Journal of Chromatography A, 1217 (2010) 1101–1105

Contents lists available at ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

Thorough evaluation of the validity of conventional enantio-gas chromatography in the analysis of volatile chiral compounds in mandarin essential oil: A comparative investigation with multidimensional gas chromatography

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ARTICLE INFO

Article history:
Available online 4 October 2009

Keywords:
Deans-switch
Enantio-gas chromatography
Enantiomeric excess
Mandarin essential oil
Heart-cutting multidimensional GC-mass spectrometry (MDGC-MS)

ABSTRACT

The present research is focused on the determination of the enantiomeric distribution of chiral compounds, contained in mandarin essential oils, by means of conventional chiral gas chromatography with flame ionization detection (enantio-GC-FID); the results attained were compared with those derived from heart-cutting multidimensional GC-mass spectrometry (MDGC/MS), to evaluate the reliability of the monodimensional technique as a tool for quality control. The Deans-switch MDGC system was equipped with two GC ovens, which were connected via a heated transfer line, a flame ionization detector (FID1) in the first dimension and a quadrupole MS as second-dimension detector. The *a priori* knowledge of potential co-elutions concerning target compounds (an enantiomer and an interfering compound), when using enantio-GC-FID, could enable the use of corrected enantiomer excess values. Correction factors could be calculated through a preliminary GC-FID analysis (using an apolar column), considering the peak areas of the known interferences. The method used for the calculation of a so-called "coelution correction factor" is described, along with some examples.

1. Introduction

Mandarin essential oils, obtained from cold-pressed fruit peels, are widely commercialized all over the world. Italian mandarin oils are considered as the most valuable, because of their organoleptic properties, due to the optimum growth conditions. Mandarin oil is used in different fields, such as food/beverage and perfumery industries, to enhance the bouquet of flavor and fragrance compositions. Mandarin essential oil is characterized by the presence of: the sesquiterpene aldehyde α-sinensal, its major odorant (also present in orange oil), the aromatic ester methyl-N-methyl anthranilate, and the aromatic alcohol thymol [1].

Reconstituted mandarin oils, which are easy to find on the market, are generally obtained by mixing natural mandarin oils with sweet orange terpenes and/or distilled oils of different origins; distilled oils can also be added with methyl-N-methyl anthranilate, α-sinensal and thymol. Several techniques have been exploited to detect these kinds of adulterations, such as gas chromatography with conventional or chiral stationary phases (enantio-GC) [1]. Enantio-GC (also abbreviated as Es-GC) is considered one of the most powerful techniques for the quality assessment of essential oils. Enantio-GC can provide useful informations on the genuineness and quality of essential oils, on the basis of the characteristic enantiomeric excess (ee) of each chiral compound. Specific pairs of enantiomers have been exploited as markers, using various chiral stationary phases (in mono- and bidimensional systems) [1–6]. On the contrary, the quantitative analysis of mandarin oil volatiles, using conventional GC, can often be of little help, due to variations that each component can undergo throughout the season [1,3]. Moreover, mandarin oil constituents are characterized by wide concentration ranges, and, hence, it is rather easy to produce reconstituted oils, altogether similar to the natural counterpart.

Dugo et al. showed that an apolar-chiral column combination, which gives a performance comparable to that of a mixed stationary phase, was useful in enhancing the resolution of target compounds and reducing matrix interferences, in lemon and mandarin oil applications [8,9]. A coupled-column system, based on the use of a low-polarity stationary phase column connected to the terminal end of an enantioselective one, was also shown to be a valid option by Shellie et al., in the analysis of tea tree oil [10].

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0021-9673/$ – see front matter © 2009 Published by Elsevier B.V.
doi:10.1016/j.chroma.2009.09.080

However, such chromatography cannot be defined as multidimensional, because the resolution achieved on the first column might be impaired on the second one.

The introduction of enantio-multidimensional GC (enantio-MDGC), first described by Schomburg et al. [11], allowed unresolved target components to be heart-cut from the primary (achiral) column and delivered to the (chiral) analytical column. The employment of chiral MDGC, in essential oil analysis, has become a very useful tool, to overcome the drawbacks of enantio-GC [12,13]. Mondello et al. established a quality range for mandarin essential oil, based on the enantiomeric ratios of β-pinene, sabinene, limonene, linalool, terpinen-4-ol and α-terpineol [7].

