GC-MS Quantitation of Fragrance Compounds Suspected To Cause Skin Reactions. 1

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Recent changes in European legislation require monitoring of 24 volatile compounds in perfumes as they might elicit skin sensitization. This paper reports a GC-MS quantitation procedure for their determination in fragrance concentrates. GC and MS conditions were optimized for a routine use: analysis within 30 min, solvent and internal standard selection, and stock solution stability. Calibration curves were linear in the range of 2−100 mg/L with coefficients of determination in excess of 0.99. The method was tested using real perfumes spiked with known amounts of reference compounds.

KEYWORDS: Allergen; GC-MS; quantitation; skin reaction; fragrances; perfumes

INTRODUCTION

In the European Union, the allergenicity of some consumer products has recently come to the forefront. Twenty-four volatile chemicals used in perfumery have been suspected to elicit dermal reaction under patch testing (**Table 1**) (*1*). Without presuming whether their possible sensitizing properties will be confirmed or invalidated, their occurrence in fragrance concentrates needs to be determined. The objective of the present work is to develop a reliable reference analytical method applicable in all quality control laboratories. In this study, the following conditions were targeted: instrument and analytical conditions usually used for fragrances; automated procedure for a high control frequency; and analysis of the 24 target compounds in a single run.

Only two papers on this subject have been previously published. Rastogi's approach consists of the identification of targeted allergens using GC-MS (*2*). The quantitation is then achieved with a GC-FID, after peak attribution according to their retention times. This does not solve the possible coelution of allergens with perfume constituents, as a FID does not exhibit any specificity to evaluate the proportion of a given compound in a complex peak. In a report by the Danish Environmental Institute, the same author used specific ions extracted from the scan acquisition to achieve the quantitation (*3*). Such a procedure is known to lead to inaccurate values (*4*). Ellendt's proposal seems to overcome these difficulties as the quantitation is

performed in GC-MS, using specific ions in SIM mode (*5*). However, this procedure still requires improvements for a general applicability to complex fragrance mixtures, due to the following potential shortcomings:

• Only one internal standard (citronellal) was used for a long elution time (80−120 min), and its stability was known to be limited.

• The paper indicates quantitation based on two ions per compound, but it does not mention whether abundance ratios of these ions were used to check the identity of compounds, as recommended in such a context (*6*).

• Standard solutions were prepared in ethanol, in which they were said to be unstable (*2, 3*).

In the present study, a conventional GC-MS was used, as it is now a common instrument in the perfumery industry. To demonstrate the capability of the method to be extended to the quantitation of other compounds used in fragrances, phenylacetaldehyde, estragole, methyleugenol, and methyl 2-nonynoate were included in the present investigation.

EXPERIMENTAL PROCEDURES

Materials. Suppliers of reference compounds, internal standards, and solvents are indicated in **Tables 1** and **3**, respectively. Fragrance models, proton, FT, and SVB, were chosen to exemplify several levels of composition complexity with 32, 57, and 168 constituents, respectively.

GC-MS System. Analyses were performed with an HP 6890 gas chromatograph (Agilent Technologies, Wilmington, DE), equipped with a programmable thermal vaporizer (PTV) and a PAL autosampler (CTC Analytics AG, Zwingen, Switzerland). The column outlet was directly coupled to the EI source of an HP 5973 mass spectrometer (Agilent Technologies). The injector and MS source temperatures were 250 and 230 °C, respectively. Four different columns were used: DB1, DB5, DB17 (J&W−Agilent Technologies), and Delta 3 (Mach-

