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Characterisation of essential oil plants from Turkey by IR and Raman spectroscopy

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Abstract

The essential oils obtained from various plant species (genera: *Origanum*, *Satureja*, *Salvia*, *Sideritis*, *Thymus*, *Calamintha*, *Lavandula*, *Ziziphora* and *Thymbra*) collected in Turkey were studied by two complementary methods, ATR/FT-IR and NIR-FT-Raman spectroscopy. The vibrational spectra of both techniques obtained from the hydro-distilled essential oils of the air-dried plant material present characteristic key bands of the individual main volatile components (e.g. carvacrol, thymol, *p*-cymene, γ-terpinene, camphor, 1,8-cineole, α- and β-pinene). Applying principal component analysis (PCA) to these spectral data, a clear discrimination of the different species can be frequently achieved. Hierarchical cluster analysis provides a fast, easy and reliable approach for chemotaxonomy characterisation. Both vibrational techniques described in this study have the potential to replace existing standard methods used for quality control purposes and continuous evaluation of distillation processes.

Keywords: Vibrational spectroscopy; Essential oils; Quality control; PCA

1. Introduction

The genus *Origanum* is represented in Turkey by 22 species, 21 being endemic to this country. Herbal parts of *Origanum* species, known as ''kekik'' in Turkey, are used for production of tea, condiments, essential oils as well as aromatic water (kekik suyu) [1,2]. The main interest is focused on the species *O. onites* (Turkish oregano), but also the other *Origanum* species such as *O. majorana* (white oregano), *O. vulgare* subsp. Hirtum, *O. minutiflorum* (Sütçüler kekigi), *O. syriacum* (*cyriacum*) var. Bevanii (Israeli oregano) are collected from wild populations for commercial use. Main components of all mentioned *Origanum* species are carvacrol, thymol, *p*-cymene and γ-terpinene, relating to the fact that all four terpenes are closely connected by biogenetical processes [3]. Carvacrol-rich essential oils are of special commercial interest as ingredients in animal feed and for the preservation of food, because of their high potency as antibacterials and antifungal agents [4–7].

Essential oils of *Thymbra spicata* have wide industrial applications for the flavouring of foods, liqueur production, perfumery and antiseptic as well as antimicrobial agents [7,8]. The chemical composition of the hydro-distilled oil is very similar to the oil obtained from *O. vulgare*, presenting also very high amounts of carvacrol and other monoterpenes such as α-pinene, myrcene, *p*-cymene and α-terpinene in lower percentages [6,9].

Thymus (Labiatae family) is a polymorphic genus comprising 60 taxa of which 39 species are growing in Turkey [10]. *Thymus zygoides*, also known as ''kekik'', contains thymol as major constituent [11]. The essential oil of *Coridothymus capitatus*, commercially known as

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''Spanish oregano oil'' is characterised by comparatively high carvacrol content [12], whereas thymol is the predominant component in *C. capitatus* essential oils [13].

Ziziphora (Labiatae family) is represented in Turkey by 6 taxa belonging to five species. It was found that *Z. persica* contains mainly thymol in the volatile fraction, whereas the essential oils of *Z. taurica* and *Z. clinopodioides* show comparatively high levels of pulegone [10].

Species belonging to the genus *Lavandula* (Labiatae family) are perennial herbaceous plants growing in some regions of Turkey [8]. *Lavandula stoechas* is an aromatic plant known as ''lavanta çiçeği'', ''karabaş lavanta çiçeği'', ''gargan'' and ''keşiş otu'' in Turkey. The herbs and their derivatives such as essential oils are commonly used in cosmetic and perfumery industries. Furthermore, infusion of the aerial parts of a number of *Lavandula* species are applied as diuretic, antiseptic, carminative, antipain as well as wound healing agents in folk medicine. The chemical compositions of essential oils obtained from various *Lavandula* species have been extensively studied [14–18].

Most *Salvia* species (69%) containing essential oils in the concentration range between 0.1 and 1.0% are offered in the market as herbal teas. *Satureja* (Labiatae family) species are well-known aromatic plants, which are used for production of essential oils as well as aromatic water in the mountain regions of the Mediterranean parts in Turkey. Carvacrol and/or thymol were detected as main components in all taxa of *Satureja* growing in Turkey [9].

