Application Note: 10024

Characterization of Essential Oils by Gas Chromatography in One Minute

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Key Words

- TRACE GC Ultra
- Chamomile Essential Oil
- Peppermint Essential Oil
- Reduction in Analysis Time
- Sage Essential Oil
- Ultra Fast GC

Introduction

Essential oils are the fragrant essences of plants in their purest, most concentrated state, most of which are primarily composed of terpenes and their oxygenated derivatives. These oils find application mainly in the flavor and fragrance industry, pharmaceutical industry, and in aromatherapy, which is the science of applying the controlled use of naturally plant extracted essences to promote physical and psychological well-being.

Essential oils are usually obtained by steam or hydro-distillation of botanicals. Different parts of plants can be used to obtain them, including the flowers, leaves, seeds, roots, stems, bark, and wood. The oil of the same plant can vary strongly in composition from supplier to supplier, depending on the species, location, ground and weather conditions, and level of expertise and care given by farmers and distillers. For such reasons, the characterization of the oils through chemical analysis is a mandatory step in the production chain, to be carried out by both researchers and quality control labs.

Conventional analytical methods based on GC and GC/MS operate with 25-30 m long columns and oven heating rates around 3 to 5 °C/min. High chromatographic efficiencies are needed to deliver baseline separation and quantitative determination of the critical groups of components. Such methods generally require 30-60 minutes to perform an overall analytical cycle. This application note reports an alternative method based on the Ultra Fast technology implemented on the Thermo Scientific TRACE GC Ultra™, which operates with 5 m long columns and heating rates of hundreds of degrees per minute. The outcome is up to a 40-fold reduction in the analysis time and high performance in repeatability and accuracy as usually requested in this field. The real-world examples shown and the comparison with respective conventional analyses prove that productivity, which is a priority for most laboratories today, can be dramatically increased in a reliable way.

Figure 1: Thermo Scientific TRACE GC Ultra with UltraFast module.

UltraFast GC Configuration

For this application, the TRACE GC Ultra is configured with a SSL injector, an UltraFast option (including the analytical column), and a Fast Flame Ionisation Detector (FFID) featuring 6 ms time constant and acquisition frequencies up to 300 Hz. Such a high speed is, in fact, a compulsory requirement for the correct acquisition (15-20 points/peak) of the extremely narrow peaks (approx. 100 ms $PW_{1/2}h$) typical for this type of chromatography.

The assembly allows the instrument to achieve heating rates up to 1200 °C/min, and fast cooling times occur rapidly, as well, taking about one minute to return to 50 °C from 350 °C compared to about 4 minutes in conventional mode.

The column module, connected to the split-splitless injector and the FID detector as a removable accessory, is completely and directly controlled by the instrument local user interface and electronics.

The TRACE GC Ultra was used to perform the same application in conventional mode with the UltraFast accessory removed. All of the components of the essential oils analyzed were identified through GC/MS technique.

The injections were performed using a Thermo Scientific AS3000 autosampler, designed to achieve maximum precision in automatic liquid injection in capillary GC.

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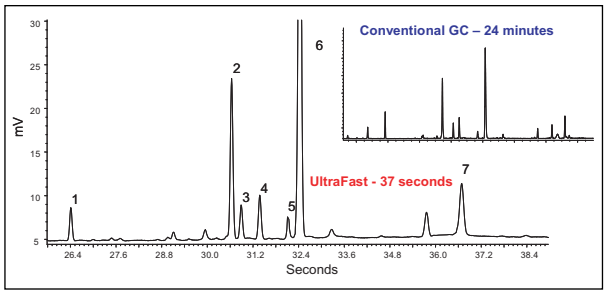
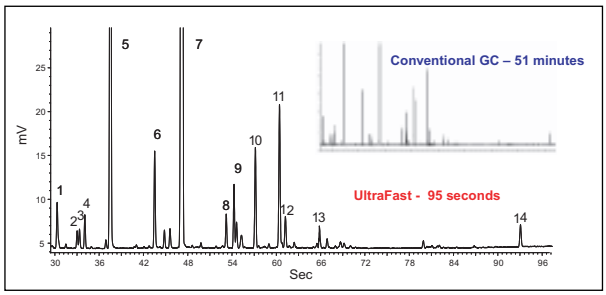


PEAK #	COMPOUND
1	Trans-β-farnesene
2	Bisabolol oxide B
3	α-bisabolol
4	α-bisabolone oxide A
5	Chamazulene
6	Bisabolol oxide A
7	Spiroether

Figure 2: Comparison between the characterization of Chamomile essential oil by the TRACE GC Ultra with UltraFast configuration and conventional GC with an OV1701 column.



