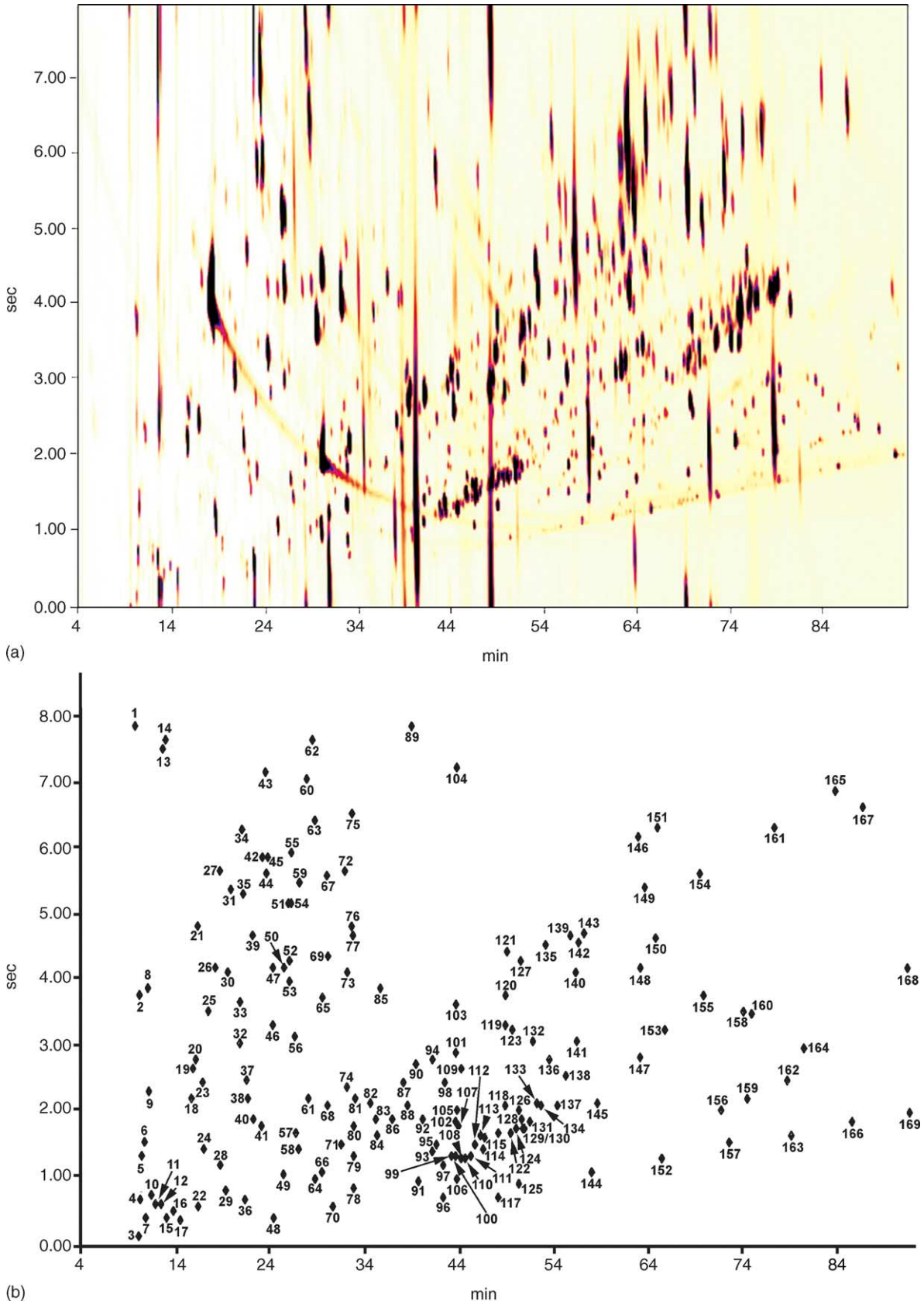

Fig. 2. (a) GC × GC–qMS perfume sample 2D result and (b) relative apex-plot containing the identified peaks (complete peak identification can be obtained via e-mail through request to the corresponding author).

