

APPLICATION NOTE**UNIQUE SOLUTION FOR
FLAVOR AND FRAGRANCE
IDENTIFICATION BY MEANS OF
SOLID PHASE FTIR GC-MS****Authors:**

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Key Points:

Flavor and Fragrance Analysis
Unequivocal Identification

Instrumentation:

DiscovIR Solid phase FTIR

Detectors:

Master GC
Master TOF-MS

Flavor and fragrance (F&F) adulteration is a frequently present problem in the perfumery industry, thus reliable determination of the volatile profile of perfume and other cosmetic products is a crucial question. However, gas chromatography coupled with mass spectrometry is a widely used technique for F&F analysis, the obtained information is not always enough for an accurate identification.

The GC-MS (TOF) system combined with a unique solid phase FTIR can provide a solution for reliable peak assignment also in the case of positional or diastereomer isomers.

The GC separates the components and gives additional information about the retention behavior through linear retention indices (LRI), while the MS and solid phase FTIR spectrometer provide structural elucidation.

The solid phase FTIR is compatible with standard GC columns and injection mode, with a simple post column flow splitting it can interface with GC-MS instrumentation. Practically, in this novel technique the separated compounds are condensed in small singular spots on a rotating disc, thus distortion of spectra is eliminated, giving an excellent spectral resolution which provides unique IR spectra for each molecule.

In this application note a commercially available perfume sample was studied, focusing on the hardly identifiable compounds.

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Experimental Conditions

The GC-MS profile was acquired by a DANI Master TOF MS Plus and DiscovIR-GC System. For the separation an SLB-5ms column (30 m × 0.25 mm id × 0.25 µm, Merck Millipore) was employed.

FTIR parameters: the FTIR spectrum were acquired from 700 to 4000 wavenumber (cm⁻¹); the rotation speed and temperature of the disc were 3 mm·min⁻¹ and -50°C, respectively; transferline and restrictor temperature were 280°C.

GC parameters: the injection of 1 µL perfume sample was performed at 280°C in split mode (1:10). Constant linear velocity: 30 cm/sec. Temperature program: 50°C to 280°C (5 min), at 3°C/min.

MS parameters: the samples were analyzed using a mass range of 40-500 m/z; acquisition rate: 5 spectra/sec; interface and ion source temperatures were 300°C and 200°C, respectively. MS ionization mode: electron ionization. For LRI calculation on non-polar stationary phase a C7-C30 saturated n-alkane (49451-U, Merck Millipore) series was used as reference standard.

DiscovIR-GC	
Spectrum	acquired from 700-4000 wavenumber (cm ⁻¹)
Disk Speed	3 mm/min
Disk Temp	-50°C
Restrictor, Transferline temp	280°C

Master GC	
Column	SLB-5ms column (30 m × 0.25 mm id × 0.25 µm film, Merck Millipore)
SLIN Inj Temp	280°C
Split Ratio	1:10
Linear Velocity	Constant @ 30 cm/sec
Oven Temp	50°C to 280°C (hold 5 min) , @ 3°C/min

Master TOF-MS	
Transfer Line Temp	300°C
El Source	70eV
Source Temperature	200°C
Mass Range	40-500 amu
Acquisition Rate	5 Hz

Table 1. Operating Conditions



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Results and discussion

The studied innovative technique provides the distinction of diastereomer or positional isomers with very similar MS spectra and retention behavior, through the specificity of the “fingerprint” region around 1100 cm⁻¹.

Exploiting the enhanced discriminating power a unique library was developed containing TOF MS and solid phase FTIR spectrum. The F&F database, including about 1500 MS and FTIR spectrum of pure standards, contains also experimental LRI values of

each compound. Boosting this comprehensive information collection a universal post-run software, namely CromatoPlus Spectra, allows the library searching using the FTIR and MS spectral similarity and LRI filter simultaneously.

The developed system was applied for the analysis of a commercially available perfume sample.

The obtained volatile fraction is shown on Figure 1.

