Fast GC for the Analysis of Citrus Oils

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Abstract

In this investigation, the gas chromatographic (GC) analysis of citrus essential oils is carried out in 3.3 min, with a speed gain of almost 14 times in comparison with traditional GC procedures. The fast method that is developed requires the application of severe experimental conditions (accelerated temperature program rates, high inlet pressures, and split ratios) and, thus, the support of adequate instrumentation. The samples investigated can be considered to be rather complex and, although a slight loss in peak resolution is observed, the overall analytical result is excellent. All data obtained are compared with that of a conventional application on the same matrices. This is done in order to evaluate the effectiveness and advantages of fast GC achieved with narrow bore columns.

Introduction

Several essential oils are obtained through steam distillation and contain only volatile compounds. Citrus essential oils are an exception to this because their complex matrix, containing volatile (90–99%) and nonvolatile (1–10%) components, is generally extracted by cold-pressing machines. In this field, sophisticated adulterations have been developed and, as such, their detection can be very difficult. The widespread production of cheaper oils altogether similar to natural ones are the cause of considerable economical losses (1). The determination of the essential oil volatile fraction profile is generally sufficient for an evaluation on quality and authenticity. This is mainly carried out by traditional gas chromatographic (GC) techniques, which are characterized by high time costs caused by the use of long capillary columns and slow temperature ramps. It is for this reason that there has always been much interest for the development of faster methods. Principles and theory for fast GC analysis were already established in the 1960s, but it has only been in the last decade that this technique has found routine application with good results (2–5). Although the most common approach for faster analysis consists in the reduction of capillary column lengths, internal diameters and film thicknesses (6–10), other important routes can be mentioned. One of these concerned the employment of multicapillary columns formed by 900 capillaries, each with an internal diameter of 40 µm. These features lead to a high sample capacity, but their low separation power confined this type of application to simple samples (11,12). Other applications regarded the use of packed columns characterized by a higher sample capacity than multicapillary columns but with even less resolving power attributable to band broadening caused mainly by eddy diffusion. This drawback was somewhat minimized by the use of smaller particles (13,14), but the reduction of particle size is accompanied by a proportionally higher required inlet pressure attributable to a reduction in column permeability. For this reason, only very short packed columns could be used, with insufficient separation power for the more complex matrices. Undoubtedly, the most important technological innovation for the development of fast GC techniques was the narrow bore capillary column. These columns are shorter than conventional ones, with a reduced internal diameter and a thin stationary phase, but they maintain a high phase ratio.

The separation of very complex matrices through GC analysis requires optimum heating rates. The greatest benefit of temperature programming is a substantial reduction of analysis time: the higher the rate, the shorter the time. Unfortunately, increasing heating rates causes a reduction in column peak capacity as well (15). An optimum temperature program rate should guarantee both a short analysis time and a minimal loss in peak capacity.

The introduction of new instrumental technologies able to satisfy the extreme parameters required for narrow bore column fast analysis (high split ratio injection systems, very high inlet pressures, rapid oven heating rates, and fast electronics for detection and data acquisition) has made faster separations of very complex matrices possible, with little or no loss in efficiency and, consequentially, resolving power.

In the present study a fast GC method has been applied to the analysis of citrus essential oils. The overall results obtained can be considered more than satisfactory because analyses were completed in 3.3 min (speed gain of 14 times), with little loss in resolution. The aims of this work were to evaluate the suitability of modern analytical instrumentation when challenged with very fast GC analysis and, furthermore, to define boundaries in which speed is accompanied by an acceptable separating power.

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Experimental

Samples

Five citrus essential oils (bergamot, bitter orange, sweet orange, mandarin, and lemon) were analyzed. The oils were diluted 1:10 (v/v) in hexane.