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Table 1. Sources and Purities of Standards [GC Areas; Ions in Bold Are Used for Quantitation, Others for Peak Recognition (See Text)]

name [CAS Registry No.][d]	supplier	purity[a] (%)	ions	impurities (>0.5%)
amylcinnamic alcohol [101-85-9]	Mane Fils (France)	92.0 + 4.5 Z + E	**133**, 115, 204	1% dihydrocinnamic alcohol
amylcinnamic aldehyde [122-40-7]	Whyte Chemicals (U.K.)	93.7 + 4.7 Z + E	**202**, 201, 129	1.3% 2-pentyl-2-nonenal
anisyl alcohol [105-13-5]	Symrise (Germany)	>99.9	**138**, 137, 109	
benzyl alcohol [100-51-6]	Whyte Chemicals (U.K.)	>99.9	**108**, 79, 107	
benzyl benzoate [120-51-4]	Symrise (Germany)	>99.9	**105**, 212, 194	
benzyl cinnamate [103-41-3]	Symrise (Germany)	99.2	**131**, 192, 193	0.75% benzyl alcohol
benzyl salicylate [118-58-1]	Quest Int'l (U.K.)	>99.9	**91**, 228, 65	
cinnamic alcohol [104-54-1]	Noveon (U.S.)	96.0	**92**, 134, 115	1.1% benzaldehyde
				1.7% cinnamic aldehyde
cinnamic aldehyde [104-55-2]	Noveon (U.S.)	1.8 + 93.63 Z + E	**131**, 132, 103	2.9% benzaldehyde
citral [5392-40-5]	BASF AG (Germany)	37.3–62.6 Z + E	neral: **69**, 94, 109	
			geranial: **69**, 84, 94	
citronellol [106-22-9]	Takasago (Netherlands)	99.3	**69**, 95, 81	
coumarine [91-64-5]	Buckton Page Ltd (U.K.)	>99.9	**146**, 118, 89	
estragole[b] [140-67-0]	Bordas SA (Spain)	98.2	**148**, 147, 117	
eugenol [97-53-0]	Indonesian Essential Oils	>99.9	**164**, 103, 149	
farnesol [106-28-5]	S. Black Ltd (U.K.)	45.9 + 53.6 ZE + EE	**69**, 93, 81	
geraniol [106-24-1]	IFF (U.K.)	98.5	**69**, 123, 93	1.5% nerol
hexylcinnamic aldehyde [101-86-0]	IFF (U.K.)	94.0 + 4.0 Z + E	**216**, 215, 129	1.5% 2-hexenyl-2-decenal
hydroxycitronellal [107-75-75]	BASF AG (Germany)	>99.9	**59**, 71, 43	
isoeugenol [97-54-1]	Indonesian Essential Oils	7.8 + 92.2 Z + E	**164**, 149, 131	
butylphenyl methylpropional [80-54-6]	S. Black Ltd (U.K.)	2.4 + 96.5 Z + E	**189**, 147, 204	
limonene [5989-27-5]	R. C. Treatt Co. Ltd (U.K.)	97.3	**68**, 93, 67	0.5% α-pinene
				2.2% myrcene
linalool [78-70-6]	Millenium Products (U.S.)	98.5	**93**, 71, 121	1.5% dihydrolinalool
hydroxyisohexyl-3-cyclohexene carboxaldehyde [31906-04-4]	IFF (U.K.)	27.5 + 72.5 (3-)[c] + (4-)[c]	**136**, 192, 149	
methyl 2-nonynoate[b] [111-80-8]	S. Black Ltd (U.K.)	99.5	**79**, 137, 100	
methyl 2-octynoate [111-12-6]	S. Black Ltd (U.K.)	>99.9	**95**, 123, 79	
methyleugenol[b] [93-15-2]	Symrise (Germany)	99.5	**178**, 163, 147	
phenylacetaldehyde[b] [122-78-1]	Symrise (Germany)	95.6	**91**, 120, 92	
α-isomethylionone [127-51-5]	IFF (U.S.)	88.0	**135**, 206, 150	1.3% γ-ionone
				3.04% β-ionone
				4.4% α-ionone
1,4-dibromobenzene	Aldrich (U.S.)		**236**, 234, 238	
4,4′-dibromobiphenyl	Aldrich (U.S.)		**312**, 310, 314	

[a] For geometrical isomers, their respective percentages are denoted (*x* + *y*). [b] Other compounds, not in the SCCPNFP list of 24 compounds (*1*). [c] Isomers (3-) and (4-) represent 3- and 4-(4-hydroxy-4-methylpentyl)-3-cyclohexene-1-carbaldehyde. [d] Supplied by the author.