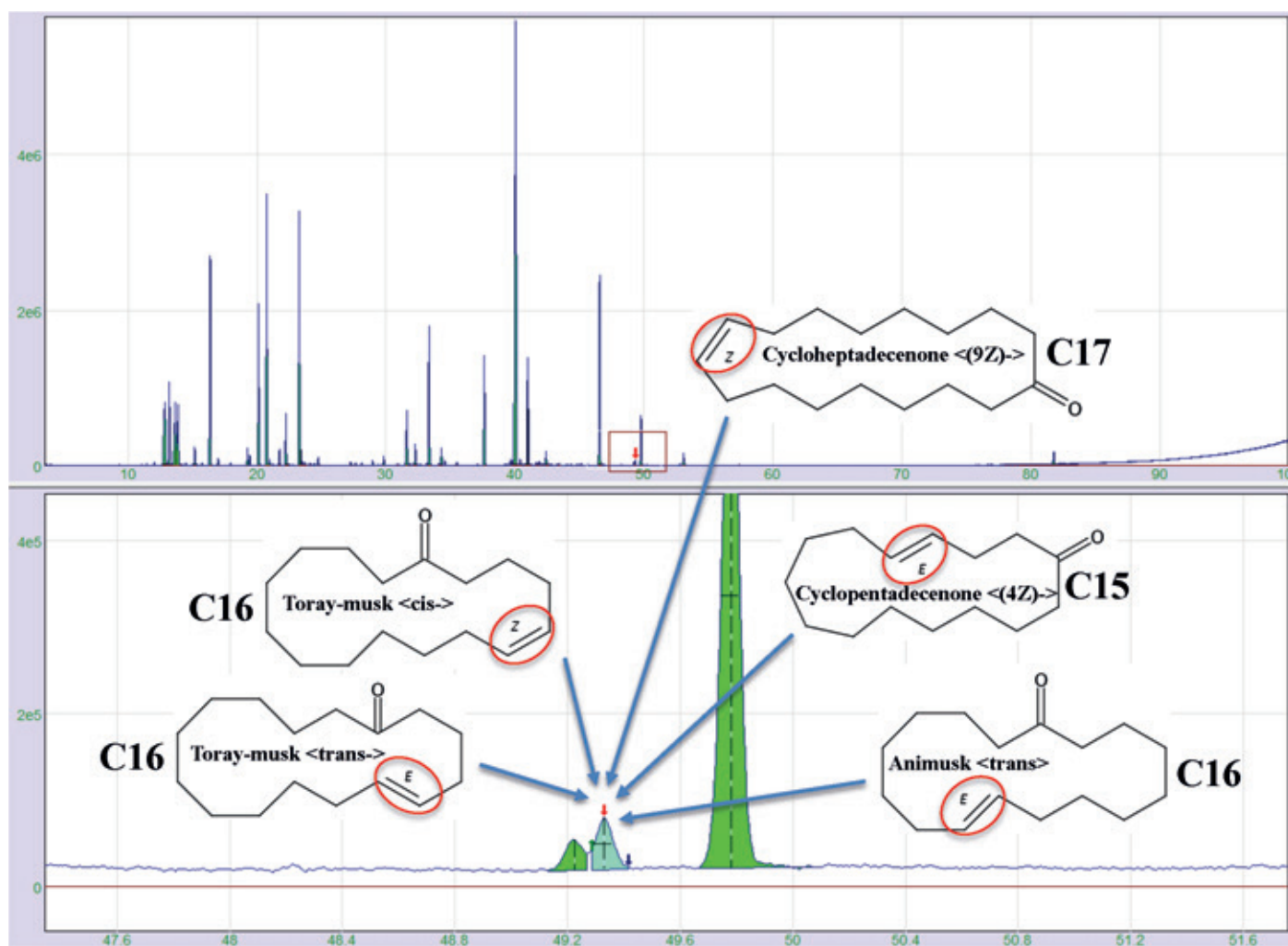


Figure 1. Chromatogram obtained by GC-TOF.
Upper: Complete Volatile profile.

Lower: Enlargement of a critical target compound peak.

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Volatiles were identified using the F&F library. The similarity filter level can be selected and personalized for each parameter. In fact, either a simple MS search can be performed or it can be supported by a second filter, namely LRI or also FTIR spectrum can be considered, and any combination of these three individual analytical information.

To demonstrate the importance of the application of all three filters to achieve a univocal identification, in the first step only mass spectral similarity was used (Figure 2 upper). Nine musk isomers with almost identical MS similarity were obtained as candidates even setting the MS filter more than 900 (90%).