Instrumentation

Conventional GC

GC–flame ionization detection (FID) analyses were performed on a Shimadzu system composed of GC-17A (ver. 3) equipped with a split/splitless injector, autosampler AOC-20i, and FID (Shimadzu, Milan, Italy). Separations were performed on a MDN-5S (Supelco, Bellefonte, PA) 30-m × 0.25-mm i.d. × 0.25-µm film thickness column. The temperature program was as follows: 50°C to 250°C at 3°C/min. The injection volume was 1.0 µL, pressure was 102 kPa at constant pressure, carrier gas was He at 30 cm/s of average linear velocity (u). The split ratio was 1:100. The detector was set at 280°C. H_2 was 60 kPa. The air was 50 kPa. The makeup was 80 kPa (He), sampling frequency was 5Hz, and the data were acquired by a Class-VP 4.3 software (Shimadzu).

GC–MS

GC–MS analyses were performed on a Shimadzu GC/MS instrument QP5050A equipped with Adams library (16). The GC conditions were the same as those reported for GC–FID analyses. The pressure was 35 kPa at pressure constant. The carrier gas was He, and u was 32.12 cm/s. The injection volume was 1.0 µL. The split ratio was 1:30 (250°C), interface temperature was 230°C, ionization energy was 1.50 kV, and acquisition mass range was 40–400 *m/z*.

Fast GC

GC–FID analyses were performed on a Shimadzu system composed of: GC-2010 equipped with split/splitless injector, autosampler AOC-20i, FID, and data acquisition was performed by the GC Solution software (Shimadzu). The column was an MDN-5S (Supelco) 10-m × 0.1-mm i.d. with a 0.1-µm film thickness. The temperature program was 40°C to 300°C at 50°C/min. The pressure was 265.3 kPa at linear velocity constant. The carrier gas was H_2 and u was 81.5 cm/s. The injection volume was 0.2-µL. The split

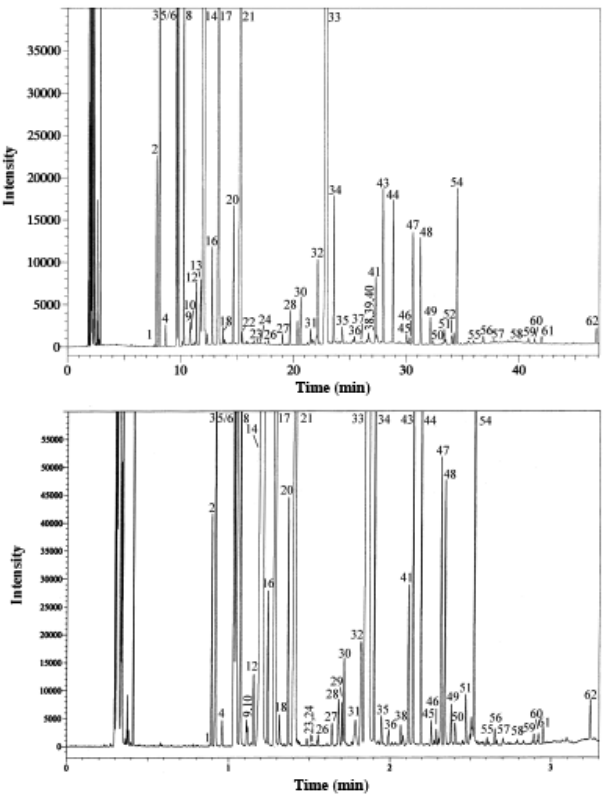

Figure 1. Conventional (top) and fast (bottom) GC chromatograms of a bergamot oil. See Table I for peak identification. Conventional: 30-m × 0.25-mm i.d., 0.25 µm, MDN-5S column. Oven temperature program: 50°C to 250°C at 3°C/min. Carrier gas: He, at 30 cm/s. Detector: FID, 280°C. Injection volume: 1.0 µL. Split ratio: 100:1. Fast: 10-m × 0.10-mm i.d., 0.10 µm, MDN-5S column. Oven temperature program: 40°C to 300°C at 50°C/min. Carrier gas: H_2, at 81.5 cm/s. Detector: FID, 350°C. Injection volume: 0.2 µL. Split ratio: 400:1.