Table 2. Separation Performances of Some Columns Tested with the Mix of 28 Compounds

column	oven program	flow[a] (mL/min)	duration (min)	$\bar{R}$	coelutions
DB1 (100% PDMS), 60 m × 0.25 mm × 0.25 μm	100 °C, 2 min; 10 °C/min; 280 °C	3.6	25	0[b] (5.17)	amyl cinnamic aldehyde, first peak of hydroxyisohexyl-3-cyclohexenecarboxaldehyde[a]
DB1 (100% PDMS), 20 m × 0.18 mm × 0.18 μm	100 °C, 2 min; 10 °C/min; 280 °C; 10 min	1.7	30	0	anisic alcohol/geranial cinnamic alcohol/methyl nonynoate
DB5 (5% phenylmethylpolysiloxane), 60 m × 0.25 mm × 0.25 μm	60 °C, 1 min; 3 °C/min; 150 °C; 6 °C/min; 280 °C	1.7	45	5.90	
DB17 (50% phenylmethylpolysiloxane), 30 m × 0.25 mm × 0.25 μm	60 °C, 1 min; 3 °C/min; 280 °C	1.3	55	9.78	
DB17 (50% phenylmethylpolysiloxane), 20 m × 0.18 mm × 0.18 μm	100 °C, 2 min; 10 °C/min; 280 °C	1.7	17	8.80	
Delta-3, methyl [75%]-biphenyl[25%]-polysiloxane, 30 m × 0.25 mm × 0.25 μm	60 °C, 1 min; 3 °C/min; 280 °C	1.0	56	0	cinnamaldehyde/anisic alcohol

[a] Flow measured at the initial temperature of the oven program. [b] Mean resolution if the mentioned coelution is taken into account. If neglected: = 5.96 (see the discussion).

erey-Nagel, Düren, Germany). Their characteristics and conditions of use are reported in **Table 2**. The carrier gas was helium supplied at a constant pressure, and samples (2 μL) were injected with a 1/100 split.

The MS was operated under an ionization energy of 70 eV, in SIM and low resolution modes, with one quantitation ion and two qualifying ions per target compound. The typical dwell time was 50 ms for each

of the three ions of a SIM window when the GC peak was fully separated from its neighbors and 20 ms when an overlap occurred, to monitor six ions (i.e., two compounds) in a given SIM window (see **Table 6**).

Quantitation. A stock solution of the 24 allergens, plus phenylacetaldehyde, estragole, methyleugenol, and methyl 2-nonynoate, was prepared in isooctane (10 g/L of each compound). From this stock
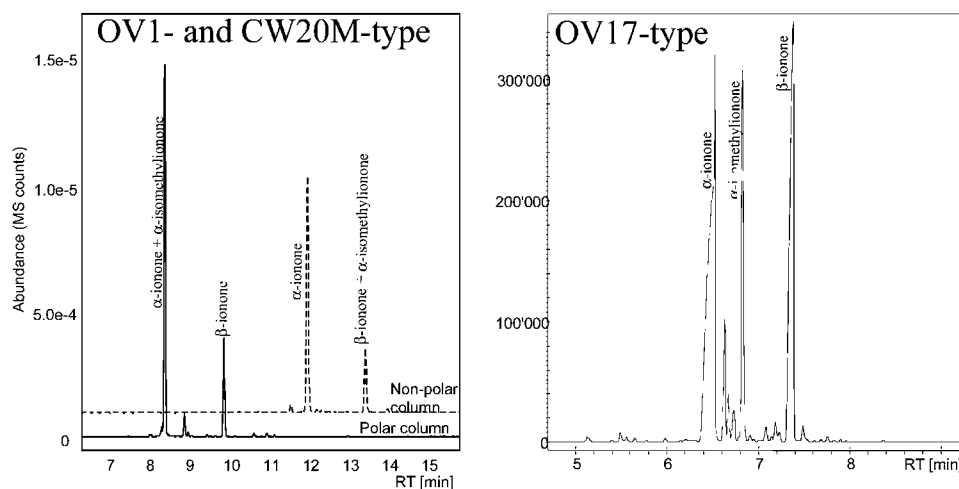
Figure 1. Coelution of α-isomethylionone with α- or β-ionone (left); resolution of the same on a DB17 column (right).