PEAK #	COMPOUND
1	Myrcene
2	Cis-β-ocimene
3	Limonene
4	Trans-β-ocimene
5	Linalool
6	α-terpineol
7	Linalyl acetate
8	Neryl acetate
9	Geranyl acetate
10	β-caryophyllene
11	Germacrene D
12	Bicyclogermacrene
13	Geraniol
14	Sclareol

Figure 3: Comparison between the characterization of Sage essential oil by TRACE GC Ultra with UltraFast configuration and conventional GC with a SE54 column.

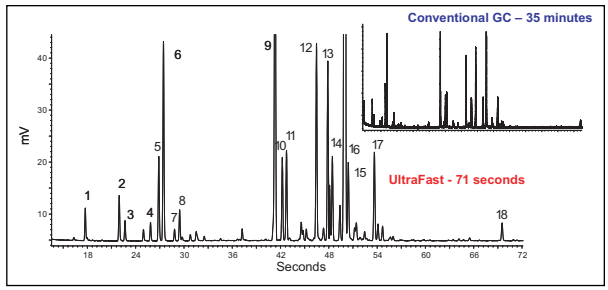


Figure 4: Comparison between the characterization of Peppermint essential oil by TRACE GC Ultra with UltraFast configuration and conventional GC with a CarboWax column.

		AREA %	
		Ultra Fast GC	Conventional GC
1	α-pinene	0.96	0.94
2	β-pinene	1.37	1.41
3	Sabinene	0.62	0.64
4	Myrcene	0.35	0.39
5	p-cymene	0.56	0.58
6	Limonane	2.58	2.47
7	1,8 cineole	6.19	6.07
8	y-terpinene	1.02	0.94
9	Menthone	14.18	14.21
10	Menthofurane	2.56	2.44
11	i-menthone	2.59	2.57
12	Methyl acetate	5.69	5.74
13	Neomenthol	5.88	5.95
14	β-cariophyllene	2.34	2.39
15	Menthol	47.26	47.49
16	Pulegone	2.58	2.54
17	Germacrene D	2.69	2.64
18	viridilflorol	0.56	0.58

Table.1: Accuracy of UltraFast analysis of Peppermint essential oil.

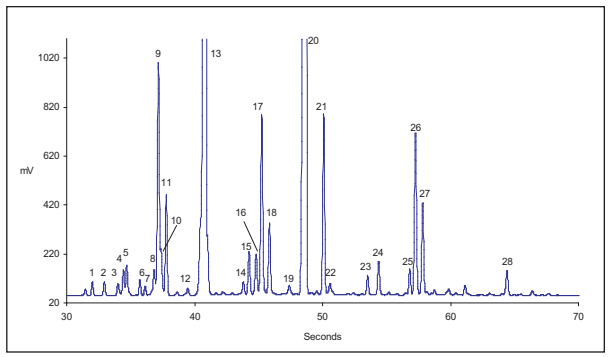


Figure 5: Characterization of Lavender essential oil by TRACE GC Ultra with UltraFast configuration.

	COMPONENT	PEAK WIDTH AT 1/2 H (S)	RETENTION TIME (S) MEAN	SD	PEAK AREA (COUNT*10⁴) MEAN	RSD %
9	Limonene	0.17	37.12	0.04	173	1.00
10	Eucalyptol	0.15	37.32	0.04	27.6	1.76
11	β-Ocimene	0.15	37.73	0.04	67.6	0.91
13	Linalol	0.23	40.79	0.04	998	0.60
15	Lavandulol	0.17	44.20	0.04	33.4	0.77
16	Borneol	0.18	44.76	0.04	33.7	0.76
17	4-Terpineol	0.18	45.20	0.04	143	0.64
18	α-Terpineol	0.17	45.80	0.04	56.9	0.78
20	Linalyl acetate	0.23	48.62	0.04	1298	0.57
21	Lavandulyl acetate	0.16	50.03	0.04	128	0.64
23	Neryl Acetate	0.16	53.45	0.04	15.3	1.28
24	Geranyl Acetate	0.16	54.31	0.04	26.8	0.94
25	α-Santalene	0.16	56.75	0.04	19.5	1.11
26	Caryophillene	0.17	57.19	0.04	127	0.63
27	β-Farnesene	0.16	57.75	0.04	69	0.82
28	Cadinol	0.19	64.35	0.04	21	0.56

Table 2: Repeatability of Lavender essential oil analysis based on 10 consecutive injections.