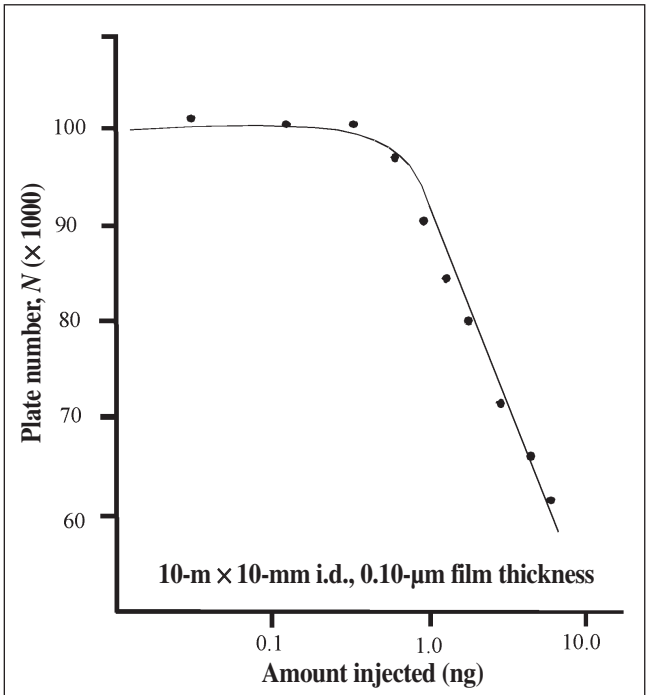

Figure 2. Sample capacity of the column MDN-5S 10-m × 0.1-mm i.d., 0.1-µm film thickness. Sample injected: tridecane.

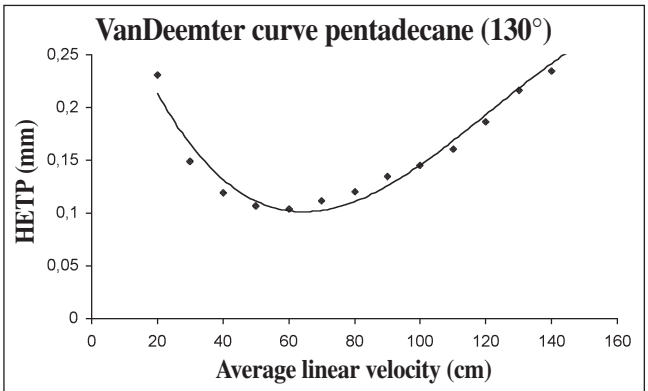

Figure 3. H versus u curve obtained for pentadecane run isothermally at 130°C. Column: MDN-5S 10-m × 0.1-mm i.d., 0.1-µm film thickness.

Table I. Peak Identification and Retention Time Values of Bergamot Oil Compounds Analyzed by Conventional and Fast GC