Table 3. Sources and Purities of Investigated Solvents (Based on GC Areas)

name	supplier	bp (°C)	purity (%)	impurities (>0.1%)
isooctane	Fluka	99	>99	isomers of isooctane
acetonitrile	Carlo-Erba	81.6	99.5	
fluorobenzene	Acros	85.1	96.3	1.6% fluorobiphenyl
				1.4% phenol
				0.7% chlorobenzene
o-fluorotoluene	Acros	114	99.8	0.2% fluorobenzene

solution, calibration solutions were prepared in isooctane at individual concentrations of 2, 5, 10, 20, 50, and 100 mg/L of each compound and 100 mg/L of each internal standard. An aliquot (2 µL) of these calibration solutions was injected with the autosampler using the above-mentioned GC-MS conditions. Target compound areas were reported to the closest eluting internal standard (ISTD), and calibration curves were drawn as

$$\frac{\text{allergen area}}{\text{ISTD area}} = f\left(\frac{\text{allergen amount}}{\text{ISTD amount}}\right)$$

The fragrance to be evaluated was spiked with both internal standards (100 mg/L) and then diluted in isooctane or fluorotoluene (100 g/L) depending on the sample polarity.

The identity of the target compound was checked by determining the Q value according to the following formula (7):

$$Q = 100 - \frac{\sum\limits_{i=1}^{i=n}(100 \times |r_i - r_i'|)(\ln[100r_i + 1])^2}{21.3 \times \sum\limits_{i=1}^{i=n} r_i} \quad (1)$$

In eq 1, n is the number of ions per compound, r_i is the reference peak area ratio, and r_i' is the observed peak area ratio.

A Q value of between 90 and 100 indicates a positive recognition of the target peak. The deviation of the determined value from the truth was calculated as

$$\Delta_i = 100\left(\frac{m_i}{\mu_i} - 1\right) \quad (2)$$

with m_i and μ_i the observed and true amounts of a given compound. The uncertainty of the latter was considered to be negligible compared to that of the former.

The mean squared error (or mean deviation from the truth) was computed as

$$\bar{\Delta} = \sqrt{\frac{1}{l}\sum\limits_{i=1}^{i=l}(m_i - \mu_i)^2} \quad (3)$$

with l the number of compounds to be evaluated.

RESULTS AND DISCUSSION

Purity of Standards. Sources of standards with a purity of >95% were selected except for α-isomethylionone, due to the absence of an alternative supplier (**Table 1**).

GC Column. As fragrances are very complex mixtures, separating all target compounds from perfume constituents may not be achieved using the sole GC column. A specific detection means, such as MS, is required to selectively detect the target compounds from coeluting ones. Conversely, this detector is not selective enough to resolve all possible coelutions, and the GC separation of target compounds must be optimized to simplify the detector task. To characterize the global separation quality using a given column and set of temperature and flow parameters, the geometric mean $\bar{R}$ of the resolution between all target peaks was calculated as

$$\bar{R} = 1.18\left[\prod\limits_{i=1}^{i=n-1}\left(\frac{t_{R,i+1} - t_{R,i}}{w_{h,i} + w_{h,i+1}}\right)\right]^{1/(n-1)} \quad (4)$$

where $t_{R,i}$ is the total retention time of the ith peak, $w_{h,i}$ is the width at half-height of the ith peak, and n is the number of peaks in the chromatogram