A Deans-switch, twin-oven MDGC system has been recently used in multiple-cut analysis, demonstrating a very high retention-time stability, due to a three-restrictor configuration [14]. The combination of a third MS dimension, greatly increases the analytical potential of the instrument [15]. The MDGC system was employed in the present research which is focused on: (I) the analysis of chiral components in natural Italian cold-pressed mandarin essential oils by means of enantio-GC; (II) the analysis of the same constituents by using MDGC/MS (apolar-chiral); (III) comparison of the results attained in order to locate possible coelutions using enantio-GC (a specific enantiomer plus one or more interferences); (IV) the analysis of the specific enantiomers, by using chiral-apolar MDGC/MS, in order to identify the interferences.

2. Materials and methods

2.1. Samples and sample preparation

118 natural Italian mandarin oils, obtained from the fruit cultivars "Avana", harvested from September to January 2008–2009, and "Tardivo di Ciaculli" harvested from mid-January to the end of February 2009. The plantations were located in Palermo (Sicily, Italy) and Reggio Calabria (Calabria, Italy). All samples were provided by Simone Gatto s.r.l. (Messina, Italy), and were extracted using two different techniques: *sfumatura* and Brown oil extractor.

Each oil was stored at 4 °C and prior to analyses, diluted 1/10 (v/v) in *n*-hexane.

2.2. Instrumentation and operational conditions

2.2.1. Conventional GC-FID and enantio-GC-FID

A Shimadzu GC2010 gas chromatograph, equipped with an AOC-20i series autoinjector, was used in all applications (Shimadzu, Kyoto, Japan).

GC-FID: column, SLB-5ms [silphenylene polymer, virtually equivalent in polarity to poly(5% diphenyl/95% methylsiloxane)] 30 m × 0.25 mm I.D. × 0.25 μm d_f (Supelco, Milan, Italy); temperature program: 50–250 °C at 3.0 °C min; split/splitless injector (250 °C); injection mode: split, 1:100 ratio; injection volume: 1.0 μL; inlet pressure: 99.5 kPa; carrier gas: He; constant gas linear velocity: 30.0 cm/s.

Enantio-GC-FID: column, Megadex DETTBS-β (diethyl-*tert*-butyl-silyl β-cyclodextrin) 25 m × 0.25 mm I.D. × 0.25 μm d_f (Mega, Legnano, Italy); temperature program: 50–200 °C at 2.0 °C min; split/splitless injector (220 °C); injection mode: split, 1:10 ratio; injection volume: 1.0 μL; inlet pressure: 96.6 kPa; carrier gas: He; constant gas linear velocity: 35.0 cm/s.

Detector: FID (220 °C); H_2: 50.0 mL/min; air: 400 mL/min; make up (N_2): 40.0 mL/min; sampling rate: 80 ms. Data were collected by the GCSolution software (Shimadzu).

2.2.2. Multidimensional enantio-GC

The MDGC system consisted of two GC2010 (defined as GC1 and GC2) gas chromatographs, equipped with a Deans-switch transfer device, an MS-QP2010 quadrupole mass spectrometer, and an AOC-20i autosampler (Shimadzu).

GC1 was equipped with a split/splitless injector and a flame ionization detector (FID1). The MDGC switching element, located inside the oven, was connected to an advanced pressure control (APC) system which supplied carrier gas (He) at constant pressure. The transfer device has been previously described [12].

GC1: the primary column was the same as used in the GC-FID experiments. The operational conditions were as follows: constant inlet pressure 220 kPa (300 °C), split mode 1:20 (gas carrier He), injected volume 1.5 μL, initial linear velocity 30 cm/s. Temperature program: 50–280 °C at 3 °C/min. The FID (300 °C) was connected, via a stainless steel retention gap, to the transfer device; sampling rate: 80 ms. APC constant pressure: 130 kPa.

GC2 was equipped with a split/splitless injector and a flame ionization detector (both not used in the present research). Transfer line between GC1 and GC2: 180 °C. The chiral column was the same as used in the enantio-GC experiments. Temperature program: 40 °C (20 min) to 100 °C at 1 °C/min, to 160 °C at 3 °C/min.