The genus *Sideritis* is represented by 46 species, and altogether 53 taxa, 39 taxa being endemic for Turkey. *Sideritis*, a member of the Labiatae family, is widely distributed in subtropical and moderate regions [19,20]. *Sideritis* species are a group of plants known as ''mountain tea'' in Anatolia. Some species are used as tea as well as flavouring agents and for various medicinal purposes in several regions. Infusion of aerial parts of a number of *Sideritis* species are used as tonics, carminatives, stomachic, antispasmodics, diuretics and digestives, and taken for cough [21].

Analytical studies performed on *Sideritis* species show that main essential oil components are β-copaene, α-pinene, δ-cadinene, β-pinene, β-caryophyllene and limonene [22–24]. Contrary to that, the plants of *Sideritis raeseri* ssp. *raeseri* growing wild in Greece contain camphor and 1,8-cineole as main constituents of the essential oil [25], whereas the oil of *Sideritis dichotoma* from Turkey presents comparatively high amounts of α- and β-pinene [26]. The essential oil obtained from aerial parts of *Sideritis hispida* collected in Turkey (Kayseri location) consisted mainly of β-caryophyllene, carvacrol, caryophyllene oxide and linalool [27]. Also, in the essential oil of *Sideritis scardica* Griseb. subsp. *scardica*, mainly α- and β-pinene as well as carvacrol have been detected [23]. Contrary to that, the essential oils of *S. cladestina* and *S. sipylea* contain mainly α- and β-pinene, myrcene and limonene [28].

In this work, we apply two complementary techniques, NIR-FT-Raman and ATR-IR spectroscopy to investigate essential oils obtained from various plants collected in Turkey. These techniques are used with the aim to distinguish the main oil components of the studied plants. Additionally, the hierarchical cluster analysis is applied to establish a model for the fast essential oil classification and selection of those plants, which meet the individual demands in an optimal way.

2. Materials and methods

The essential oils analysed in this study were isolated from the following plant species: *Calamintha nepeta* L., *Lavandula stoechas* L., *T. zygoides* Griseb. var. Lycaonicus (Celak) Ronniger, *Z. clinopodioides* Lam., *Satureja cilicica* P.H. Davis, *Origanum spyleum* L., *Salvia officinalis* L., *Rosmarinus officinalis* L., *O. onites* L. *O. vulgare* ssp. *hirtum*, *O. minutiflorum* Schwarz et Davis, *O. majorana* L., *O. syriacum* L. var. Bevanii, *C. capitatus* L., *T. spicata* L., *Satureja cuneifolia* Teu., *Satureja thymbra* L., *Salvia tomentosa* Miller, *Salvia fructicosa* Miller, *Sideritis libanotica* Labill. ssp. *linearis* (Bentham) Bornm. Most herbs were collected from June to August at altitudes of 250–1900 m.

The air-dried plant material was hydro-distilled according to the standard method described in the European Pharmacopoeia [29].

Pure standard substances (carvacrol, thymol, *p*-cymene, γ-terpinene, 1,8-cineole, camphor, β-caryophyllene, α-pinene, β-pinene, pulegone) were purchased from Roth (Karlsruhe, Germany) and Sigma–Aldrich (Taufkirchen, Germany). The other analytes were tentatively identified by using the NBS75K and Wiley 138 library databases of the GC–MS system described below.

2.1. Reference analysis

The hydro-distilled essential oils were analysed by gas chromatography/flame ionisation detector (GC/FID) using a Hewlett-Packard gas chromatograph 6890, fitted with an HP-5 column (50 m × 0.32 mm i.d.; film thickness 0.52 μm). Detector and injector temperature were set at 280 and 250 °C, respectively. The following oven temperature was used: beginning at 60 °C and then 4 °C/min up to 220 °C. Carrier gas was nitrogen with a constant flow rate of 1 mL/min (split 1:40). The percentage composition was computed from the GC peak areas according to the 100% method without using any correction factors.

Identification of the detected compounds was based on their relative retention time in comparison to the pure standard substances as well as on MS reference data. GC–MS analyses of the isolated essential oils were performed using an Hewlett-Packard MSD 5972/HP 5890 series plus 2, equipped with a 15 m × 0.25 mm i.d.; 0.25 μm Permabond OV-1-DF column. The ionisation energy was set at 70 eV.

2.2. ATR-IR measurements

The mid IR spectra were recorded in the range between 650 and 4000 cm^{-1} with a portable diamond ATR/FT-IR spectrometer "TravelIR" (Resultec Analytical Equipment, Oberkirchberg, Germany) in a single reflection configuration. The instrument (weight: 12 kg, easily operated by a 12 V car battery) was fitted with a Michelson interferometer with fixed and moving corner-cube mirrors and a DLATGS detector. ca. 5–10 μL of the essential oil were placed on the surface of the diamond-ZnSe ATR crystal (diameter 0.5 mm^2).