Considering also the LRI values with a filter of ± 5 LRI units the long list of candidates obtained for the target molecule (LRI:1916) was reduced to three compounds

with very similar retention behavior (Figure 2. center). The C16 musk compound isomers due to the excellent specificity of the FTIR spectrum, difference in similarity is one order of magnitude, can be distinguish reliably (Figure 2 down). In the presented case the correct identification of the right compound, trans-Toraymusk, is very important. It is noteworthy, that use of animal derived musk is prohibited, thus musk odor is substituted mainly with synthetic polymer or macrocyclic musk-type fragrances.

According to the number of carbon atoms in the ring and double bond position and geometry, musk compounds provide different odor sensation, in addition to musky they can have secondary odors such as dry and powdery or floral or fatty and soapy (1, 2).

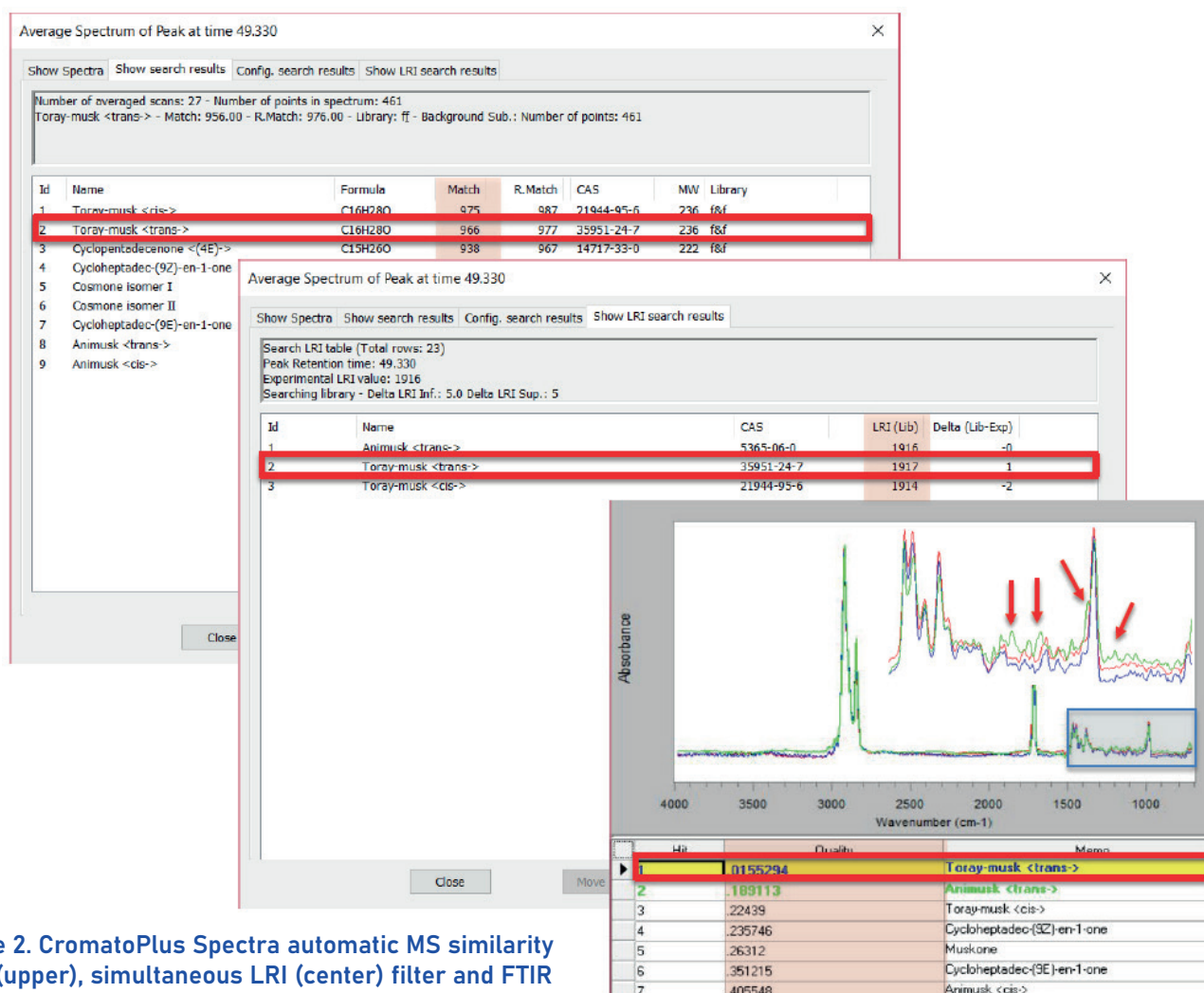


Figure 2. CromatoPlus Spectra automatic MS similarity filter (upper), simultaneous LRI (center) filter and FTIR spectral similarity filter (lower, red line: spectra of the target compound).