As a single coelution is enough to give a null value of $\bar{R}$, this situation was representative of an unfavorable separation to allow the MS quantitation. Various columns and conditions were tested (**Table 2**). Carbowax-type phases were not considered due to their lower stability under intense use. The best results were observed for DB17 columns, with a short analysis time (17 min) when the column length and diameter were reduced. In contrast with Carbowax- and OV1-type phases, DB17 allowed the separation of α-isomethylionone from other ionones that frequently occur together in violet-like fragrances (**Figure 1**).

Due to its wide availability in perfume laboratories, the conditions were also optimized for a DB1 phase. Contrary to the DB17 column, decreasing the column diameter and length did not lead to a satisfactory separation. However, a reasonable

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Table 4. Recoveries from Stock Solutions Containing 100 mg/L of Each of the 28 Compounds (Except[b]), Stored under Different Conditions (Recoveries of Nonreported Compounds Do Not Significantly Differ from 100%, Except for the Experiment at −21 °C, after 56 Days)

	isooctane, 22 °C		fluorobenzene, 4 °C				isooctane −21 °C		isooctane −196 °C
compound	31 days	58 days	43 days	58 days	43 days	58 days	35 days	56 days	58 days
phenylacetaldehyde	25.6	22.4[a]	84.1	81.2	97.3[b]	91.7[b]	97.1	84.2	99.5
isoeugenol	84.0	83.3[a]	90.3	87.3	97.3[b]	96.5[b]	97.5	86.9	100.6
amyl cinnamic ald.	101.7	115.8[a]	91.2	88.1	100.5[b]	94.7[b]	97.9	85.2	96.0

[a] These concentrations must be lowered by 10% as 10% solvent losses were observed under these conditions. [b] Storage as two different mixtures: aldehydes and nonaldehydic compounds.
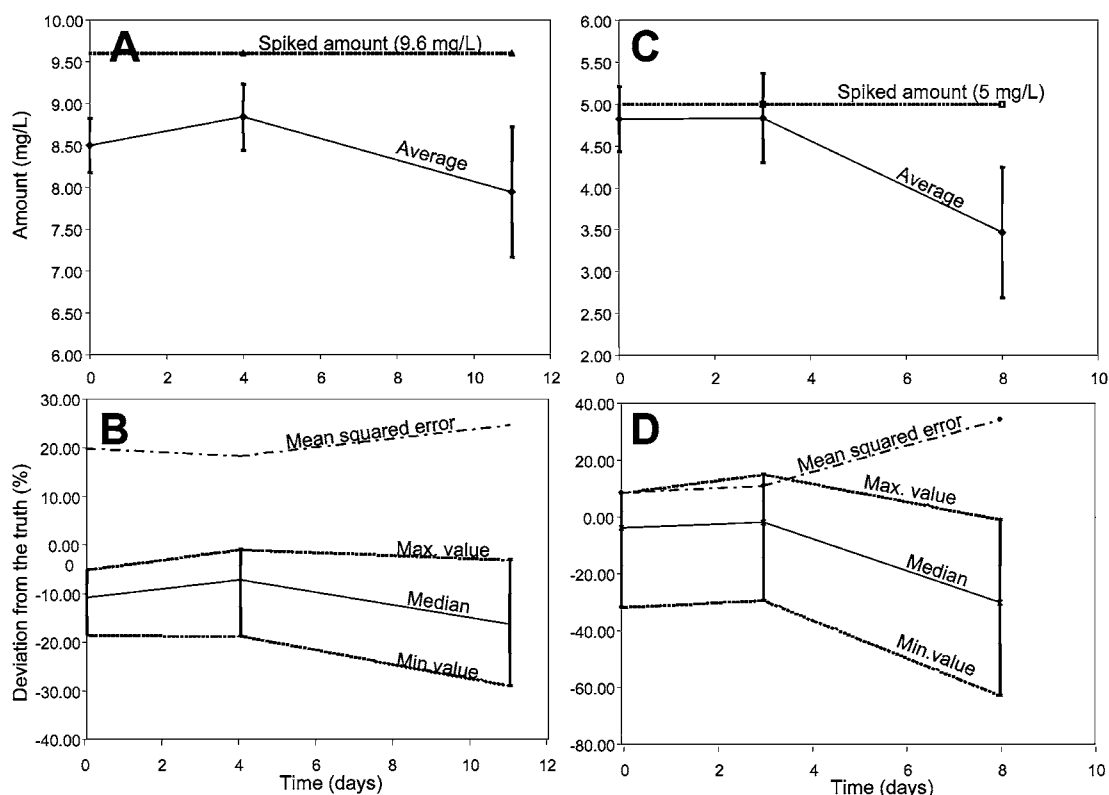