		Conventional			Fast		
		X t_R	s	CV%	X t_R	s	CV%
1	Tricyclene	7.720	0.003	0.039	–	–	
2	α-Thujene	7.864	0.002	0.029	0.894	0.00	0.104
3	α-Pinene	8.128	0.002	0.021	0.916	0.001	0.101
4	Camphene	8.684	0.002	0.027	0.960	0.000	0.000
5	Sabinene	9.636	0.002	0.024	1.030	0.001	0.091
6	β-Pinene	9.803	0.000	0.000	1.046	0.000	0.000
7	6-Methyl-5-hepten-2-one	10.187	0.004	0.034			
8	Myrcene	10.299	0.002	0.017	1.071	0.001	0.088
9	Octanal	10.827	0.004	0.032	1.110	0.001	0.085
10	α-Phellandrene	10.882	0.002	0.016	1.117	0.000	0.000
11	δ-3-Carene	11.142	0.002	0.016	1.139	0.001	0.083
12	α-Terpinene	11.414	0.002	0.020	1.153	0.001	0.082
13	*p*-Cymene *	11.786	0.002	0.020	1.210	0.001	0.077
14	Limonene*	12.122	0.004	0.033			
15	(*Z*)-β-Ocimene*	12.345	0.004	0.033			
16	(*E*)-β-Ocimene	12.810	0.003	0.023	1.241	0.001	0.079
17	γ-Terpinene	13.377	0.004	0.026	1.286	0.001	0.074
18	*cis*-Sabinene hydrate	13.749	0.002	0.013	1.314	0.001	0.072
19	Octanol	14.401	0.003	0.024	1.355	0.001	0.070
20	Terpinolene	14.690	0.003	0.020	1.367	0.001	0.069
21	Linalool	15.326	0.006	0.038	1.411	0.001	0.068
22	Nonanal	15.462	0.002	0.011	1.485	0.001	0.102
23	*cis*-Limonene oxide	16.898	0.005	0.030	1.502	0.001	0.089
24	*trans*-Limonene oxide	17.113	0.004	0.021	1.509	0.001	0.067
25	Camphor	17.495	0.004	0.023	1.550	0.001	0.062
26	Citronellal	17.809	0.002	0.010	1.554	0.001	0.061
27	Terpinen-4-ol	19.030	0.003	0.016	1.640	0.001	0.057
28	α-Terpineol	19.694	0.002	0.012	1.681	0.001	0.056
29	Decanal	20.350	0.003	0.015	1.703	0.001	0.056
30	Octyl acetate	20.639	0.003	0.017	1.715	0.001	0.055
31	Nerol	21.518	0.002	0.008	1.785	0.000	0.000
32	Neral	22.143	0.004	0.016	1.820	0.000	0.000
33	Geraniol	22.983	0.006	0.025	1.868	0.001	0.051
34	Geranial	23.584	0.002	0.010	1.902	0.001	0.050
35	Bornyl acetate	24.338	0.002	0.007	1.946	0.001	0.049
36	Undecanal	25.247	0.004	0.014	1.992	0.000	0.000
37	Nonyl acetate	25.329	0.002	0.007	2.035	0.001	0.086
38	Methyl geranoate	26.497	0.004	0.013	2.066	0.001	0.046
39	Linalyl propionate*	26.648	0.002	0.006	2.082	0.001	0.045
40	δ-Elemene*	26.800	0.000	0.000			
41	α-Terpinyl acetate*	27.296	0.002	0.008	2.114	0.001	0.045
42	Citronellyl acetate*	27.405	0.007	0.025			
43	Neryl acetate	27.952	0.002	0.006	2.142	0.001	0.044
44	Geranyl acetate	28.847	0.000	0.000	2.192	0.001	0.043
45	Dodecanal	30.163	0.000	0.000	2.257	0.000	0.000
46	Decyl acetate	30.337	0.004	0.012	2.288	0.001	0.041
47	β-Caryophyllene	30.600	0.000	0.000	2.316	0.001	0.040
48	*trans*-α-Bergamotene	31.262	0.002	0.006	2.341	0.000	0.000
49	*cis*-β-Farnesene	32.144	0.002	0.007	2.380	0.001	0.039
50	β-Santalene	32.303	0.003	0.008	2.404	0.002	0.056
51	Germacrene D	33.371	0.002	0.005	2.471	0.001	0.039
52	Sesquiterpene	33.488	0.002	0.005	2.505	0.001	0.038
53	Bicyclogermacrene	34.231	0.001	0.003	2.511	0.001	0.037

* Coeluted in fast.

ratio was 1:400 (300°C). The detector was 350°C, H_2 was 50 mL/min, air was 400 mL/min, and makeup was 50 mL/min (N_2). The sampling rate was 4 ms, and the filter time constant was 50 ms.

For method translation, a GC Transform 1.0 software (Avantech, Angri, SA, Italy) was used.

Results and Discussion

Figure 1 shows two chromatograms (conventional and fast, respectively) relative to a sample of bergamot oil. It is evident that, in the fast chromatogram, the analysis time is drastically reduced with a speed gain of almost 14 times.

During the development of the fast method applied in the present investigation, several factors were taken into consideration. The first challenge was to shorten the analysis time while affecting, as least as possible, resolution. As aforementioned, essential oils have a complex volatile fraction characterized also by the presence of trace components. For this reason, our interest was focused in evaluating the sample capacity of the narrow bore column in relation to efficiency in terms of *N* (plate number). A standard compound (tridecane) was injected in 10 different quantities ranging from 9 to 0.05 ng. Column plate numbers relative to each quantity were calculated and plotted in a graph illustrated in Figure 2. As can be seen, the maximum efficiency was reached in the 0.8–0.05-ng range and corresponded to a plate number of approximately 100,000.

