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Comprehensive two-dimensional gas chromatography–time-of-flight mass spectrometry for the analysis of volatile components in Neroli essential oil

Kai Wang,* Rui-zhi Zhu, Rong-fen Qu and Zhi-yu Li

R&D Center of Hongta Tobacco (Group) Co., Ltd., Yuxi 653100, P. R. China.
Fax: +86 877 296 5000; e-mail: 27922573@163.com

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As found using comprehensive two-dimensional gas chromatography–time-of-flight mass spectrometry, the main components (92.01 vol%) of Neroli oil are terpenoid compounds, such as linalool, β-pinene, α-terpineol, limonene, sabinene, nerol, nerolidol and linalyl acetate.

Comprehensive two-dimensional gas chromatography[1] (GC×GC) has become a well-known technique for the separation of complex samples. GC×GC technologies have advantages over one-dimensional GC, such as high resolution, large peak capacity, high sensitivity, short analysis time and large quantity of information.[2–5] This analytical technique has been applied to environmental analysis, petrochemical, food, flavor and fragrance industries, *etc*.[6–11] Time-of-flight mass spectrometry (TOFMS), possessing higher collection frequency than a conventional mass spectrometry, is the preferred option as a detector for GC×GC. The combination of GC×GC and TOFMS provides a solution to analytical identification and quantification strategies for complex samples.[12–15]

Neroli essential oil is obtained from *Citrus auranthium* or *Citrus sinensis* using steam distillation. It is primarily used in small quantities as a modifier in flavors such as citrus and fruit flavors for candies, soft drinks, *etc*.[16] Here, we report the analysis of the volatile components of Neroli essential oil by GC×GC–TOFMS.†

The analytical results are shown in Figures 1 and 2.

The influence of a modulation period on separation is also considered under experimental conditions. Because of the short length of the second column (1.5 m, including a transfer line), the components cannot be separated if the modulation period is too long. If the period is shorter, the orthogonal separation of GC×GC is difficult to perform, and strongly polar compounds can enter the next modulation cycle. So, we chose the experimental modulation period of 4 s.

The Pegasus 4D workstation (Leco Corporation) was used for data processing, including automated peak find, spectral deconvolution and GC×GC modulation slice combination. This workstation can provide information such as 'similarity', 'reverse' and 'probability'. In our work, the compounds with the value of 'similarity' over 800 are shown as analytical result. A total of 115 compounds are detected in the Neroli essential oil; 87 of these compounds have individual volume fractions > 0.02%, and their total volume percentage is 99.66%. Under the same conditions, just 62 compounds are found using traditional one-dimensional gas chromatography. In GC×GC, the number of peaks with the value of signal-to-noise ratio over 100 recognized by workstation automatically is more than 250.

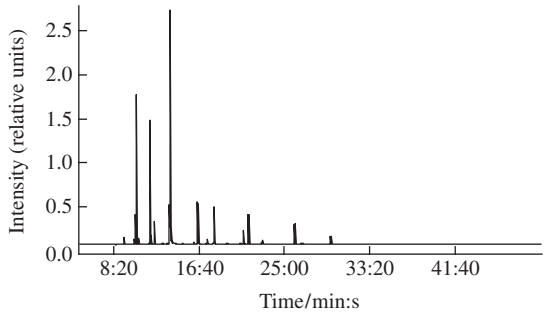

Figure 1 GC one-dimensional chromatography of Neroli essential oil.

From the results, the main constituents of Neroli essential oil are terpenoid compounds, such as linalool, β-pinene, α-terpineol, limonene, sabinene, nerol, nerolidol, linalyl acetate and α-pinene. The volume content of these terpenoid compounds is up to 92.01% in all 115 components. Among 54 terpenoid compounds, there are 37 terpenes, 16 sesquiterpenes and 1 diterpene. The reten-

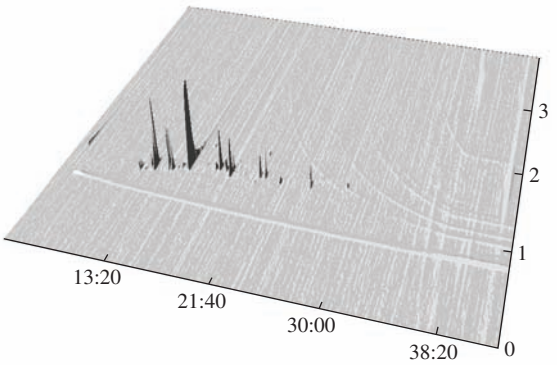

Figure 2 GC×GC 3D chromatography of Neroli essential oil (1st and 2nd dimensional retention time/s).