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Table I: Identification of F&F using 3 independent analytical information

Compound name	Area%	t _{ret}	LRI _{exp}	LRI _{lib}	MS (TOF) match	FTIR match
Myrcene	0.04	11.43	989	991	-	-
Acetate <hex-(3E)-enyl->	0.08	12.05	1004	1001	876	-
Dipropylene glycol	4.84	12.88	1023	1018	921	0.05377
Limonene	2.38	13.2	1030	1030	968	0.06538
Unknown diol isomer I	3.33	13.42	1041	-	-	-
Unknown diol isomer II	3.62	13.66	1046	-	-	-
Linalool	6.86	16.37	1101	1101	979	0.01591
Phenethyl alcohol	0.25	16.97	1114	1113	867	-
Acetate <benzyl->	0.56	19.25	1163	1167	872	0.03174
Linalool ethyl ether	0.31	19.43	1167	1166	953	-
Linalool <ethyl-, (Z)->	5.25	20.13	1181	1181	983	0.05385
Linalool <ethyl-, (E)->	9.71	20.76	1195	1193	981	0.06552
Rozanol <cis->	0.17	20.97	1200	1200	863	-
Rozanol <trans->	0.54	21.74	1216	1218	911	0.34219
Citronellol	1.76	22.24	1227	1228	941	0.00119
Linalyl acetate	10.44	23.27	1250	1250	964	0.02419
Geranyl acetate <trans->	0.16	28.96	1378	1380	892	0.27042
Vanillin	0.33	29.82	1397	1394	955	0.06866
Coumarin	2.38	31.62	1440	1438	941	0.01674
Vanillal	0.76	32.27	1456	1457	927	0.02925
Ionone <(E)-, beta->	4.95	33.34	1481	1482	981	0.00108
Bulnesene <alpha->	0.75	34.31	1505	1505	909	-
Ionone <alpha-, 6-methyl-, trans->	0.16	34.57	1512	1511	785	-
Ionone <alpha-, 6-methyl-, cis->	0.12	35.49	1535	1535	790	-
Phthalate <diethyl->	4.06	37.63	1589	1589	948	0.01019
Dihydrojasmonate <methyl-, cis->	21.29	40.07	1653	1650	955	0.02230
Patchuli alcohol	3.17	40.97	1678	1678	970	0.11503
Dihydrojasmonate <methyl-, trans->	2.15	41.02	1680	1678	943	0.03318
Pentadecanolide	7.15	46.57	1834	1836	985	0.07941
Toray-musk <cis->	0.10	49.22	1914	1914	912	0.25457
Toray-musk <trans->	0.17	49.33	1917	1917	966	0.01553
Ambrettolide	1.75	49.78	1930	1929	971	0.03669

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A total number of 30 F&F was identified in the analyzed perfume: 1.88% of the volatile fraction with almost two independent analytical information, 90.76% with all three confirmations was identified.

However, two major compounds were not present in the library, due to the functional group specific FTIR spectrum and similar matches found in the library they were classified as unknown diol compounds.

In the case of the fragrances at lower concentration FTIR spectral similarity was also lower, but as a third confirmation giving the best match for the target compound it can be a further support in the identification.

Conclusions

The combination of the novel GC-TOF/solid phase FTIR with the F&F library with embedded LRI and CromatoPlusSpectra provide an unsurpassed support for a univocal identification of F&F molecules in a single analysis for the target compounds present in the library.

But it can give a unique possibility also for the prediction of unknown or low-concentration molecules using all three independent analytical information: due to the spectral data the molecular class or family can be individualize according to compounds with similar spectrum in the search list, while LRI information can confirm or exclude candidates.

References

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