In Figure 3, data obtained for a hydrocarbon (pentadecane) run isothermally at different carrier gas linear velocities (u) are plotted; after a threshold value of 60 cm/s, H increases. The Van Deemter curve shows that at 81.5 cm/s, the u value set for the fast method, the correspondent H value, is still acceptable (N = 83500). In addition, the H_{min} value (0.104) observed at the optimal u (60 cm/s) is in good agreement with the theoretical value predicted (0.10). In fact, for capillary columns with a high phase ratio (250 or more), the H_{min} value approaches the d_c (column internal diameter), which is, in this case, 0.10 mm.

Table I reports the mean retention times for each component of the bergamot oil, relative to three repetitions. The coefficient of variation percent (CV%) values are also reported, and they demonstrate the excellent repeatability of fast GC analysis under severe experimental conditions. As can be seen when comparing the conventional with the fast results, the fast method leads to a loss of some peaks as well as to some coelutions. In particular, a peak triplet (13-14-15) and two peak pairs (39-40 and 41-42) undergo coelution, yet

peaks 1 and 7 are not present in the fast chromatogram. Table II lists the relative percentage areas and the CV% values for the same components as seen in Table I; once again, data produced by the two methods proved to be in good agreement. Furthermore, CV% values confirm the excellent repeatability of both methods, as they are always lower than 3. There were a few exceptions to this, as some trace components were characterized by higher CV% values. This can be considered of secondary importance when dealing with essential oils because the accurate determination of the major components is sufficient for quality control and the detection of adulterations. In order to provide additional information concerning column efficiency in such extreme experimental conditions, a comparison was made between the conventional and the fast applications in terms of the following chromatographic parameters: retention times (t_R), peak widths at the base (w_b), selectivity (α), and resolution (R_s) (Table III). The w_b values emphasize the fast peak shapes, much narrower than in conventional GC. On the other hand, high

Table I (continued). Peak Identification and Retention Time Values of Bergamot Oil Compounds Analyzed by Conventional and Fast GC

		Conventional			Fast		
		X t_R	s	CV%	X t_R	s	CV%
54	β-Bisabolene	34.512	0.002	0.005	2.523	0.000	0.000
55	β-Sesquiphellandrene	35.972	0.002	0.005	2.603	0.001	0.036
56	(*E*)-γ-Bisabolol	36.834	0.002	0.006	2.651	0.002	0.108
57	(*E*)-α-Nerolidol	37.792	0.005	0.013	2.702	0.000	0.000
58	Tetradecanal	39.727	0.000	0.000	2.828	0.002	0.083
59	2,3-Dimethyl-3-(4-methyl-3-pentenyl)-2-norbornanol	40.699	0.005	0.013	2.894	0.001	0.055
60	Campherenol	40.848	0.004	0.010	2.922	0.001	0.031
61	α-Bisabolol	41.025	0.011	0.026	2.951	0.000	0.000
62	Nootkatone	46.853	0.000	0.000	3.245	0.001	0.028

* Coeluted in fast.

Table II. Relative Area Percent and CV% for Conventional and Fast GC Analyses of Bergamot Oil