† The GC×GC–TOFMS system was based on an Agilent 7890A gas chromatograph coupled with a Leco Pegasus 4D TOF mass spectrometer with a 4D thermal modulator (Leco Corporation); the first column was Agilent HP-5MS 30 m × 0.25 mm × 0.25 μm; the second column was Agilent DB-17ht 1.5 m × 0.10 mm × 0.10 μm; the carrier gas was helium, and the flow rate was 1.0 ml min^{-1}; the modulation period was 4 s. Column 1 was held at 60 °C for 1 min and then heated at a rate of 5.0 K min^{-1} to 270 °C and held for 5 min at this temperature. Column 2 was initially set at 75 °C and followed the same temperature program as column 1. The ion source and transfer line temperatures were 200 and 250 °C, respectively. Mass channels *m*/*z* 40–600 were collected at 100 spectra per second after a 300 s solvent delay. The raw mass spectrograms were processed by the Leco ChromaTOF software v4.33, and the mass spectral libraries were NIST08 and Wiley9N. Dichloromethane was used as a solvent to dilute the analyte (by a factor of 100).

Table 1 Terpene components of Neroli essential oil detected by GC×GC–TOFMS.

Component	Retention time/min:s	Similarity	Area (%)	CAS no.	Formula
3-Thujene	11:08, 1.130	904	0.1405	2867-05-2	$C_{10}H_{16}$
α-Pinene	11:24, 1.160	950	3.0511	7785-26-4	$C_{10}H_{16}$
Camphene	11:52, 1.160	935	0.1771	79-92-5	$C_{10}H_{16}$
Sabinene	12:20, 1.210	921	1.5838	3387-41-5	$C_{10}H_{16}$
2(10)-Pinene	12:32, 1.240	946	17.6565	127-91-3	$C_{10}H_{16}$
2-Isopropenyl-5-methyl-5-vinyltetrahydrofuran	12:40, 1.230	838	0.0782	13679-86-2	$C_{10}H_{16}O$
Limonene	13:44, 1.250	953	9.2162	138-86-3	$C_{10}H_{16}$
1,8-Cineole	13:52, 1.260	863	0.1202	470-82-6	$C_{10}H_{18}O$
3,7-Dimethyl-1,3,6-octatriene	14:04, 1.220	933	1.6019	3779-61-1	$C_{10}H_{16}$
Terpinene	14:28, 1.250	869	0.1917	99-85-4	$C_{10}H_{16}$
Linalool oxide (2)	14:44, 1.280	875	0.5206	5989-33-3	$C_{10}H_{18}O_2$
Terpinolen	15:08, 1.280	922	0.4159	586-62-9	$C_{10}H_{16}$
Linalool	15:20, 1.290	953	26.5791	78-70-6	$C_{10}H_{18}O$
trans-Sabinene hydrate	15:36, 1.290	877	0.01792	17699-16-0	$C_{10}H_{18}O$
trans-1,2-Limonene oxide	16:04, 1.320	883	0.1969	4959-35-7	$C_{10}H_{16}O$
cis-Limonene oxide	16:20, 1.330	837	0.0749	4680-24-4	$C_{10}H_{16}O$
trans-Pinene hydrate	16:36, 1.310	828	0.0527	35408-04-9	$C_{10}H_{18}O$
Pinocarveol	16:40, 1.370	887	0.0607	5947-36-4	$C_{10}H_{16}O$
Camphene hydrate	17:04, 1.360	869	0.0094	465-31-6	$C_{10}H_{18}O$
Epoxylinalol	17:16, 1.370	821	0.0535	14049-11-7	$C_{10}H_{18}O_2$
4-Terpineol	17:36, 1.330	948	0.9447	562-74-3	$C_{10}H_{18}O$
α-Terpineol	17:52, 1.360	950	9.2578	98-55-5	$C_{10}H_{18}O$
Myrtenol	18:00, 1.380	802	0.0095	515-00-4	$C_{10}H_{16}O$
Myrtenal	18:00, 1.450	918	0.0171	564-94-3	$C_{10}H_{14}O$
trans-Piperitol	18:12, 1.340	803	0.0145	16721-39-4	$C_{10}H_{18}O$
trans-Carveol	18:24, 1.390	801	0.0112	1197-07-5	$C_{10}H_{16}O$
Nerol	18:28, 1.340	915	1.2944	106-25-2	$C_{10}H_{18}O$
Linalyl acetate	19:00, 1.290	946	6.6451	115-95-7	$C_{12}H_{20}O_2$
Geraniol	19:00, 1.360	948	0.4359	106-24-1	$C_{10}H_{18}O$
1-Carvone	19:04, 1.440	864	0.0400	99-49-0	$C_{10}H_{14}O$
(*E*)-Citral	19:28, 1.380	880	0.0878	141-27-5	$C_{10}H_{16}O$
Bornyl acetate	20:00, 1.350	896	0.0324	76-49-3	$C_{12}H_{20}O_2$
Geraniol formate	20:08, 1.330	907	0.1972	105-86-2	$C_{11}H_{18}O_2$
Linalyl propionate	20:52, 1.280	875	0.0087	144-39-8	$C_{12}H_{22}O_2$
Neryl acetate	21:28, 1.330	946	2.4608	141-12-8	$C_{12}H_{20}O_2$
Geranyl acetate	21:52, 1.350	954	4.9315	105-87-3	$C_{12}H_{20}O_2$
(*E*)-Geranylacetone	23:28, 1.360	948	0.2111	3796-70-1	$C_{13}H_{22}O$