2.3. Raman measurements

The Raman spectra were recorded on a Bruker Spectrometer RFS 100 with a diode-pumped Nd:YAG laser, emitting at 1064 nm and a Germanium detector cooled with liquid nitrogen. The instrument was equipped with a *xy* stage, a mirror objective and a prism slide for redirection of the laser beam. Compared with the standard vertical sampling arrangement, the samples were mounted horizontally; approximately 3–5 μL of the essential oil sample was placed in the middle of a metal ring. The spectra were accumulated from 128 scans measured with a resolution of 4 cm^{-1} in the range of 1000–4000 cm^{-1} with a laser power of 150 mW supplied by a nonfocused laser beam.

2.4. Chemometric algorithms

Hierarchical cluster analysis was performed for NIR-FT-Raman spectra obtained from essential oils applying the OPUS programme (Bruker, Germany). All spectra were not baseline corrected. Individual spectral distances were calculated with the standard algorithm after applying vector normalisation. The cluster analysis was performed for the wavenumber range from 500 to 1800 cm^{-1}.

3. Results and discussion

In Table 1 the amounts of the main volatile components (amount > 5.0% of the individual essential oil) are presented. It can be seen there that essential oils obtained from species related to the genera *Origanum*, *Satureja*, *Thymbra*, *Coridothymus* and *Thymus* contain mainly carvacrol, thymol, *p*-cymene and γ-terpinene. According to the literature [30], *R. officinalis*, *L. stoechas* and the different *Salvia* species consist predominantly of camphor and 1,8-cineole. Finally, the essential oils of *C. nepeta* and *Z. clinopodioides* are characterised by comparatively high percentages of pulegone, menthone and menthol. The major volatile components of *S. libanotica* are various terpene hydrocarbons such as α- and β-pinene as well as β-caryophyllene representing together more than 80% of the total essential oil content.

3.1. Essential oil composition investigated by cluster analysis

The chemical composition of individual essential oils is usually determined by gas chromatography methods, but during the last ten years also several vibrational spectroscopy methods using Raman [31–38], infrared [33–36,39,44], and near infrared spectroscopy [33,34,39–43] have been described in this context. Based on the spectral data sets, cluster analysis can be established presenting the specific differences of the individual chemotypes [33,36,39] as well as quantitative predictions of individual essential oil substances are generally possible [32,34–36,39–44].

In this study, 25 samples of laboratory-distilled essential oil plants collected in Turkey were measured by two complementary methods, FT-Raman and ATR-IR spectroscopy. As demonstrated in Fig. 1, cluster analysis established on the basis of all FT-Raman spectra obtained in this study shows a remarkable variation relating to the different genetic background of the individual plant species. Furthermore, it was found that the GC composition of the investigated essential oils correlates very well with the related spectral results. It can be also seen in Fig. 1 that the whole spectral set splits into three clusters, where one of them is separating further into three subclusters. These clusters can be identified based on reference GC data indicating the main components of the essential oils: carvacrol, thymol, 1,8-cineole/camphor, β-pinene, β-caryophyllene and pulegone. The essential oil of the carvacrol type shows high percentages of carvacrol (41–87%) and contains only small amounts of thymol (0–9%). In contrast to that, the composition of the thymol type is characterised by a comparatively high level of thymol (10–42%) and medium or not detectable amounts of carvacrol (0–39%). As can be seen in Fig. 1, the carvacrol and thymol clusters are close together and present both a significant spectral distance to the third essential oil group. The composition of essential oils belonging to the third cluster is quite

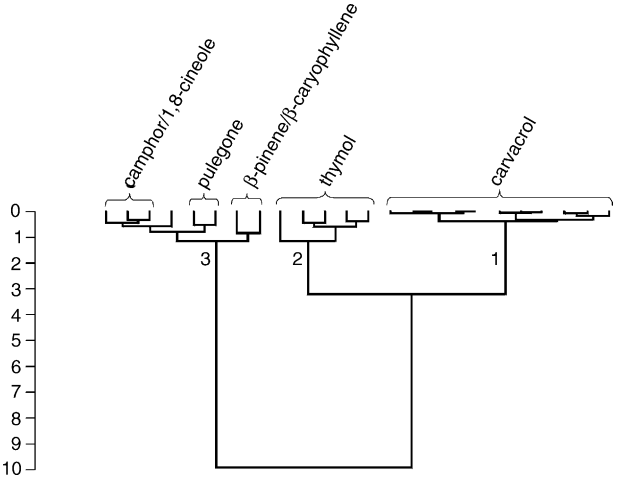

Fig. 1. Cluster analysis (Ward's algorithm) based on the NIR-FT-Raman spectra of essential oil plants collected in Turkey.