Figure 2. Drift of the determination of a standard solution of the 28 compounds at the same concentration after the day of calibration, without (A, B) and with (C, D) injector cleaning: (A, C) average of the 28 determinations and standard deviations; (B, D) deviation from the truth of the 28 compounds

analysis time was achieved when a rapid temperature program (10 °C/min) was used. Under these conditions a coelution was observed between amyl cinnamaldehyde and the first peak of hydroxymethylpentyl cyclohexenecarbaldehyde (isomer 3-, **Table 2**). However ions of the latter compound were different from those of the former; therefore, amyl cinnamaldehyde was quantifiable in SIM mode without any interference with other target compounds.

Internal Standard and Solvent Selection. Internal standards were chosen so that they fit several criteria: (i) no coelution with target compounds; (ii) satisfactory purity; (iii) chemical inertness; (iv) nonoccurrence in nature and/or in perfumes; and (v) exhibition of at least one characteristic and intense ion in mass spectrometry. Due to their characteristic molecular ion patterns, dibrominated derivatives, especially 1,4-dibromobenzene and 4,4′-dibromobiphenyl, are good candidates.

Ideally the solvent should elute before the first eluting target compounds, without any peak interference. Volatile or protic solvents were rejected as the former were prone to evaporation from standard solutions, and the latter could react with some reference compounds (e.g., acetal formation between ethanol and aldehydes). Isooctane and *o*-fluorotoluene were selected for lipophilic and hydrophilic fragrances, respectively, as they fit the previous requirements for a satisfactory commercial purity (>99%) (**Table 3**).

Stability of the Mix of Standards. As the mix of allergens has been reported to be unstable (*2*), its optimal storage conditions were investigated. As mentioned in Internal Standard and Solvent Selection, protic solvents were not suitable for the preparation of a stock solution. An ethanolic solution stored for 8 weeks at 4 and −18 °C exhibited a decrease of concentrations between 10 and 70% for most of its constituents (data not shown). In isooctane and fluorobenzene, only two or three compounds were found to deviate from a quantitative recovery after 1 month (**Table 4**). This deviation was lowered by decreasing the temperature and was negligible when the solution was stored for 1 month in the freezer (−21 °C), but longer storage under these conditions resulted in degradation. Alternatively, separating aldehydes and nonaldehydic compounds into two different stock solutions gave a satisfactory stability at 4 °C for 2 months. It must be noted that the sample stored at room temperature underwent solvent losses, although it appeared to be hermetically closed. This solvent loss was not observed at lower temperatures tested in **Table 4**.