Reversed column set conditions were as follows: in GC1 the chiral column was the same as used in the enantio-GC experiments, temperature program: 50–250 °C at 3.0 °C min, initial linear velocity: 35 cm/s; split/splitless injector (250 °C); injection mode: split, 1:100 ratio; injection volume: 1.0 μL; GC2 column was the same as used in the GC-FID experiments. Temperature program: 50 °C (10 min) to 200 °C at 3 °C/min. All data were collected using the MDGC Solution software 1.0 (Shimadzu).

3. Results and discussion

Conventional enantio-GC-FID is commonly employed for the assessment of essential oil quality, through the determination of the enantiomeric excesses of volatile chiral compounds; one of the most popular chiral selectors is the diethyl-*tert*-butyl-silyl β-cyclodextrin stationary phase, the selectivity of which is well known [1,2]. As an example, the enantio-GC separation of α-thujene, α-pinene, camphene, β-pinene, sabinene, α-phellandrene, β-phellandrene, limonene, linalool, citronellal, terpinen-4-ol and α-terpineol enantiomers, in a mandarin essential oil, is illustrated in Fig. 1. The position of the camphor isomers is illustrated, even if the chromatographic signal is below the detection limit (S/N > 3).

The overall resolution level, between optical isomers, appears to be generally satisfactory, and no complete co-elutions seem to occur. In fact, most compounds, *viz.*, α-thujene, β-pinene, sabinene, α-phellandrene, linalool, terpinen-4-ol and α-terpineol are baseline resolved. In the case of the camphene enantiomers, while (+)-camphene was entirely separated, overlapping occurred between (−)-camphene (peak 3) and (−)-α-pinene (peak 4), while the latter partially co-eluted with its (+) isomer (peak 5). A further lack of satisfactory separation was observed between (−)-limonene and (+)-β-phellandrene (a phenomenon also dependent on the dilution level) and between the citronellal enantiomers. For the compounds separated at the baseline, the information obtained can be considered as reliable, correspondent to the real enantiomer composition. On the contrary, substantial deviations from the real values could be expected for the partially overlapping compounds. For example, in the case of camphene, the low on-column amounts and the partial coelution could clearly lead to unreliable ee results; similar considerations can also be made for (−)-citronellal (peak 21) and (+)-terpinen-4-ol (peak 23). The aforedescribed chromatography performance is very typical of a monodimensional separation.

At this point, an MDGC method was developed and applied (a first dimension boiling point separation, followed by a chiral one) to the analysis of the same essential oil samples, with the objective of verifying the reliability of the monodimensional information. The

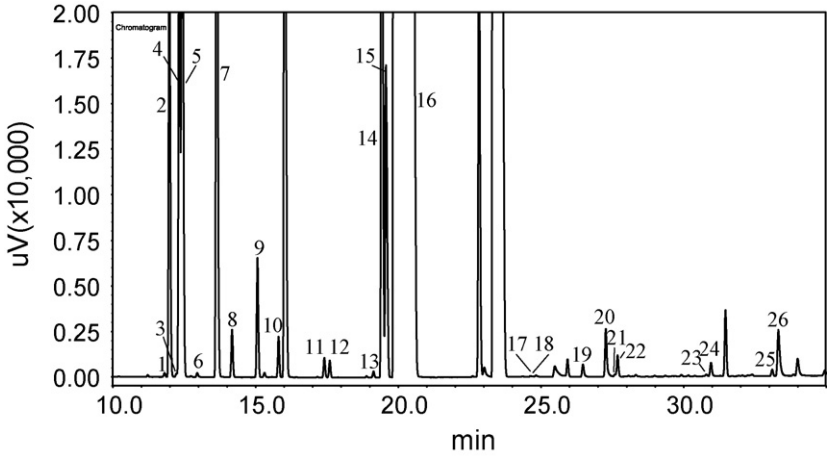

Fig. 1. Conventional enantio-GC-FID chromatogram of mandarin essential oil. (1) (−)-α-thujene; (2) (+)-α-thujene; (3) (−)-camphene; (4) (−)-α-pinene; (5) (+)-α-pinene; (6) (+)-camphene; (7) (+)-β-pinene; (8) (−)-β-pinene; (9) (+)-sabinene; (10) (−)-sabinene; (11) (−)-α-phellandrene; (12) (+)-α-phellandrene; (13) (−)-β-phellandrene; (14) (−)-limonene; (15) (+)-β-phellandrene; (16) (+)-limonene; (17) (+)-camphor; (18) (−)-camphor; (19) (−)-linalool; (20) (+)-linalool; (21) (−)-citronellal; (22) (+)-citronellal; (23) (+)-terpinen-4-ol; (24) (−)-terpinen-4-ol; (25) (−)-α-terpineol; (26) (+)-α-terpineol.