Table 1
Typical gas chromatographic composition of the individual investigated essential oil plants collected in Turkey (A) cluster 1 and 2 and (B) cluster 3 (according to the classification presented in Fig. 1)

Species	Main volatile components (%)			
	Carvacrol	Thymol	*p*-Cymene	γ-Terpinene
A				
Thymbra spicata	62.3		9.4	17.4
Thymbra spicata	71.7		8.5	9.8
Satureja thymbra	41.6		7.7	34.0
Satureja cuneifolia	72.3		6.4	5.8
Origanum minutiflorum	82.9			
Origanum syriacum	60.5		7.4	
Origanum majorana	86.7			
Origanum onites	69.0	5.7	5.1	
Coridothymus capitatus	60.4	8.8	6.7	9.2
Origanum spyleum	35.4	41.0	11.0	5.3
Origanum vulgare	39.1	22.2	9.3	13.5
Satureja cilicica	18.9	22.8	19.5	13.4
Satureja cuneifolia	10.1	10.1	19.3	10.2
Thymus zygoides		42.6	16.8	

Species	Main volatile components (%)															
	1,8-Cineole	Camphor	β-Caryophyllene	β-Pinene	α-Pinene	Verbenone	α-Thujone	β-Thujone	Menthol	Menthone	Isomenthone	Pulegone	Piperitone	Fenchone	Bornyl acetate	Borneol
B																
Lavandula stoechas		50.9												24.0		
Rosmarinus officinalis	7.6	13.12	5.6			7.6									7.6	12.3
Salvia fructicosa	47.2	12.5						6.6								
Salvia tomentosa	23.0	6.0			27.9											
Salvia officinalis	14.1		9.0	9.2			21.5	5.8								
Sideritis libanotica			5.9	50.6	24.5											
Calamintha nepeta												76.5	6.1			
Ziziphora clinopodioides	7.4								8.9	17.1	8.0	33.0				

complex and only the presence of some characteristic components allow to distinguish three subclusters, namely: 1,8-cineole/camphor, β-pinene/β-caryophyllene and pulegone.

3.2. Vibrational analysis of the pure terpenoids

Detailed spectral analysis of the investigated oils is based on their vibrational spectra. First of all, FT-Raman and ATR-IR spectra of terpenoid compounds, which are present in the investigated essential oils in higher amount, were recorded (see Figs. 2 and 3, respectively). All of them show some characteristic key bands, which can be used for discrimination between carvacrol (A), thymol (B), *p*-cymene (C), γ-terpinene (D), 1,8-cineole (E), camphor (F), β-pinene (G), β-caryophyllene (H) and pulegone (I). Isomeric compounds like thymol and carvacrol show significant differences in FT-Raman as well as in ATR-IR spectra. In FT-Raman spectra ring vibration of thymol is seen at 740 cm^{-1}, while for carvacrol this corresponding signal appears at 760 cm^{-1} (Fig. 2A and B). In the ATR-IR spectrum the most intense bands are seen at 804 cm^{-1} (thymol) and 811 cm^{-1} (carvacrol) (Fig. 3A and B). These bands can be attributed to out-of-plane CH wagging vibrations, which are the most significant signals used in distinguishing different types of aromatic ring substitution [45]. These bands are usually weak in Raman, but very intensive in IR. Likewise key bands

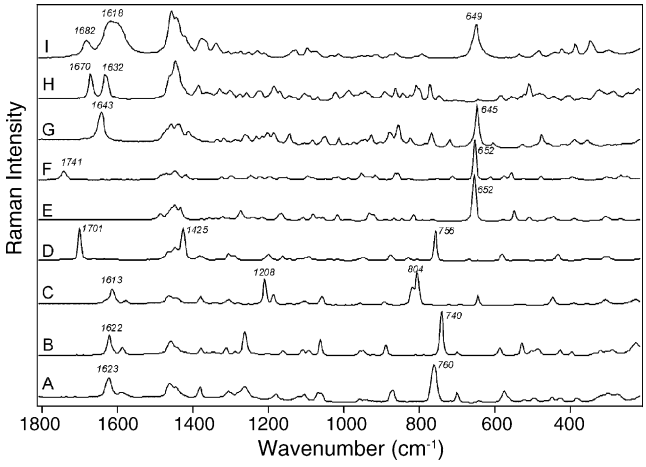

Fig. 2. NIR-FT-Raman spectra of carvacrol (A), thymol (B), *p*-cymene (C), γ-terpinene (D), 1,8-cineole (E), camphor (F), β-pinene (G), β-caryophyllene (H) and pulegone (I).

