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Essential oil counterfeit identification through middle infrared spectroscopy

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ABSTRACT

Infrared spectroscopy (FTIR) has been employed for a fast quality control of commercial essential oils from different plant species. 47 samples were obtained from Algerian and Spanish market and directly measured, without any previous treatment, by attenuated total reflectance Fourier transform Infrared spectroscopy (ATR-FTIR), in the wavenumber region between 4000 and 550 cm^{-1}. Pure essential oils were obtained by hydro- and steam-distillation extraction methods and their ATR spectra obtained. Results found evidenced the presence of solvents in some commercial formulations and permitted a rapid authentication of pure essential oils correctly extracted from those diluted. The proposed method offers a fast and environmentally friendly methodology which can be used as an alternative to the commonly employed chromatography methods to evidence the quality of commercial essential oils.

1. Introduction

Essential oils are natural, volatile, complex mixtures of compounds with strong odor. These oily liquids, are produced by different aromatic plant as secondary metabolites from their buds, flowers, leaves, stems, twigs, seeds, fruits, roots, wood or bark, and are stored in secretory cells [1]. Essential oils are obtained from aromatic plants mainly localized in temperate countries like Mediterranean, where these plants represent a major category, and also in tropical countries [2,3].

Essential oils are extracted by several methods including, expression, enfleurage, solvent extraction, supercritical carbon dioxide extraction, microwave or ultrasound [4] assisted treatments being hydro- and steam-distillation the most frequently used procedures. Essential oil compositional analysis is mainly achieved by gas chromatography [5].

Essential oils are unstable and fragile complex mixtures of volatile compounds. Monoterpenes represent more than 80% of essential oil composition, together with sesquiterpenes and oxygenated derivatives of these two chemical groups [4]. There are more than 60 compounds, at different concentrations, in an extracted oil with one, two or three major components at high concentration [2]. So major compounds of citrus essential oils are Limonene with (79%) in *C. limon* L. (lemon) [6], (93%) in *C. reticulate* L. (mandarin) and (97%) in *C. sinensis* L. (orange) [7]. Carvone (54%) and limonene (46%) are the major compounds of the *C. carvi* L. (caraway) seeds essential oil [8] and for *C. longa* L. (Turmeric) rhizomes essential oil, ar-turmerone (13%), α-turmerone (43%) and β-turmerone (16%) are the principal compounds [9]. Other components are present only at trace levels [5].

The chemical composition which determines the biological properties of essential oils, can be influenced by various factors mainly, the species, geographic location, the part of the plant collected and the system employed for oil extraction [10,11].

Essential oils have been largely used as food flavours and for their bactericide, fungicide and insecticide properties, and recently for therapeutics in human medicine; being reported, as an example, that *R. officinalis* (rosemary) and *M. piperita* (pepper mint) have a positive effect on the human memory [12].

The interest in essential oils and their compounds is increasing due to their high acceptance by consumers [13]. An estimated number of 3000 essential oils are known, 300 of which are commercially important especially for the pharmaceutical, agronomy, food, sanitary, cosmetic and perfume industries [2,5]. The market of essential oils is rapidly expanding and generates several billions of dollars every year, and unfortunately has resulted in adulteration for dishonest profits [14,15].

Different factors can cause an essential oil adulteration due to the use of diluted solutions of natural oils or the addition of cheaper synthetic material and cheap volatile compounds from other natural products. These adulteration methods can degrade the quality of the oil and provide deleterious effects on its consumers. So the authentication of essential oils is an important subject for consumer protection and also for the quality control of their production [15].

Several techniques have been used for the determination of adulteration of essential oils, including physical, chemical, chromatography and spectroscopy techniques [16]. The quality of the essential oil can be

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Table 1
Plant essential oils evaluated in this study together with their main components (in % w/w) as reported in the literature.