		Conventional		Fast				Conventional		Fast	
		X area %	CV%	X area %	CV%			X area %	CV%	X area %	CV%
1	Tricyclene	tr†	2.49	–	–	32	Neral	0.24	0.30	0.27	0.23
2	α-Thujene	0.32	0.22	0.21	0.20	33	Geraniol	27.34	0.05	31.64	0.33
3	α-Pinene	1.27	0.21	0.95	0.29	34	Geranial	0.36	0.18	0.36	0.60
4	Camphene	0.04	0.26	0.03	0.40	35	Bornyl acetate	0.05	0.22	0.04	4.96
5	Sabinene	1.16	0.14	0.88	0.41	36	Undecanal	0.01	2.85	tr	1.76
6	β-Pinene	7.04	0.16	6.06	0.30	37	Nonyl acetate	0.01	0.86	0.02	1.89
7	6-Methyl-5-hepten-2-one	0.01	0.50	–	–	38	Methyl geranoate	0.01	3.22	0.02	2.76
8	Myrcene	0.98	0.11	0.80	0.13	39	Linalyl propionate*	0.03	2.25	0.01	4.07
9	Octanal	0.05	1.34	0.03	0.34	40	δ-Elemene*	tr	3.26	–	–
10	α-Phellandrene	0.03	3.10	0.02	1.77	41	α-Terpinyl acetate*	0.17	0.18	0.19	0.61
11	δ-3-Carene	tr	3.09	tr	3.48	42	Citronellyl acetate*	0.03	3.75	–	–
12	α-Terpinene	0.15	0.19	0.10	0.64	43	Neryl acetate	0.39	0.15	0.38	0.07
13	*p*-Cymene*	0.62	8.55	39.89	0.78	44	Geranyl acetate	0.36	0.10	0.34	0.91
14	Limonene*	42.07	0.06	–	–	45	Dodecanal	0.01	3.73	0.02	0.82
15	(*Z*)-β-Ocimene*	0.02	0.75	–	–	46	Decyl acetate	0.02	3.84	0.02	1.46
16	(*E*)-β-Ocimene	0.21	0.28	0.16	1.66	47	β-Caryophyllene	0.33	0.09	0.29	0.39
17	γ-Terpinene	7.84	0.12	7.57	0.25	48	*trans*-α-Bergamotene	0.29	0.22	0.28	2.60
18	cis-Sabinene hydrate	0.04	0.54	0.03	0.31	49	*cis*-β-Farnesene	0.07	0.26	0.05	0.77
19	Octanol	tr	0.72	tr	2.99	50	β-Santalene	0.03	0.70	0.05	0.97
20	Terpinolene	0.32	0.14	0.26	0.26	51	Germacrene D	0.05	1.73	0.04	2.32
21	Linalool	7.53	0.11	7.79	0.08	52	Sesquiterpene	0.02	2.20	0.06	1.36
22	Nonanal	0.03	0.48	0.01	3.24	53	Bicyclogermacrene	0.03	2.47	0.04	2.65
23	*cis*-Limonene oxide	0.00	4.04	tr	3.05	54	β-Bisabolene	0.43	0.08	0.41	1.31
24	*trans*-Limonene oxide	tr	3.15	tr	2.97	55	β-Sesquiphellandrene	0.01	3.42	0.02	1.35
25	Camphor	0.01	2.30	tr	5.81	56	(*E*)-γ-Bisabolol	0.02	1.05	0.01	3.56
26	Citronellal	0.01	1.16	0.01	1.51	57	(*E*)-α-Nerolidol	0.01	2.07	0.02	4.92
27	Terpinen-4-ol	0.03	3.80	0.03	1.77	58	Tetradecanal	0.01	3.83	tr	4.20
28	α-Terpineol	0.09	0.23	0.08	1.63	59	2,3-Dimethyl-3-(4-methyl-3-pentenyl)-2-norbornanol	tr	3.47	0.02	1.77
29	Decanal	0.06	0.39	0.05	1.19	60	Campherenol	0.01	2.65	0.02	1.84
30	Octyl acetate	0.12	0.40	0.10	1.53	61	α-Bisabolol	tr	3.05	0.02	3.33
31	Nerol	0.05	3.30	0.07	0.84	62	Nootkatone	0.05	0.60	0.05	1.29

* Coeluted in fast.
† tr < 0.01.

Table III. Comparison of Some Chromatographic Parameters Obtained for Conventional and Fast GC Analyses

		Conventional				Fast			
		t_R	w_b	α	R_s	t_R	w_b	α	R_s
2	α-Thujene	7.864	0.069			0.894	0.006		
3	α-Pinene	8.128	0.071	1.040	3.8	0.916	0.009	1.033	1.9
47	β-Caryophyllene	30.600	0.111			2.316	0.007		
48	*trans*-α-Bergamotene	31.262	0.105	1.020	6.1	2.341	0.007	1.010	1.8

analytical speed had a cost in regard to resolution, which had values somewhat lower in fast GC but still sufficient to allow the baseline separation of nearly all components. After testing the ruggedness and reliability of the fast method on bergamot oil, the other four oils were analyzed (Table IV) at the same experimental conditions. Even in this case, the comparison between fast and conventional GC highlights the fact that quantitative values are in good agreement as well as with quality ranges established for essential oils by international regulations.