tion times of terpenes vary from 11 to 23.28 min, and that of sesquiterpenes is from 21.12 to 39.32 min. The content of terpenes in Neroli oil is 88.40 vol%; 37 terpenes are listed in Table 1.

In conclusion, a GC×GC–TOFMS system has been applied to analyze Neroli essential oil. More than 250 peaks have been detected, and 115 components have been structurally identified. Terpene compounds are the main constituents of Neroli oil. The GC×GC–TOFMS technique, having high resolution, large peak capacity and high sensitivity, is very suitable for the analysis of such a complex sample.

References

1 Z. Liu and J. B. Phillips, *J. Chromatogr. Sci.*, 1991, **29**, 227.
2 P. Marriott, R. Sheellie and C. Cornwell, *J. Chromatogr. A*, 2001, **936**, 1.
3 J. Beens, H. Boelenns and R. Tijssen, *J. High Resolut. Chromatogr.*, 1998, **21**, 47.
4 H. Degeus, J. Deboer and J. B. Phillips, *J. High Resolut. Chromatogr.*, 1998, **21**, 411.
5 C. H. Ruan, G. W. Xu and X. Lu, *Chromatographia*, 2003, **57**, 5265.
6 J. C. Hernan, B. Winniford, J. Luong and P. Matthias, *J. Sep. Sci.*, 2009, **32**, 883.
7 E. M. Rachel, M. D. Kenneth, C. H. Jamin and T. Y. Elton, *Anal. Chem.*, 2006, **78**, 2700.
8 M. P. Karisa, L. H. Janiece, C. H. Jamin and R. E. Synovec, *Talanta*, 2006, **70**, 797.
9 J. M. Sanchez and R. D. Sacks, *Anal. Chem.*, 2006, **78**, 3046.
10 P. Ognjen and G. Tadeusz, *Anal. Bioanal. Chem.*, 2006, **386**, 1013.
11 K. Bester, *J. Chromatogr. A*, 2009, **1216**, 470.
12 M. Adahchour, J. Beens, R. J. Vreuls and U. A. Brinkman, *J. Chromatogr. A*, 2003, **1019**, 157.
13 S. K. Zhu, X. Lu, K. Ji and K. Guo, *Anal. Chim. Acta*, 2007, **597**, 340.
14 F. Bianchi, M. Careri, C. Conti, M. Musci and R. Vreuls, *J. Sep. Sci.*, 2007, **30**, 527.
15 C. Vonmuhlen, C. A. Zini, E. B. Caramao and P. J. Marriott, *J. Chromatogr. A*, 2008, **1200**, 34.
16 Y. T. Zhang and G. Wang, *J. Agr. Sci. China*, 2009, **8**, 441.

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