are also seen for the other terpenes; in the FT-Raman spectrum characteristic ring deformation vibrations appear at 804 cm^{-1} for α-terpinene, at 756 cm^{-1} for γ-terpinene, at 652 cm^{-1} for 1,8-cineole and camphor and at 649 cm^{-1} for pulegone (see Fig. 2). Only β-caryophyllene, which does not possess a 6-membered ring in the molecular structure, shows no intensive Raman bands in the range between 600 and 800 cm^{-1}. Most of the discussed compounds show also

Table 2
Assignment for the most characteristic Raman and IR bands of the essential oil compounds discussed in the paper

Compounds	FT-Raman (cm^{-1})	Assignment	ATR-IR (cm^{-1})	Assignment
Carvacrol	1623	ν (C=C)	811	ω (C–H)
	760	δ (ring)		
Thymol	740	δ (ring)	804	ω (C–H)
p-Cymene	1613	ν (ring)	1515	
	1208	δ (ring)	813	ω (C–H)
	804	δ (ring)		
γ-Terpinene	1701	ν (nonconjugated C=C)	947	ω (CH_2)
	756	δ (ring)	781	ω (C–H)
1,8-Cineole	652	δ (ring)	1374	δ_{sym} (CH_3(CO))
			1214	ν_{as} (C–O–C)
			1079	ν_s (C–O–C)
			984	ω (CH_2)
			843	
Camphor	1741	ν (C=O)	1739	ν (C=O)
	652	δ (ring)		
α-Pinene	1659	ν (C=C)	1658	ν (C=C)
	666	δ (ring)	886	ω (C–H)
			787	
β-Pinene	1643	ν (C=C)	1640	ν (C=C)
	645	δ (ring)	873	
β-Caryophyllene	1670	ν (C=CH)	885	ω (CH_2)
	1632	ν (C=CH_2)	875	
Pulegone	1682	ν (C=O)	1681	ν (C=O)
	1618	ν (C=C)	1285	
	647	δ (ring)	1209	

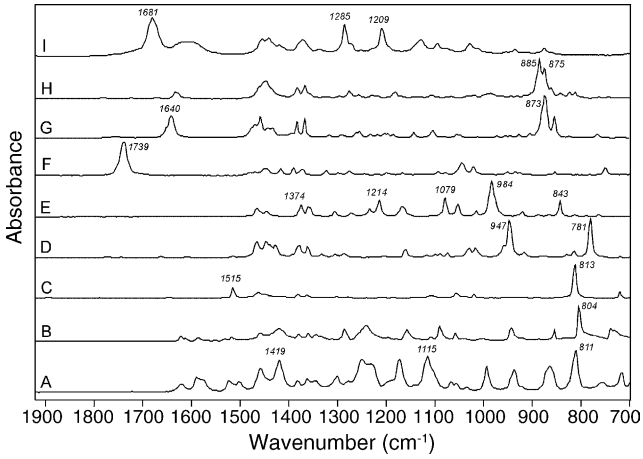

Fig. 3. ATR-IR spectra of carvacrol (A), thymol (B), *p*-cymene (C), γ-terpinene (D), 1,8-cineole (E), camphor (F), β-pinene (G), β-caryophyllene (H) and pulegone (I).

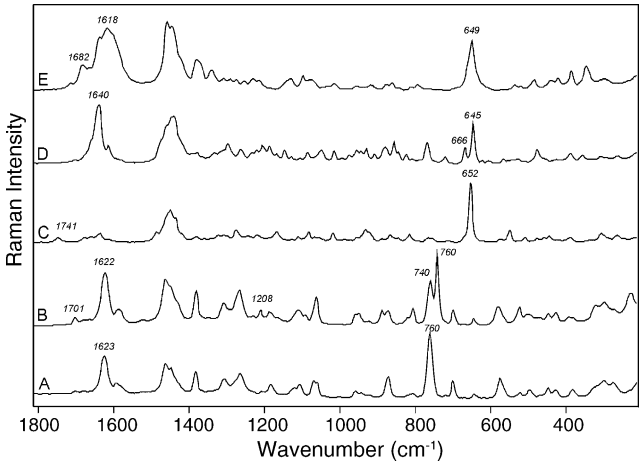

Fig. 4. NIR-FT-Raman spectra of essential oils obtained from plants collected in Turkey: (A) *Origanum majorana* (carvacrol type), (B) *Origanum spyleum* (thymol type), (C) *Salvia fructicosa* (β-pinene/β-caryophyllene type), (D) *Sideritis libanotica* (camphor/1,8-cineole type) and (E) *Calamintha nepeta* (pulegone type).