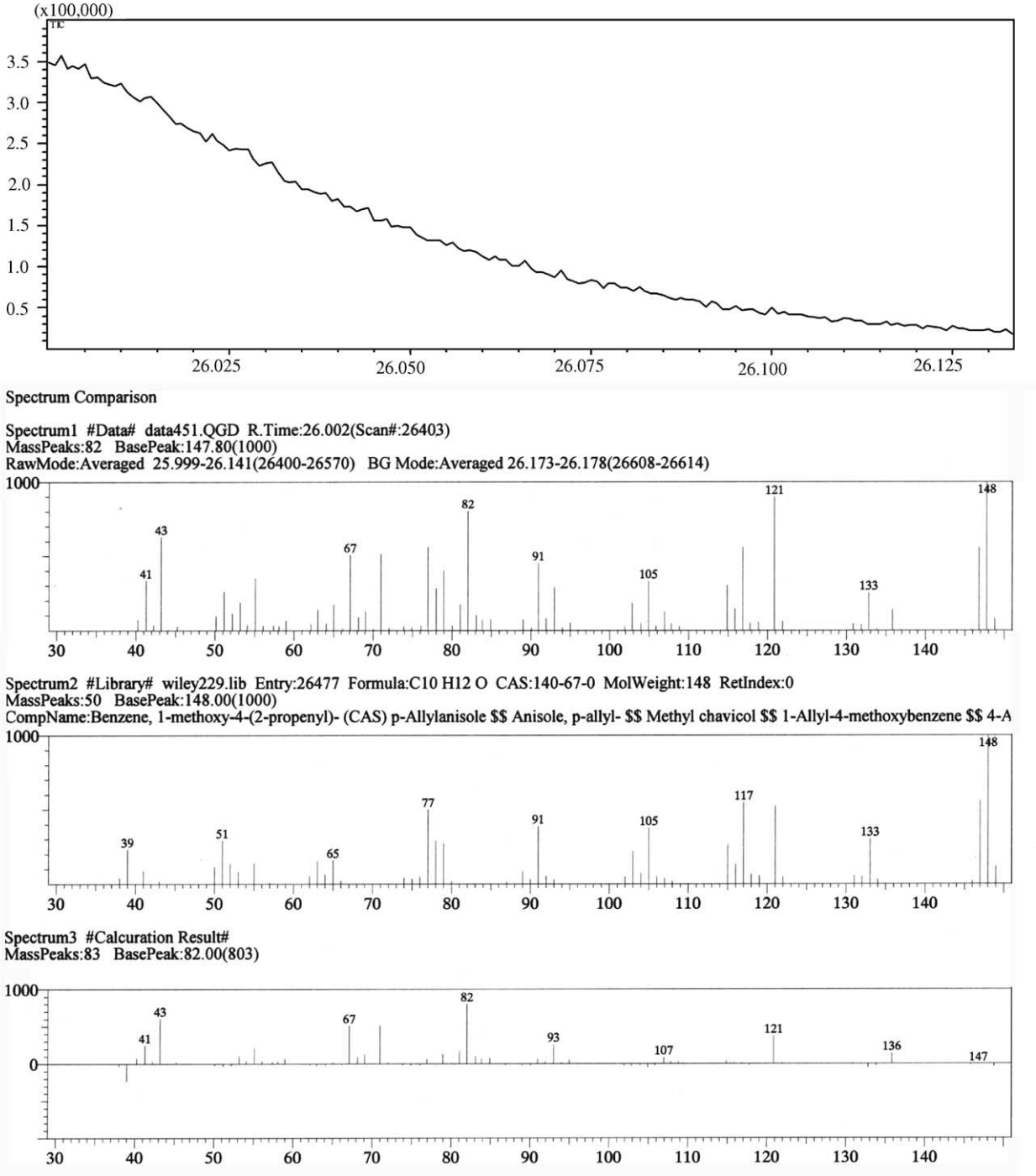

Fig. 3. Eight second (0.133 min) expansion relative to Fig. 1 and, from top to bottom, correspondent corrected mass spectrum, best library match and subtracted result.