Table 5. Quantitation of Five Spiked Compounds at a Level of 20 mg/L, in the Fragrance Sample SVB, Using Two Ions/Compound

compound	spiking (mg/L)	found (mg/L)	Q	comments
limonene	0	9.3	89	not added
linalool	20	49.7	1	not recognized, wrong amount
anisic alcohol	20	123.5	95	recognized
cinnamic alcohol	0	74.8	96	not added
eugenol	20	90.5	39	not recognized, wrong amount
α-isomethylionone	20	9.2	18	not recognized, wrong amount
benzyl benzoate	20	7.9	56	not recognized, wrong amount

Choice of Ions and Calibration. A compromise was made between the specificity and the abundance of ions for a given compound as the most specific ones were sometimes too weak for a satisfactory detection in complex mixtures. It must be noted that, whatever the ion choice, evaluating compounds such as farnesol or benzyl alcohol in EI mode imposes the selection of ions that are normally too common for an MS quantitation. In this work, three ions per compound were used (see Experimental Procedures): one for the quantitation and two others for the peak recognition (**Table 1**).

Calibration curves were linear in the range of 2–100 mg/L with coefficients of determination in excess of 0.99 for all compounds. As the instrument calibration is time-consuming, the period of the calibration validity was investigated. A first experiment was launched using a GC-MS routinely used for the control of allergens in fragrances and without special precautions. When re-injecting a reference solution containing the 28 compounds, determined amounts were found to deviate from the true level even just after the calibration (**Figure 2A**,**B**). As real fragrances often contain ingredients with low volatility, these substances were suspected to accumulate in the injector and/or in the column head, giving rise to a memory effect and biased determinations. This assumption was also supported by the greater deviation of later eluting compounds (e.g., approximately the highest boiling ones) than others.

To test this hypothesis, the experiment was repeated after the injector had been cleaned and the first 5 cm of the column had been cut. Re-injection of a freshly prepared standard solution containing 5 mg/L of each of the 28 compounds showed that the mean of all determinations fell close to the truth, with low median deviation and mean squared error (**Figure 2C**,**D**). A subsequent similar test later confirmed this conclusion: re-injecting a calibration solution (10 mg/L) on an instrument daily used for allergens, but with a regularly cleaned injector, gave an overall mean amount of 9.2 mg/L with a coefficient of variation of 4.2% 1 week after the injector cleaning.

In both series of experiments (with or without injector cleaning), the calibration seemed to be stable for 3–4 days, but a drift was observed after 1 week. In contrast with the first experiment (40 injections of fragrance concentrates over the experiment duration, **Figure 2A**,**B**), only two concentrates were analyzed during the second test (**Figure 2C**,**D**). Therefore, the calibration deviation after 1 week cannot be attributed to only the chromatographic system, but seems to be inherent in the MS detection. Such a negative drift, as a function of the number of analyses, has also been observed with headspace-MS sytems used as electronic noses (8). As practical conclusions, (1) the calibration should be done and used within the same week, and (2) cleaning the injector weekly is a useful precaution.

Quantitation. Figure 2C,**D** clearly shows that the simultaneous quantitation of these 28 compounds in a single injection is feasible from a simple solution. Using a recent calibration,

Table 6. Evaluation of Spiked Fragrances Using a DB17 Column [Elution Order, GC Conditions in Table 2; Dwell Times = 50 ms, Except for Windows 6, 9, and 10 (20 ms)]; Added Compounds Are Reported in Bold (Amounts in Footnotes)