Analysis of Essential Oils

Three essential oils with different complexities were characterized through UltraFast GC and conventional GC: chamomile, sage and peppermint. These oils can be obtained by hydro-distillation according to the method described in the European Pharmacopoeia [1]. Each is then diluted 1:200 in cyclohexane, and 1 µL of the solution is injected in the TRACE GC Ultra.

For each UltraFast analysis, the injector temperature is 230 °C, and the FID is set at 280 °C; all the columns used are 5 m long, 0.1 mm i.d., 0.1 mm film thickness. In the conventional mode, 25 m long, 0.25 mm i.d., 0.3 mm f.t. columns are used at heating rates of 3-5 °C/min.

Chamomile

Well known to be effective against problems of sleeplessness and anxiety, the chamomile essential oil is characterized by seven sesqui-terpenoids, present at different amounts as a function of quality and origin. Polar columns are not suitable to compensate the loss of efficiency derived from operating at ultra fast heating rates, so a highly selective stationary phase is necessary. The OV1701 features the winning compromise, being able to deliver base-line separation of the most critical pair a-bisabolone oxide A / α-bisabolol at the shortest analysis time.

The carrier gas (hydrogen) flow is 0.7 ml/min (constant flow), with a split ratio 1:300 and a temperature program from 50 °C to 250 °C at 500 °C/min. Figure 2 shows the comparison between the chamomile chromatograms acquired in UltraFast (37 seconds) and in conventional (24 minutes) modes, together with the list of the characteristic components. The reduction in the analysis time is almost 40 times, not including the contribution of the shorter cooling time.

Sage

Known to be a natural pain killer, the sage essential oil is a medium- complexity oil, whose composition can vary greatly depending on its origin. The version featured in this application belongs to the linalool-linalyl acetate chemotype and is characterized by 30 components of differing volatilities.

The apolar SE54 column is used. The carrier gas (hydrogen) flow is 0.5 ml/min (constant flow) with a split ratio 1:300 and a temperature program from 50 °C (0.1 min) to 250 °C at 150 °C/min.

The latter eluting component is a minor diterpenoid, called sclareol, that requires the extension of the analysis time up to 51 minutes to be eluted in conventional mode. Figure 3 reports the chromatograms acquired both in conventional and UltraFast (1.5 minutes) modes, pointing out a 30-fold reduction of analysis time.

Peppermint

Helpful in treating headaches and digestive disorders, the peppermint essential oil is a medium-complexity oil characterized by about 30 mono- and sesqui-terpenoids. The concentration of some of them (e.g. pulegone, menthofurane) is legally limited because of their toxicity. This oil is generally analyzed with a polar phase, CarboWax, since apolar phases are not selective enough to provide complete separation of some critical components. The carrier gas (hydrogen) flow is 0.8 ml/min (constant flow), with a split ratio 1:300 and a temperature program from 50 °C to 250 °C at 500 °C/min.

Figure 4, showing the peppermint chromatograms acquired in UltraFast (71 seconds) and in conventional (35 minutes) modes, points out an almost 30-fold reduction in the analysis time. Table 1 reports the excellent accordance between conventional and UltraFast peak area percentage for each component.

Repeatability Test

To test the repeatability of the system, a lavender essential oil is analyzed with a OV5 column. The carrier gas (hydrogen) flow is 0.5 ml/min (constant flow), with a split ratio 1:200 and a temperature program from 50 °C to 300 °C at 180 °C/min. Figure 5 reports the chromatogram, and Table 2 shows the excellent repeatability of the retention times and peak areas obtained over 10 consecutive injections. Standard deviations of the retention times, far lower than the peak widths, lead to unambiguous identification of the components.

Conclusions

The Thermo Scientific TRACE GC Ultra equipped with the UltraFast option can provide both qualitative and quantitative characterization of essential oils of different complexity, featuring 30-40 fold reduction in analysis time and comparable accuracy with respect to the conventional analytical methods.

The reported examples prove that it is possible to compensate the loss of efficiency deriving from the use of shorter columns at such high heating rates by choosing the column stationary phase that is properly selective towards critical pairs.

The technique has demonstrated to be suitable for the analysis of real-world samples, which (for the wide range of volatility of their components) are representative of everyday separation problems in this field.

Reference

[1] European Pharmacopoeia, 3rd Edition, Council of Europe publishing, Strasbourg (France), (1997), 1146.

Acknowledgements

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"Direct resistively heated column gas chromatography (Ultrafast module-GC) for high-speed analysis of essential oils of differing complexities".

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