MDGC peak capacity can be considered approximately as that of the first dimension summed to that of the second dimension, the latter multiplied by the number of cuts. Average ee values, relative to the mandarin essential oil ($n = 3$; 113 mandarin oil samples) analyzed by using conventional Es-GC and MDGC, are reported in Table 1. For most of the enantiomers, the ee values were in good agreement, with slight variations due probably to the use of different instruments and columns. However, considerable variations were observed for campheneand linalool, while the ee values of camphor and citronellal could be effectively calculated only in the multidimensional applications. The monoterpene limonene presented values of 96.5 and 96.1, in the Es-GC and Es-MDGC experiments,

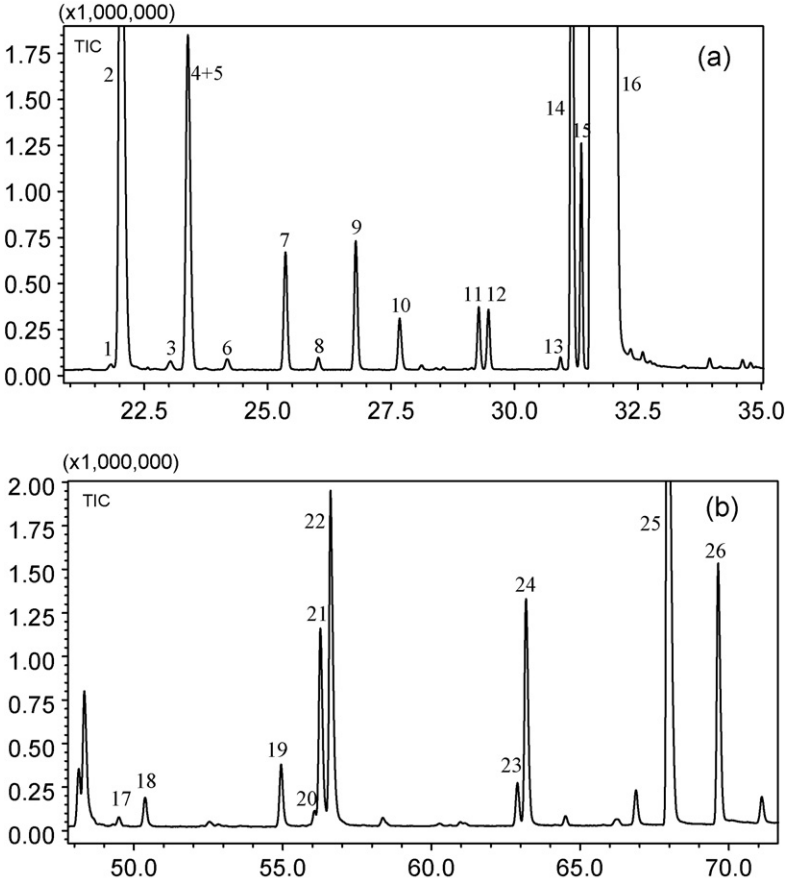

Fig. 2. (a) 20–35 min and (b) 48–72 min expansions of the 2D enantio-chromatogram relative to the MDGC/analysis. (1) (−)-α-thujene; (2) (+)-α-thujene; (3) (−)-camphene; (4 + 5) (±)-α-pinene; (6) (+)-camphene; (7) (+)-β-pinene; (8) (−)-β-pinene; (9) (+)-sabinene; (10) (−)-sabinene; (11) (−)-α-phellandrene; (12) (+)-α-phellandrene; (13) (−)-β-phellandrene; (14) (−)-limonene; (15) (+)-β-phellandrene; (16) (+)-limonene; (17) (+)-camphor; (18) (−)-camphor; (19) (−)-linalool; (20) (−)-citronellal; (21) (+)-citronellal; (22) (+)-linalool; (23) (+)-terpinen-4-ol; (24) (−)-terpinen-4-ol; (25) (−)-α-terpineol; (26) (+)-α-terpineol.