SIM window	name	FT[a] amount (mg/L)	FT[a] Q	proton[a] amount (mg/L)	proton[a] Q	SVB[b] amount (mg/L)	SVB[b] Q
1	benzyl alcohol	11.8[d]	97				
2	phenylacetaldehyde	**50.1**	95	4.7	75	20.2	54
3	limonene	296.9	16				
4	linalool			2.9	26	**127.6**	97
5	methyl 2-octynoate						
6	estragole[c]			46.5	99		
7	citronellol	49.5	96	329.5	24	3700	25
8	citral (neral)						
9	geraniol[c]			45.1	99	30.0	1
9	cinnamic aldehyde[c]						
10	citral (geranial)[c]			4.0	1		
10	anisic alcohol[c]					98.0	97
11	hydroxycitronellal			44.5	99		
12	methyl 2-nonynoate	4.2	50	42.7	98	1548	25
13	cinnamic alcohol	18.9	27				
14	eugenol	**45.2**	99			96.6	92
15	methyleugenol			47.7	98		
16	coumarine						
17	isoeugenol						
18	α-isomethylionone	364.2	33			**98.9**	98
19	butylphenyl methyl-propional						
20	amyl cinnamic aldehyde	**49.5**	97	14.7	26	112.3	28
21	hydroxymethylpentyl cyclohexene-carbaldehyde	8.4	1	11.8	1	72.1	1
22	amyl cinnamic alcohol	16.2	1	442.15	80[e]	5460	62
23	farnesol	49.8	80[e]	28.7	1	204.2	1
24	hexyl cinnamic aldehyde			6.7	66[e]	32.8	78
25	benzyl benzoate			3.7	69[e]	**145.6**	99
26	benzyl salicylate	14.1	11	47.1	77[e]	459.3	86
27	benzyl cinnamate						

[a] Spiking with 50 mg/L of each five compounds reported in bold. [b] Spiking with 100 mg/L of each five compounds reported in bold. [c] Peak overlap, dwell time = 20 ms. For estragole, the overlap occurs with 1,4-dibromobenzene. [d] Present in the nonspiked sample (11.6 mg/L). [e] Presence/absence checked in scan mode.

all peaks deviated by <10% except two: the first peak of farnesol (29%) and amyl cinnamaldehyde (23%). Therefore, only the second peak of farnesol was used for its quantitation. However, as the real application of this method is the determination of allergens in fragrance concentrates, the evaluation of spiked samples was investigated.

SIM with Two Ions. Because abundant constituents may saturate the column, and/or low volatile ingredients could quickly pollute the injector, fragrance samples were diluted to 10% prior to analysis. A first quantitation attempt was achieved, using a real fragrance concentrate (SVB), free of target compounds, that was spiked with five reference compounds at individual concentrations of 20 mg/L. Ellendt used two ions per compound for the quantitation, but his paper does not report their use for the peak recognition (5). In the present study, this recognition was achieved by the calculation of the Q value (eq 1) from the area ratio between one qualifier and the target ions. With two ions, results gave the identification of an absent compound, the nonidentification of added compounds, and five wrong evaluations from the five added references (**Table 5**). This clearly shows that, in complex fragrances, attempting to evaluate an amount of 20 ppm with only two ions per compound is beyond the capability of the method. This observation also invalidates the limit of detection previously published [2 ppm (5)], as compounds occurring at a 10 times higher concentration were not detected.

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SIM with Three Ions. Using three ions per compounds, a series of spiked samples was evaluated (**Table 6**). To detect the occurrence of possible false positives, and because all target compounds rarely occur simultaneously in the same fragrance, each sample was spiked with only five of them, randomly selected from the list (**Table 1**). Samples were previously checked for the absence of target compounds (one exception noted in **Table 6**). The mean recovery calculated from results of **Table 6** was 100.5%, with a coefficient of variation of 16%. Two compounds (linalool and benzyl benzoate) were over-evaluated in SVB due to the coelution of isobaric ions despite the previously described precautions. This was inherent in the low specificity of all ions in their MS spectra. In proton and FT samples, some peaks with Q values below 90 required a confirmation in scan mode of a possible absence or presence of a target compound.

Conclusion. This work shows that a reliable verification of the identity of target peaks is required, due to the great composition complexity of fragrances. Satisfactory results have been achieved with GC-MS in SIM mode, using three ions for the quantitation and peak recognition. However, verifying the occurrence of a given compound in scan mode sometimes appears to be necessary. The applicability limits of the present method are currently under investigation and will be published in a second paper.

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