characteristic signals in the ATR-IR spectrum due to wagging vibrations of CH and CH_2 groups e.g. at 813 cm^{-1} for *p*-cymene, at 947 and 781 cm^{-1} for γ-terpinene, at 984 cm^{-1} for 1,8-cineole, at 873 cm^{-1} for β-pinene and at 885 and 875 cm^{-1} for β-caryophyllene. Camphor and pulegone cause only weak IR bands in this range, but reveal intensive bands due to C=O stretching vibrations at 1739 and 1681 cm^{-1}, respectively. Other characteristic bands identified for the main pure essential oil substances are presented in Figs. 2 and 3 and are assigned in Table 2. The data collected there are in agreement with some previous publications reporting interpretation of vibrational spectra of essential oils isolated from *Lamiaceae* species [31–34,36]. For all these components listed in Table 2, it is possible to choose indicator signals in the FT-Raman as well in the ATR-IR spectra, which can be therefore used for their identification.

3.3. Spectral identification of the individual main essential oil substances

The analysed essential oil samples corresponding to the different types were measured by FT-Raman and ATR-IR spectroscopy (see Figs. 4 and 5, respectively). Based on GC data, main components of these essential oils are listed in Table 1. A comparison of the spectral features between the essential oils (Figs. 4 and 5) and the standard substances (Figs. 2 and 3) clearly shows that different main substances occurring in the individual essential oils dominate the resulting vibrational spectra. Consequently, the spectra of the individual essential oils present very similar profiles as their main components and all key bands listed in Table 2 were found to be characteristic for the essential oil types. Those compounds, which occur in essential oils only in low percentages, do not influence the FT-Raman or ATR-IR spectrum significantly. As can be seen in Fig. 4A, the spectrum of *O. majorana* oil is dominated by bands at 760 and 1623 cm^{-1} attributed to its main component, carvacrol (87%). The same conclusion can be drawn from its ATR-IR spectrum (Fig. 5A), where strong signals at 811, 864, 1115, 1173, 1250, 1419 cm^{-1} are seen. The Raman spectrum of *O. spyleum* oil (Fig. 4B), which shows intensive bands at 740 and 760 cm^{-1}, reflects the complex composition of this essential oil: 41% of thymol and 35% of carvacrol, respectively. The corresponding ATR-IR spectrum is less resolved (Fig. 5B) and demonstrates a strong signal at 808 cm^{-1}, which arises from overlapping of thymol and carvacrol bands (804 and 811 cm^{-1}, respectively). The presence of the intensive band at 652 cm^{-1} in the Raman spectrum of *S. fructicosa* essential oil (Fig. 4C) allows to indicate 1,8-cineole and camphor as its main components. In

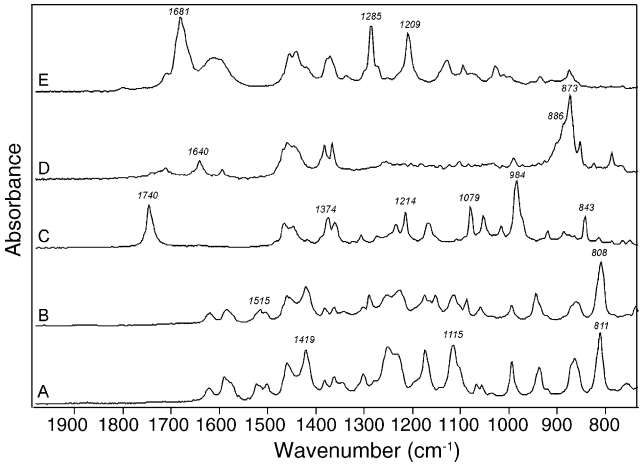

Fig. 5. ATR-IR spectra of essential oils obtained from plants collected in Turkey: (A) *Origanum majorana* (carvacrol type), (B) *Origanum spyleum* (thymol type), (C) *Salvia fructicosa* (β-pinene/β-caryophyllene type), (D) *Sideritis libanotica* (camphor/1,8-cineole type) and (E) *Calamintha nepeta* (pulegone type).