in the present investigation. Altogether, 58 perfume analytes (reference LRI were not available in six cases) were assigned (numbered peaks in the figure). The highest library match, in terms of probability, was in 32 cases (approximately 55%) within the 94–97% range, while at least three library hits per peak were obtained in 35 cases (approximately 60%). Twelve identified components are recognized contact allergens whose identification was supported by the use of standard components (in bold in Table 1). Amongst the allergens, just two (peaks 82 and 135) presented a library spectra similarity of under 94%, while only peaks 135 and 154 were identified with less than three library hits. The GC–qMS result, both in terms of separation and mass spectra quality, can be considered satisfactory.

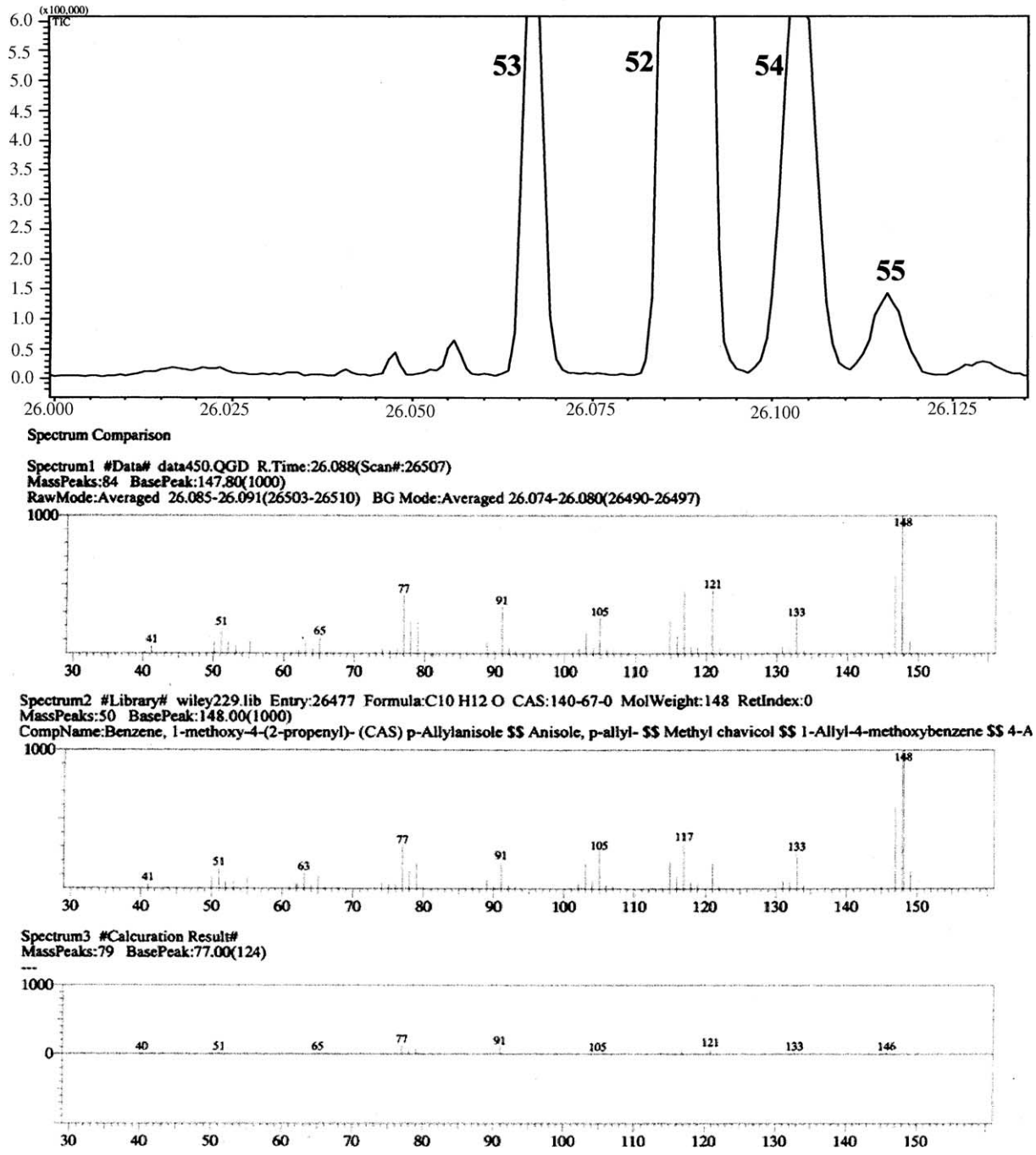

Fig. 4. The result of a single modulation applied to the peak fraction reported in Fig. 3 and, from top to bottom, correspondent corrected mass spectrum, best library match and subtracted result. Peak numbering as in Table 1.

3.2. GC × GC–qMS perfume analysis

The double axes TIC chromatogram relative to the GC × GC–qMS application on the same perfume is illustrated in Fig. 2a. The effective entrapment of low-boiling perfume volatiles was achieved through the use of a pressurized CO_2 cylinder (see Section 2) previously reported [22]. Two factors are evident after a brief observation of the chromatogram: the bidimensional peaks are spread over great part of the space plane and are characterized by a series of wrap-arounds relative to the more polar compounds. This last aspect is less than what would be desired from a chromatographic standpoint. The exploitation of low pressure conditions, although enabling a considerable increase in the secondary elution speed, did not completely resolve this problem. Furthermore, the use of an undiluted sample (see Section 2) while enabling the detection of trace-level amount analytes, was the cause of peak distorsion for the more abun-