Family	Plant species	Common name	Main components	Ref.
Apiaceae	*Pimpinella anisum* L.	Anise	*trans* Anethole (88.49%), γ himachalene (3.13%)	[20]
			trans Anethole (81.33%), γ himachalene (12.32%)	[21]
	Apium graveolens L.	Celery	Limonene (63.90%), β selinene (16.40%)	[22]
			β Selinene (37.40%), phellandral (17.20%), limonene (16.00%)	[23]
	Foeniculum vulgare Mill.	Fennel	*trans* Anethole (59.970%, 63.23%), fenchone (21.42%, 25.04%), estragole (3.76%, 4.75%), limonene (2.68%, 2.99%).	[24]
			trans Anethole (81.60%, 79.0%), fenchone (8.70%, 10.90%), estragole (4.00%, 4.20%), limonene (3.50%, 3.2%).	[25]
			trans Anethole (72.86%), fenchone (12.93%), estragole (3.41%), limonene (6.37%).	[26]
	Carum carvi L.	Caraway	Carvone (76. 37%), limonene (19.52%)	[13]
			Carvone (77.35%), limonene (16.15%)	
			Carvone (61.58%), limonene (29.11%)	
			Carvone (53.60%), limonene (45.59%)	[8]
	Cuminum cyminum L.	Cumin	γ Terpinene (24.30%), cumin aldehyde (21.07%), *p* cymene (16.56%), β pinene (13.74%), safranal (12.95%)	[27]
			γ Terpinene (12.62%), cumin aldehyde (38.50%), *o* cymene (10.98%), β pinene (11.50%)	[28]
			γ Terpinene (16.30%), cumin aldehyde (32.80%), *o* cymene (9.74%), β pinene (10.30%)	
Asteraceae	*Artemisia herba-alba*	White wormwood	α and β Thujone (57.00%), camphre (24.00%)	[2]
			β Thujone (25.10%), α thujone (22.90%), 1,8 cineole (20.10%), camphre (10.50%)	[29]
			1,8 Cineole (25.80%), *p* cymene (15.50%), α pinene (11.30%)	[30]
			1,8 Cineole (41.10%), *p* cymene (12.70%), α pinene (8.20%)	
			1,8 Cineole (8.6%), *p* cymene (19.9%), α pinene (17.20%), myrcene (10.90%)	
	Matricaria chamomilla L.	Chamomile	Spathulenol (12.50%), (E) β farnesene (10.4%), α bisabolol oxide B (6.50%)	[31]
			Spathulenol (7.3.00%), (E) β farnesene (6.00%), α bisabolol oxide B (11.40%)	
			Spathulenol (6.70%), (E) β farnesene (6.00%), α bisabolol oxide B (20.00%), α bisabolol oxide A (11.90%)	
			α-Bisabolol oxide A (48.22%), α bisabolol oxide B (23.31%), α bisabolol (12.10%).	[32]
Geraniaceae	*Pelargonium graveolens*	Geranium	Citronellol (30.20%), citronellyl formate (9.30%), geraniol (7.60%), guai 6,9 diene (5.40%)	[33]
			β Citronellol (24.14%), citronellyl formate (11.75%), geraniol (16.45%), linalool (7.99%)	[34]
Cupressaceae	*Cupressus sempervirens*	Cypress	α Pinene (48.10%), δ 3 carene (24.40%)	[35]
			Sabinene (14.80), terpinen 4 ol (11.40), α pinene (9.90%), δ 3 carene (4.20%)	[36]
	Juniperus communis L.	Juniper	Sabinene (48.40%), limonene (20.00%), α pinene (16.50%)	[37]
			α Pinene (80.00%), sabinene (02.00%), limonene (1.00%)	
			α Pinene (34.00%), sabinene (22.00%), limonene (5.00%)	
			α Pinene (57.00%), limonene (12.00%), sabinene (3.00%)	
			Sabinene (39.00%), α pinene (20.00%), limonene (5.00%)	
			α Pinene (40.00%), sabinene (18.00%)	
Lamiaceae	*Lavandula angustifolia* Mill.	Lavender	1,8 Cineole (33.0%, 44.4%), camphor (23.10%, 25.10%), α bisabolol (14.10%, 6.50%)	[25]
			Linalool (25.31%), linalyl anthranilate (18.35%), lavandulyl acetate (11.14%)	[38]
	Mentha piperita	Piper mint	Menthol (26.53%), menthone (25.83%)	[39]
			Menthol (59%), menthone (19%)	[2]