the ATR-IR spectrum (Fig. 5C) these components can be distinguished by the following key bands: 1374, 1214, 1079, 984 and 843 cm^{-1} (1,8-cineole) and 1740 cm^{-1} (camphor). The composition of *S. libanotica* essential oil is reflected in its spectrum presented in Fig. 4D, where mainly bands at 645 and 666 cm^{-1} can be observed. The first one is attributed to β-pinene, present in the oil in amounts of 51% and the second signal is due to α-pinene (25%) (for band assignment, see Table 2). The ATR-IR spectrum (Fig. 5D) is less resolved and demonstrates a broad signal in the range between 850 and 900 cm^{-1}; however, the obtained data allow to draw a similar conclusion as from the corresponding Raman spectrum. Vibrational spectra of *C. nepeta* essential oil (Figs. 4E and 5E) are dominated by bands due to its main component pulegone (77%), which can be seen at 649, 1618, 1682 cm^{-1} (Raman) and 1209, 1285, 1681 cm^{-1} (IR).

4. Conclusions

In this paper some applications of FT-Raman and ATR-IR techniques for the characterisation of essential oils obtained from various plants collected in Turkey are presented. It has been found that in particular, hierarchical cluster analysis can be successfully applied for fast essential oil classification and selection of requested individual essential oil types. More detailed analysis of the essential oil composition can be based on the characteristic key bands of the individual volatile substances observed in their vibrational spectra.

The special advantage of NIR-FT-Raman spectroscopy is the possibility of applying fibre-optics for remote measurements in a reaction vessel or a distillation apparatus to control the individual refining steps. The mobile ATR-IR instrument presented in this study is especially useful for rapid monitoring of wild populations with regard to the individual essential oil profiles.