dant components. It must be emphasized, though, that the main goal was the development of an approach capable of achieving the separation/identification of the highest possible number of fragrance analytes. This was accomplished after a considerable expenditure of time in method development. The total number of entirely or partially resolved peaks in the contour plot is 866; nearly five-fold more compared to the unmodulated application. Peak identification was carried out in the same manner as in the monodimensional analysis. LRI were calculated through data derived from unconverted GC × GC chromatograms and was carried out as follows: the retention time of the central component was considered in the case of an odd number of modulated analyte peaks, while in the case of an even number of modulated peaks the central retention time between the two most internal peaks was considered.

The qMS instrumentation, operated at a wide mass scan range (40–400 u), supplied a good performance in terms of data acquisition rate (20 Hz). The attainment of three to four high quality MS spectra, for the narrower GC × GC peaks, proved to be sufficient for peak assignment in many cases. This was linked to the separation of pure component peaks in the second dimension and to the great reduction of background interference. Furthermore, the observed differences of mass spectra relative to different points across a given peak were negligible demonstrating a low qMS skewing effect. The number of peaks identified with a match quality of at least 90% were 169 (reference LRI were not available in 38 cases). A numbered apex-plot, constructed using the identified peak apex retention time coordinates and enabling the easier visualization of the identified analytes, is illustrated in Fig. 2b. The substantial improvement, in terms of GC × GC spectra quality, was demonstrated by the fact that, for 133 components (approximately 79%), the highest probability match was in the 94–98% range. Approximately, 60% of all assigned peaks (102 analytes) presented at least three library hits, which was the same as observed in the monodimensional analysis. Furthermore, an additional two skin sensitizors (eugenol and α-isomethylionone), not detected in the single column analysis, were separated and positively identified. As it can be seen in Table 1, all of the 14 GC × GC–qMS identified allergens were characterised by a highest library match in the 94–98% range, while four (peaks 63, 92, 117 and 135) presented less than three library hits (a complete list of the GC–qMS and GC × GC–qMS identified analytes can be obtained via e-mail through request to the corresponding author).