Table IV. Relative Area Percent for Conventional and Fast GC Analyses of Lemon, Sweet Orange, Bitter Orange, and Mandarin Oils

	Lemon		Sweet orange		Bitter orange		Mandarin	
	X conv.	X fast	X conv.	X fast	X conv.	X fast	X conv.	X fast
Tricyclene	0.01	–	–	–	–	–	–	
α-Thujene	0.42	0.37	0.03	0.03	0.01	0.01	0.74	0.62
α-Pinene	1.89	1.67	0.64	0.52	0.62	0.53	2.21	1.79
Camphene	0.06	0.06	0.01	0.01	0.01	0.01	0.02	0.02
Sabinene	1.97	1.71	0.52	0.40	0.29	0.23	0.24	0.20
β-Pinene	12.56	11.83	0.91	0.73	1.01	0.85	1.47	1.22
6-Methyl-5-hepten-2-one	–	–	–	–	–			
Myrcene	1.47	1.48	2.03	1.72	1.90	1.70	1.79	1.58
Octanal + α-phellandrene	0.12	0.11	0.18	0.14	0.20	0.14	0.13	0.11
δ-3-Carene	–	–	0.16	0.12	tr	tr	tr	tr
α-Terpinene	0.16	0.14	0.02	0.01	tr	tr	0.32	0.26
p-Cymene + limonene	66.40	69.01	93.33	93.51	93.26	93.12	73.84	73.46
(*Z*)-β-Ocimene	0.08	–	0.01	0.01	0.01	tr	tr	tr
(*E*)-β-Ocimene	0.12	0.08	0.62	0.61	0.62	tr	0.02	tr
γ-Terpinene	9.16	8.65	0.59	0.46	0.08	0.06	17.06	16.09
cis-Sabinene hydrate	0.03	0.02	0.04	0.04	tr	tr	0.01	tr
Octanol	–	–	–	–	–	–	0.01	tr
Terpinolene	0.35	0.31	0.05	0.05	0.01	tr	0.73	0.61
Linalool	0.12	0.09	0.30	0.27	0.32	0.30	0.09	0.08
Nonanal	0.12	0.09	0.04	0.02	0.03	0.01	0.03	0.02
cis-Limonene oxide	tr	tr	0.01	0.01	0.01	0.01	–	–
trans-Limonene oxide	tr	tr	0.02	0.02	tr	tr	–	–
Miroxide	–	–	–	–	–	–	0.02	0.02
Camphor	0.01	tr	–	–	–	–	–	–
Citronellal	0.10	0.10	0.04	0.04	tr	tr	0.02	0.03
Terpinen-4-ol	0.05	0.05	tr	tr	tr	tr	0.02	0.02
α-Terpineol	0.17	0.15	0.06	0.04	0.03	0.03	0.08	0.07
Decanal	0.05	0.06	0.17	0.16	0.13	0.11	0.08	0.09
Octyl acetate	tr	tr	tr	tr	0.04	0.03	–	–
Nerol	0.04	0.03	0.02	0.03	–	–	0.01	0.02
Neral	0.77	0.67	0.06	0.05	0.03	0.03	tr	tr
Geraniol	0.03	0.03	0.01	0.01	0.01	tr	–	–
Linalyl acetate	–	–	–	–	1.04	0.97	–	–
Geranial	1.29	1.20	0.13	0.11	0.05	0.04	0.04	0.03
Perillaldehyde	0.02	0.03	tr	tr	0.02	0.02	–	–
Bornyl acetate	–	–	0.01	tr	–	–	–	–
Undecanal	0.03	0.03	0.01	0.01	0.01	0.01	0.01	tr
Thymol	–	–	–	–	–	–	0.04	0.05
Nonyl acetate	0.01	tr	–	–	0.01	tr	–	–

* tr < 0.01.