	Mentha spicata L.	Spear mint	Carvone (65.40–46.70%), menthol (8.70–2.00%), menthone (6.90–1.50%), pulegone (7.90–1.40%)	[40]
Lamiaceae	*Mentha spicata* L.	Spear mint	Carvone (76.65%), limonene (9.57%)	[41]
Lamiaceae	*Melissa officinalis*	Melissa	Citronellal (31.10%), citronellol (18.3%), E citral (11.20%), β caryophyllene (12.00%)	[42]
			Citronellal (10.20%), Z citral (19.60%), β caryophyllene (13.20%)	
			Citronellal (14.40%), geraniol acetate (10.20%), caryophyllene oxide (11.00%)	[43]
			p Mentha-1, 2, 3 triol (13.10%), *p* menth 3 en 8 ol (8.80%), pulegone (8.80%)	[44]
	Rosmarinus officinalis	Rosemary	1,8 Cineole (55,90%), camphor (10,58%), α-pinene (9,38%)	[45]
			Camphor (52.12%), 1,8 cineole (9.65%), camphene (7.55%), α-pinene(6,05%)	[46]
			α Pinene (28.20%, 21.9%), verbenone (11.60%, 12.70%), camphor (7.90%, 9.90%), 1,8 cineole (7.40%, 9.40%)	[25]
	Salvia officinalis	Sage	1,8 Cineole (33.27%), β thujone (18.40%), α thujone (13.45%)	[47]
			α Thujone (20.10%), camphor (16%), 1,8 cineole (7.00%), β thujone (5.00%)	[48]
			β Thujone (16.40%), α thujone (15.80%), 1,8 cineole (2.70%)	
			Camphor (21.30%), α thujone (15.40%), 1,8 cineole (9.50%), β thujone (3.70%)	
			Camphor (23.80%, 37.30%), 1,8 cineole (13.70%, 17.90%)	[19]
	Thymus vulgaris	Thyme	Thymol (40.97%), *p* cymene (13.11%), γ terpinene (10.96%), carvacrol (8.35%)	[49]
			Thymol (47%), p cymene (34%)	[50]
			o Thymol (38.71%), furan, tetrahydro 3 methyl (12.19%), *p* cymene (2.77%)	[10]
Lauraceae	*Laurus nobilis* L.	Laurel	1,8 Cineole (38.76%), α-terpinyl acetate(13.35%), α pinene (10.17%), linalool (10.03%)	[51]
			1,8 Cineole (24.55%), linalool (17.67%), eugenyl methyl ether (12.40%)	[52]
			1,8 Cineole (34.62%), linalool (12.57%)	
			1,8 Cineole (38.86%), linalool (9.45%), isovaleraldehyde (10.47%)	
	Cinnamomum cassia	Cinnamum	*trans* Cinnamaldehyde (84.4%), cinnamyl acetate (2.50%)	[53]
			trans Cinnamaldehyde (79.6%), β caryophyllene (3.60%)	
			trans Cinnamaldehyde (30.36%), 3-methoxy-1,2-propanediol (29.30), *o*-methoxy-cinnamaldehyde (25.39%)	[54]
Myrtaceae	*Eucalyptus globulus*	Eucalyptus	1,8 Cineole (55.29%), spathulenol (7.44%), α-terpineol (5.46%)	[55]
			1, 8 Cineole (63.81%), α pinene (16.06%)	[56]
	Myrtus communis L.	Myrtle	Myrtenyl acetate (23.70–39.00%), 1, 8 cineole (12.7–19.6%), α pinene (10.10–11.60%), linalool (7.00–15.80%)	[57]
			1, 8 Cineole (29.60%), α pinene (24.71%), myrtenyl acetate (10.60%)	[3]
			1, 8 Cineole (21.90%), α pinene (50.90%), linalool (2.70%)	[58]
			1, 8 Cineole (13.30%), α pinene (33.60%), linalool (14.80%)	
	Syzygium aromaticum L.	Clove	Eugenol (81.60, 79.00%), eugenol acetate (6.40%), caryophyllene (5.10%, 24.80%)	[25]
			Eugenol (57.17%), eugenol acetate (5.93%), caryophyllene (29.94%)	[59]
			Eugenol (63.64%), eugenol acetate (4.61%), caryophyllene (23.20%)	
			Eugenol (54.97%), eugenol acetate (2.45%), caryophyllene (31.46%)	
Pinaceae	*Pinus halepensis*	Aleppo pine	z β Caryophyllene (24.40–25.90%), α pinene (10.90–13.70%), myrcene (20.20–24.10%), *p* cymene (10.50–11.90%), caryophyllene oxide (10.50–12.50%)	[60]
			z β Caryophyllene (15.60–16.70%), α pinene (6.70–8.50%), myrcene (16.70–17.10%), *p* cymene (13.70–14.60%)	