In the present research, many major monodimensional GC–MS peaks remained unidentified essentially because they were the result of several co-eluting compounds. It is obvious that, when such unresolved analytes are delivered to the mass spectrometer, high quality spectra cannot be obtained. A good example of this major drawback can be observed in Fig. 3, which illustrates the descending part of a peak, contained in a 8 s (0.133 min) expansion relative to the conventional GC–MS application. The background corrected averaged mass spectrum, the best reference library match and the subtraction result are also reported. A poor 72% spectrum similarity was observed for the most similar reference match estragole. Hence, the peak was not assigned in the conventional GC–qMS application. The subtraction result, as it can be seen, belies the probable presence of co-eluting analytes.

The greater potential of the GC × GC–qMS method, in this type of application, is fully demonstrated in Fig. 4, which shows the result of a single modulation applied to the same peak fraction reported in the previous figure. The raw GC × GC chromatographic expansion is characterized by the presence of eight fully-resolved compounds; three minor and one major peak were identified and numbered in accordance with data reported in Table 1. The eight components were quantified through GC × GC–qMS data. As it can be seen from the spectra illustrated in Fig. 4, peak 52, identified as estragol, was characterized by a high quality spectrum (98% library match). This analyte was present in a relative quantity (in respect to the other seven peaks) of approximately 87% (peak responses relative to compounds 52–55 were measured through the employment of standard components), obviously in both expansions. The other now-resolved components (especially peaks 53–55), were the cause of the unacceptable spectra quality seen in Fig. 3. It must be noted, that baseline resolution, between components that are characterized by very similar LRI (peaks 52–55 have LRI reference values all in the 1493–1499 range) and in the aforeseen quantities, would be very complicated to achieve on a single capillary.

Table 2
GC × GC–qMS unfiltered, with filter 1 and filter 1/2 search results relative to peak 130 (β-bisabolene)

Unfiltered library search	Filter 1 (90% minimum similarity)	Filter 1 and 2 (90% minimum similarity and 1463–1513)
β-Bisabolene 94% (1506)	β-Bisabolene 94% (1506)	β-Bisabolene 94% (1506)
(*E*)-β-Farnesene 92% (1457)	(*E*)-β-Farnesene 92% (1457)	
(*Z*)-Caryophyllene 90% (1409)	(*Z*)-Caryophyllene 90% (1409)	
(*E*)-Caryophyllene 90% (1419)	(*E*)-Caryophyllene 90% (1419)	
(*Z*)-β-Farnesene 89% (1443)		
(*Z*)-α-Bisabolene 89% (1507)		
Sesquisabinene 86% (1460)		
(*Z*)-α-Bergamotene 85% (1413)		

Also reported for each component is the spectrum similarity (%) and the reference LRI.

Finally, the aforementioned automated library search procedure was of substantial, even if reduced help (in respect to monodimensional GC), in component identification. A good example of this is reported in Table 2, which illustrates the GC × GC–qMS search result relative to β-bisabolene (peak 130), respectively without, with filter 1 and filter 1/2. The unfiltered library search, carried out with the four aforementioned libraries, provided eight possible sesquiterpene matches (Table 2) for the initially unknown peak (a LRI of 1508 was calculated). The application of filter 1 (minimum 90% similarity) lead to the exclusion of four components, while the additional employment of filter 2 (1463–1513 LRI window) eliminated a further three sesquiterpenes giving only one possible match. This type of approach, in general, is of great support in the attainment of reliable structural information.

4. Conclusions

The GC–MS determination of a perfume formulation is a cumbersome challenge. This, even when dual analysis on different stationary phases is carried out, as the presence of several major and trace-level components, as well as target allergens must be identified within a very complex sample.

The GC × GC–qMS method, developed in the present research, proved to be a more suitable alternative in this type of application. A great improvement, in the analysis of a completely unknown matrix, was achieved in terms of separation, number of identified peaks and mass spectral quality. It must be noted, that although nearly 870 resolved and partially overlapping peaks were visible on the space plane, the authors retain that co-elutions still occur. In fact, a series of mass spectra, even relative to major components, were characterized by insufficient quality denoting the presence of interfering analytes. It must be observed, though, that this factor could be linked to the lack of the relative mass spectra in the commercial libraries. Future research will be dedicated to further method improvements, as aforementioned, on this and other more complex fragrances and to the development of dedicated libraries.

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