Table 1
Enantio-GC-FID and MDGC/MS % enantiomeric excess average values derived from 113 genuine mandarin oil samples; enantio-GC-FID and MDGC/MS % enantiomeric results for sample C. The corrected values, considering the interferences, are reported in parenthesis.

	Es-GC average	MDGC average	Es-GC sample C	MDGC sample C
(+)-α-Thujene	98.2	98.6	98.2	98.4
(−)-α-Pinene	11.8	n.d.	12.2	n.d.
(+)-Camphene	36.3	6.5	28.1	8.7
(+)-β-Pinene	92.9	93.3	93.8	94.0
(+)-Sabinene	57.2	57.4	57.5	57.8
(−)-α-Phellandrene	7.2	7.0	2.4	2.2
(+)-β-Phellandrene	96.4	94.6	96.6	94.3
(+)-Limonene	96.5	96.1	96.3 (97.0)	97.0
(−)-Camphor	n.d.	53.1	n.d.	53.0
(+)-Citronellal	n.d.	87.7	n.d.	86.4
(+)-Linalool	54.4	69.4	54.7 (63.1)	63.0
(−)-Terpinen-4-ol	75.1	75.7	75.2	75.5
(−)-α-Terpineol	45.7	44.9	48.5	48.3

respectively. Although the difference between the two values is not relevant (0.4), the issue is worthy of discussion because limonene is the predominant component of the volatile fraction, and therefore possible coelutions could explain such fluctuations. Observing the MDGC second-dimension separation (Fig. 2a and b), it is evident that (−)-camphene (peak 3) is now completely separated from α-pinene (peaks 4 and 5) while the resolution between (−)-limonene (peak 14) and (+)-β-phellandrene (peak 15) is improved, due to the lower amounts of limonene isolated and injected onto the second dimension.

Five genuine mandarin oil samples (labelled from A to E), not used for the calculation of the average ee values, were subjected to Es-GC and Es-MDGC analyses. The results attained for sample C are reported in Table 1: the lower enantiomeric excess of (+)-limonene, calculated in the enantio-GC analysis (the value was however compatible with a genuine sample), and with respect to the MDGC application, was studied. The difference in the ee values was due to the known coelutions of (−)-limonene with α-terpinene, and (+)-limonene with (E)-β-ocimene and *p*-cymene [1]. Such coelutions were overcome using MDGC, by cutting the central part of the limonene peak, at the outlet of the apolar column. β-Phellandrene was transferred with (±)-limonene, because these volatiles coelute completely in the first dimension. A similar case was observed for (−)-linalool and *trans*-limonene oxide, a peak pair that underwent complete coelution using enantio-GC, this finding was confirmed by using a reversed MDGC column set, namely chiral-apolar, and by transferring (−)-linalool onto the second dimension (Fig. 3). The MS system confirmed the identity of the two constituents.

On the basis of the knowledge relative to the coelutions that occur in monodimensional conditions, the data obtained in enantio-GC can be corrected. For this purpose, the relative % composition of mandarin essential oil was obtained by means of GC-FID analysis (Table 2), using a conventional apolar column (the GC-FID profile of mandarin oil is well-known).

Using GC-FID information, it is possible to correct the areas of the coeluting peaks in enantio-GC, such as in the case of the limonene enantiomers and (−)-linalool. Limonene and linalool enantiomers ratio, for example, were corrected using GC-FID data as follows: (−)-limonene by calculating the relative % (*f*) of α-terpinene, (+)-limonene by calculating the relative % of (E)-β-ocimene and *p*-cymene while, (−)-linalool was corrected considering the relative % of *trans*-limonene oxide. It was not possible to estimate the contribution of (Z)-β-ocimene, on the (−)-limonene ratio, due to the fact that these compounds coeluted both in GC-FID and in enantio-GC analyses. However, the small amount of (Z)-β-ocimene in mandarin