Table IV (continued). Relative Area Percent for Conventional and Fast GC Analyses of Lemon, Sweet Orange, Bitter Orange, and Mandarin Oils

	Lemon		Sweet orange		Bitter orange		Mandarin	
	X conv.	X fast	X conv.	X fast	X conv.	X fast	X conv.	X fast
δ-Elemene	–	–	–	–	0.03	0.02	–	–
α-Terpinyl acetate	–	–	–	–	tr	0.01	0.03	0.02
Citronellyl acetate	0.03	0.03	0.01	0.03	0.01	0.01	tr	tr
Neryl acetate	0.44	0.42	0.04	0.04	0.03	0.02	0.01	0.02
α-Copaene acetate	–	–	0.02	tr	–	–	–	–
Geranyl acetate	0.35	0.34	0.03	0.03	0.12	0.11	tr	0.02
β-Cubebene+β-elemene	–	–	0.03	0.02	–	–	–	–
Dodecanal	tr	–	tr	0.03	0.02	0.02	tr	–
Decyl acetate	0.02	0.02	0.01	tr	–	–	–	–
N-Methyl-methylanthranilate	–	–	–	–	–	–	0.34	0.26
Sesquithujene	0.02	0.02	–	–	–	–	–	–
β-Caryophyllene	0.21	0.17	0.03	0.03	0.06	0.05	0.07	0.07
β-Copaene	–	–	0.02	0.02	–	–	–	–
trans-α-Bergamotene	0.38	0.35	0.03	0.02	0.02	0.02	–	–
cis-β-Farnesene	–	–	0.02	0.01	0.02	0.01	–	–
α-Humulene	0.05	0.02	tr	tr	–	–	0.01	tr
Germacrene D	0.02	0.04	0.02	0.03	0.12	0.11	–	–
Sesquiterpene	–	–	–	–	–	–	–	–
Valencene	0.05	0.03	–	–	–	–	–	–
α-Selinene	–	–	–	–	–	–	0.03	0.01
α-Farnesene + Sesquiterpene	0.06	0.05	0.17	0.16	–	–	0.15	0.12
Bicyclogermacrene	0.04	0.04	–	–	0.01	0.01	–	–
β-Bisabolene	0.57	0.54	–	–	0.01	0.01	–	–
β-Sesquiphellandrene	–	–	–	–	–	–	–	–
δ-Cadinene	–	–	0.02	0.03	–	–	–	–
E-γ-Bisabolol	–	–	–	–	–	–	–	–
E-α-Nerolidol	–	–	–	–	0.09	0.08	–	–
trans-Sesquisabinene hydrate	–	–	–	–	–	–	–	–
Tetradecanal	0.01	0.01	0.01	0.01	tr	tr	–	–
Tetradecanal	0.01	0.01	0.01	0.01	tr	tr	–	–
2,3-Dimethyl-3-(4-methyl-3-pentenyl)-2-norbornanol	0.02	0.02	0.01	0.01	tr	tr	–	–
Campherenol	0.02	0.02	–	–	–	–	–	–
α-Bisabolol	0.03	0.03	–	–	–	–	–	–
β-Sinensal	–	–	0.02	0.02	–	–	–	–
cis-trans-Farnesol	–	–	–	–	–	–	tr	tr
α-Sinensal	–	–	0.01	0.01	–	–	0.29	0.26
Nootkatone	0.01	tr	0.02	0.02	0.01	0.01	0.01	tr

* tr < 0.01.

Conclusion

The described work was accomplished to demonstrate the effectiveness of fast GC, through the use of a narrow bore capillary column and extreme operational conditions, in the separation of very complex matrices such as citrus essential oils. This technique did not seriously affect analytical quality and proved its reliability for quick and correct identification. This is an important tool in such analytical areas in which hundreds of analyses per day are carried out for the routine control on quality and genuineness. The application of fast GC for the characterization of the volatile fraction of citrus essential oils was performed successfully, drastically reducing the analysis time (~ 47 vs. 3 min) while maintaining a good standard in terms of resolution.

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