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References

[1] S. Kokkini, in: S. Padulosi (Ed.), Taxonomy, Diversity and Distribution of *Origanum* Species, Oregano, IPGRI, Rome, 1997, pp. 2–12.
[2] T. Baytop, K.H.C. Başer, On essential oils and aromatic waters used as medicine in Istanbul between 17th and 19th centuries, in: K.H.C. Baser (Ed.), Proceedings of the 13th International Congress of Flavours, Fragrances and Essential Oils, vol. 2, Istanbul, Turkey, 15–19 October, AREP Publishers, 1995, pp. 99–107.
[3] A.J. Poulose, R. Croteau, Arch. Biochem. Biophys. 187 (1978) 307.
[4] DeLuca, D.L., Sparks, W.S., Ronzio, R.A., DeLuca, D.R., 1999. Oregano for the treatment of internal parasites and protozoa. United States Patent No. 5,955,086 (21 September).
[5] Nitsas, F.A., 2000. Pharmaceutical compositions containing herbal-based active ingredients, methods for preparing same and uses of same for medical and veterinary purposes. United States Patent No. 6,106,838 (22 August).
[6] H. Baydar, O. Sagdic, G. Özkan, T. Karadoğan, Food Control 15 (2004) 169.
[7] G. Özkan, O. Sagdic, M. Özcan, Food Sci. Tech. Int. 9 (2003) 85.
[8] H.B. Heath, M.B.E. Pharm, Flavor Technology: Profiles, Products, Applications, AVI Publishing Company, Westport, CT, USA, 1978.
[9] B. Simandi, M. Oszagyan, E. Lemberkovics, A. Kery, J. Kaszags, F. Thyrion, T. Matyas, Food Res. Int. 31 (1998) 723.
[10] K.H.C. Başer, Pure Appl. Chem. 74 (2002) 527.
[11] K.H.C. Başer, N. Kirimer, N. Ermin, M. Kürkçüoğlu, J. Essent. Oil Res. 8 (1996) 615.
[12] Z. Fleisher, A. Fleisher, J. Essent. Oil Res. 14 (2002) 105.
[13] U. Ravid, E. Putievsky, Planta Medica 49 (1983) 248.
[14] Koca, F., Alan, S., 2002. Türkiye’de yetişen *Lavandula stoechas* L. ssp. stoechas in morfolojik ve anatomik özellikleri, 14. Bitkisel İlaç Hammaddeleri Toplantisi, 29–31 Mayis. Eskişehir, Turkey.
[15] N. Tanker, E. Sarer, V. Basaran, J. Fac. Pharm. 7 (1977) 61.
[16] S. Zrira, B. Benjilali, J. Essent. Oil Res. 15 (2003) 68.
[17] G. Valentini, N. Arnold, B. Bellomaria, Plant Med. Phytother. 224 (1993) 289.
[18] M. Skouda, C. Agabeydi, E. Kokkalou, Biochem. Susut. Ecol. 24 (1996) 255.
[19] P.H. Davis, Flora of Turkey and East Aegean Islands, vol. 7, University Press, Edinburgh, 1982, pp. 178–199.
[20] N. Kirimer, N. Tabanca, T. Özek, K.H.C. Başer, G. Tümen, H. Duman, J. Essent. Oil Res. 15 (2003) 221.
[21] E. Yeşilada, N. Ezer, Int. J. Crude Drug Res. 27 (1989) 38.
[22] T. Azet, S. Conigueral, C. Ibanez, R. Vila, Herba Hungarica 28 (1989) 59.
[23] K.H.C. Başer, N. Kirimer, G. Tümen, J. Essent. Oil Res. 9 (1997) 205.
[24] M. Özcan, J.C. Chalchat, A. Akgül, Food Chem. 75 (2001) 459.
[25] E.M. Galati, M.P. Germano, A. Rossitto, O. Tzakou, H. Skaltsa, V. Roussis, J. Essent. Oil Res. 8 (1996) 303.
[26] N. Kirimer, K.H.C. Başer, G. Tümen, E. Sezik, J. Essent. Oil Res. 4 (1992) 641.
[27] N. Kirimer, K.H.C. Başer, T. Özek, G. Tümen, J. Essent. Oil Res. 6 (1994) 435.
[28] V. Gergis, N. Argyriadou, C. Poulos, J. Sci. Food Agric. 47 (1989) 501.
[29] European Pharmacopoeia, 1983. Part 1. Maisonneuve SA, Sainte Ruffine, p. V.4.5.8.
[30] Schulz, H., 2004. Near-infrared spectroscopy in agriculture, Application in analysis of coffee, tea, cocoa, tobacco, spices, medicinal and aromatic plants, and related products, in: Roberts, C., Workman, J., Reeves, J. (Eds.). American Society of Agronomy/Crop Science of America/Soil Science Society of America, Madison, USA, Agronomy Monograph No. 44, pp. 345–376.
[31] D.J. Daferera, A.P. Tarantilis, M.G. Polissiou, J. Agric. Food. Chem. 50 (2002) 5503.
[32] N.G. Siatis, A.C. Kimbaris, C.S. Pappas, P.A. Tarantilis, D.J. Dafarera, M.G. Polissiou, J. Agric. Food. Chem. 53 (2005) 202.
[33] H. Schulz, M. Baranska, H.-H. Belz, P. Rösch, M.A. Strehle, J. Popp, Vib. Spectr. 35 (2004) 81.
[34] H. Schulz, B. Schrader, R. Quilitzsch, S. Pfeffer, H. Krüger, J. Agric. Food. Chem. 51 (2003) 2475.

[35] H. Schulz, B. Schrader, R. Quilitzsch, B. Steuer, Appl. Spectrosc. 56 (2002) 117.
[36] M. Baranska, H. Schulz, H. Krüger, R. Quilitzsch, Anal. Bioanal. Chem. 381 (2005) 1241–1247.
[37] M. Baranska, H. Schulz, P. Rösch, M.A. Strehle, J. Popp, Analyst 129 (2004) 926.
[38] M.A. Strehle, P. Rösch, M. Baranska, H. Schulz, J. Popp, Biopolymers 77 (2005) 44.
[39] H. Schulz, R. Quilitzsch, H. Krüger, J. Mol. Struct. 661 (2003) 299.
[40] H. Schulz, H. Krüger, B. Steuer, F. Pank, Z. Arzn. Gew. Pfl. 4 (1999) 62.
[41] H. Schulz, H-H. Drews, H. Krüger, J. Essent. Oil Res. 11 (1999) 185.
[42] H. Schulz, R. Quilitzsch, H.-H. Drews, H. Krüger, Int. Agrophysics 14 (2000) 249.
[43] B. Steuer, H. Schulz, E. Läger, Food Chem. 72 (2001) 113.
[44] G. Lösing, M. Degener, G. Matheis, Dragoco Report 45 (1998) 180.
[45] D. Lin-Vien, N.B. Colthup, W.G. Fateley, J.G. Grasselli, The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules, Academic Press, Inc., San Diego, 1991.