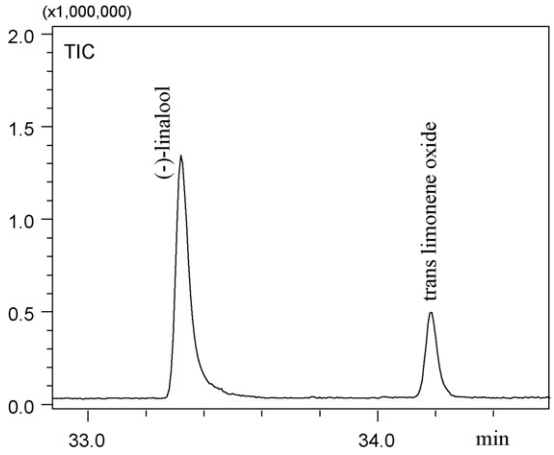

Fig. 3. 2D separation of (−)-linalool and *trans*-limonene oxide, using a chiral-apolar column set.

essential oil [1] has a neglectable influence on the (−)-limonene ratio. The formula used for the (−)-linalool area correction was:

$$f = \frac{\%_{coel}}{\%_{linalool}} \times 100$$

where $\%_{coel}$ represents the % area of *trans*-limonene oxide, and $\%_{linalool}$ represents that of linalool. In order to adjust the area of (−) linalool (A_{corr}), the following equation was applied:

$$A_{corr} = A_{(-)linalool} - \left(\frac{A_{(-)linalool} + A_{(+)linalool}}{100} \right) \times f$$

where $A_{(-)linalool}$ and $A_{(+)linalool}$ refer to the enantio-GC analysis. At this point, the enantiomeric excesses of the coeluting chiral compounds were calculated. Table 1 shows how the corrected

Table 2
GC-FID relative % composition of sample C.

Compound	rel. %	Compound	rel. %
α-Thujene	0.56	Citronellol	0.02
α-Pinene	1.65	Thymol methyl ether	>0.01
α-Fenchene	>0.01	Neral	0.05
Camphene	0.01	Ascaridole	>0.01
Sabinene	0.20	Carvone	>0.01
β-Pinene	1.42	Piperitone	>0.01
Myrcene	1.38	(2E)-Decenal	0.01
Decane	>0.01	Geranial	0.01
Octanal	0.13	Perillaldehyde	0.04
α-Phellandrene	0.04	Thymol	0.06
δ-3-Carene	>0.01	Undecanal	0.01
α-Terpinene	0.26	(2E,4E)-Decadienal	0.01
p-Cymene	0.76	Citronellyl acetate	>0.01
Limonene + (Z)-, β-ocimene	70.61	Neryl acetate	>0.01
(E)-, β-ocimene	0.02	Undec-(8Z)-enol	>0.01
γ-Terpinene	20.08	α-Copaene	0.01
cis-Sabinene hydrate	0.04	β-Cubebene	0.01
Terpinolene	0.68	Methyl-N-methyl anthranilate	0.54
p-Cymenene	>0.01	(E)-Caryophyllene	0.08
Linalool	0.14	(2E,6Z)-Dodecadienal	0.01
trans Sabinene hydrate	0.08	α-Humulene	0.01
Nonanal	0.03	(2E)-Dodecenal	0.02
p-Mentha-1.3.8-triene	>0.01	Germacrene D	>0.01
cis-Limonene oxide	0.01	Viridiflorene	>0.01
trans-Limonene oxide	0.01	α-Selinene	0.03
Camphor	>0.01	(E,E)-α-Farnesene	0.13
Citronellal	0.03	Tridecanol	>0.01
Terpinen-4-ol	0.03	δ-Cadinene	0.01
p-Cymen-8-ol	0.01	Tetradecanal	>0.01
α-Terpineol	0.20	Tetradec-(2E)-enal	0.01
Decanal	0.09	α-Sinensal	0.31
cis-Carveol	0.01		

results (reported in parenthesis), obtained for (+)-limonene and (+)-linalool in sample C, are in good agreement with the MDGC data.

A considerable advantage of chiral MDGC is the possibility to inject high amounts of sample, and then transfer the appropriate quantity of each peak in the second chiral dimension; in fact, enantiomeric ratios are not affected by analyte quantities. In the case of trace-amount compounds, higher signal-to-noise ratios can be achieved. For example, information relative to camphor (not detected using enantio-GC), citronellal and terpinen-4-ol enantiomers was attained (Fig. 2b) by increasing the volume of the sample injected, and then transferring the entire peaks. With regards to high-amount compounds, only small peak fractions were transferred; for example, in the case of limonenea 0.01 min fraction, of a 0.9 min peak, was transferred, thus avoiding both column overloading and vicinal-peak overlapping [*e.g.* (−)-limonene with (+)-β-phellandrene and (+)-citronellal with (+)-linalool].

The data obtained through chiral MDGC must be considered as more reliable, since all the values obtained in this study were in good agreement with the ranges reported in the literature for mandarin oil [7]. Considering enantio-GC, as was seen, most ee values were in good agreement with the MDGC values, although the use of corrected values was necessary for two chiral constituents. Although some enantio-GC values were within the genuineness range, such as in the case of limonene, it was possible to demonstrate that ee values can fluctuate in relation to the amounts of the co-eluting compounds.

When a multidimensional system is not available, the knowledge of the coelutions that can occur in conventional enantio-GC provides the possibility to adjust the results obtained considering the data of a common GC-FID analysis.

4. Conclusions

The goal of the present research was to compare enantio-GC and enantio-MDGC results, in the chiral analysis of mandarin essential oil, and to propose a route to overcome the problems that derive from overlapping, under single column conditions. In fact, as demonstrated, in a series of cases the 1D methodology generated incorrect results. Data obtained using enantio-GC can be adjusted considering the amounts of co-eluting compounds, calculated using conventional GC-FID analysis. Such an approach can be useful to attain reliable information even when a multidimensional system is not available.

However, the MDGC approach, remains the best option in this type of application, due to its versatility and enhanced separation-power. Finally, the instrumentation employed in this study is user-friendly, equipped with dedicated software for MDGC operation, and can be used by inexperienced operators in routine analysis.

Acknowledgements

The project was funded by the Italian Ministry for the University and Research (MUR) with a PNR 2005-2007 Project no. RBIP06SXMR "*Sviluppo di metodologie innovative per l'analisi di prodotti agroalimentari*". The authors gratefully acknowledge Shimadzu and Sigma–Aldrich/Supelco Corporations for the continuous support.

References

[1] G. Dugo, A. Di Giacomo, Citrus, The Genus Citrus, Taylor & Francis, London, England, 2002.
[2] C. Bicchi, A. D'Amato, V. Manzin, A. Galli, M. Galli, J. Chromatogr. A 742 (1) (1996) 161.
[3] G. Dugo, G. Lamonica, A. Cotroneo, I. Stagno D'Alcontres, A. Verzera, M.G. Donato, P. Dugo, G. Licandro, Perfumer Flavorist 17 (5) (1992) 57.
[4] B. Solomon Mitiku, M. Sawamura, S.M. Njoroge, H. Koaze, J. Essent. Oil Res. 14 (3) (2002) 196.
[5] M. Catalfamo, F. Gionfriddo, C. Mangiola, R. Manganaro, D. Castaldo, Ess. Deriv. Agr. 74 (2004) 57.
[6] C. Bicchi, A. D' Amato, P. Rubiolo, J. Chromatogr. A 843 (1999) 99.
[7] L. Mondello, M. Catalfamo, A.R. Proteggente, I. Bonaccorsi, G. Dugo, J. Agric. Food Chem. 46 (1998) 54.
[8] G. Dugo, I. Stagno d'Alcontres, A. Cotroneo, P. Dugo, J. Essent. Oil Res. 4 (1992) 589.
[9] G. Dugo, I. Stagno d'Alcontres, M.G. Donato, P. Dugo, J. Essent. Oil Res. 5 (1993) 21.
[10] R. Shellie, L. Mondello, G. Dugo, P.J. Marriott, Flavour Fragr. J. 19 (2004) 582.
[11] G. Schomburg, H. Husmann, E. Hübinger, W.A. König, J. High Resolut. Chromatogr. 7 (1984) 404.
[12] L. Mondello, A. Casilli, P.Q. Tranchida, M. Furukawa, K. Komori, K. Miseki, P. Dugo, G. Dugo, J. Chromatogr. A 1105 (2006) 11.
[13] L. Mondello, A. Verzera, P. Previti, F. Crispo, G. Dugo, J. Agric. Food Chem. 46 (1998) 4275.
[14] L. Mondello, A. Casilli, P.Q. Tranchida, D. Sciarrone, P. Dugo, G. Dugo, LC-GC Europe 21 (3) (2008) 130.
[15] P.J. Marriott, R. Shellie, C. Cornwell, J. Chromatogr. A 936 (2001) 1.