



Authenticity of essential oils

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ABSTRACT

Essential oils are natural materials widely used in many fields all over the world and have become an integral part of everyday life. There is increasing demand for essential oils, which has resulted in cases of adulteration. Authentication is thus a matter of critical importance for both consumers and chemical companies. This comprehensive overview covers known adulterations in essential oils, and some analytical methodologies adopted for their detection. We first list recommended tests, and then we explain and discuss common analytical techniques, such as chiral gas chromatography, isotope-ratio mass spectrometry, and nuclear magnetic resonance spectroscopy. We also present (high-performance) thin-layer chromatography, vibrational spectroscopy, coupled and multidimensional chromatography, high-performance liquid chromatography, and combination with chemometrics-metabolomics. This review provides a critical overview of existing techniques.

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Abbreviations: AFNOR, Association Française de Normalisation; AED, Atomic emission detector; ANRT, Association Nationale de la Recherche et de la Technologie; BS, British Standard; DSC, Differential scanning calorimetry; EFSA, European Food Safety Authority; EO, Essential oil; FID, Flame-ionization detector; FTIR, Fourier-transform infrared spectroscopy; GC, Gas chromatography; HPTLC, High-performance thin-layer chromatography; IFRA, International Fragrance Association; IR, Infrared; IRMS, Isotope-ratio mass spectrometry; ISO, International Standard Organization; LC, Liquid chromatography; MDGC, Multidimensional gas chromatography; MS, Mass spectrometry; NIR, Near-infrared; NMR, Nuclear magnetic resonance; Ph. Eur, European Pharmacopoeia; PS, Photoacoustic spectroscopy; SFE, Supercritical fluid extraction; SNIF, Site-specific natural isotopic fractionation; TLC, Thin-layer chromatography; TOF, Time of flight; USP, United States Pharmacopoeia.

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1. Introduction

Essential oils have been widely used all over the world and their use is constantly increasing because of the strong demand for pure natural ingredients in many fields. Thus, large quantities of essential oil are produced worldwide to fuel the industries of flavors and fragrances, and cosmetics, and the health industry with aromatherapy and phytomedicine [1,2]. Some essential oils are produced on a very large scale (e.g., in 2008, production of orange oils was ~51,000 tons, corn mint oils ~32,000 tons, and lemon oils ~9200 tons). Essential oils of citrus, which included a great number of fruits from genus *Citrus*, are the most popular natural essential oils and account for the largest proportion of commercial natural flavors and fragrances [3]. Some others are produced on a much smaller scale due to their rarity, but are traded at very high prices [e.g., agar wood oil (6000–11,000 €/kg), iris (6200–100,000 €/kg depending on the concentration of irones), or rose oil (6000–10,000 €/kg)]. These prices vary and may be related to the scarcity of the raw material, harvesting issues, climate dependence, or extraction yield. Essential oil industries' cumulative sales represented several billions US\$ in 2008 [2,4].

The use of natural extracts is seen as a strong marketing advantage in the manufacture of many goods, but the prices for natural extracts are often much higher than those of synthetic materials, so there are many cases of adulteration [5]. Authenticity can be defined as free from adulteration in the sense of absence of foreign bodies or extraneous matter, but it also suggests free from impurities in the raw material itself [6]. Thus, authentication is an important subject for consumers. From the regulatory point of view, quality standards have been established through the requirement for quality labels that specify the chemical composition of each essential oil. From an economic point of view, authentication is of critical importance to avoid unfair competition that can destabilize the market and disrupt local and even national economies of producing countries [7].

This comprehensive overview covers analytical techniques that could be used in detecting known adulterants. It is known that the chemical constituents of essential oils may vary depending on harvest season, habitat, drying processes, extraction and isolation techniques used and many other factors. Thus, it is necessary to determine a profile of the constituents of essential oils. Several regulations take into account the variability in chemical composition. In this way, authenticity is controlled using the quantitative values in the monographs. In general, few compounds or markers in essential oils have been used to evaluate their quality and their authenticity. Out of the scope of this review are cases of non-compliance of essential oils caused by degradation. We consider different analytical methods, including physical, chemical, chromatographic, spectroscopic and thermal techniques. We present an overview on essential oils and their different known problems of authentication and adulteration, followed by the recommended analytical techniques for each case.

2. Overview on essential oils

2.1. Definition and composition

According to the “Association Française de Normalisation” (AFNOR) and to the European Pharmacopoeia (Ph. Eur.), an essential oil is

clearly defined as a manufactured product from pure, identified raw materials of plant origin, obtained by hydrodistillation and steam distillation, mechanical processes (e.g., EO from *Citrus*), or by “dry” distillation for some woods (Table 1).

The essential oil is then separated from the aqueous phase by physical processes [9,10]. Essential oils can be terpene-less, sesquiterpene-less, corrected, or deprived of a substance by partial removal, such as methyleugenol in rose oil or furocoumarines in citrus oil [11]. Due to the various processes and the multiple parameters involved, essential oils are complex matrices comprising hundreds of compounds with various structures and functional groups (Table 2). These compounds are mainly derived from three biosynthetic pathways: mevalonate, methyl erithrytol and shikimic acid [4].

Among these components, the most common are volatile terpenoid compounds derived from a common precursor: isopentenyl diphosphate. Once biosynthesized, terpenes are diversified through various enzymatic reactions, such as isomerization and oxidation [1,2,13,14]. This chemical diversity could also be enhanced by chemical modification during the extraction process by thermal activation of chemical reactions. For example, distillation by dry vapor stream is known to reduce the risk of hydrolysis of esters (e.g., linalyl acetate), flame distillation is known to promote “burnt” olfactory notes, and cohobating is known to increase the content of certain compounds (e.g., sulfur compounds) [15]. Essential oils can also be produced from different chemotypes (providing distinct chemical entities within the same botanical species), such as thyme essential oil that is known

Table 1

Differences in term of composition of lime oil with different processes of extraction, obtained by GC/FID on apolar column [8]

Hydrodistillation (SD)	Expression
Limonene (36.0–46.0%)	Limonene (38.0–44.0%)
γ -terpinene (10.0–13.0%)	β -pinene (17.0–19.0%)
α -terpineol (6.0–8.0%)	β -bisabolene (4.0–4.5%)
p-cymene (1.5–2.8%)	α -pinene (1.7–2.0%)

Table 2

Examples of compounds found in essential oils [12]

Compound	Essential oil
Menthol	Mint
Linalool	Lavender, cardamom
Thymol	Thyme
Eugenol	Clove
Carvone	Caraway
α -vetivone, β -vetivone	Vetiver
Benzoic acid	Almond
Cinnamic acid	Cinnamon
Citral	Lemon
Cinnamic aldehyde	Cinnamon
Geranyl acetate	Geranium
Linalyl acetate	Lavender
Limonene	Orange, lemon
Pinene	Geranium, star anise
Caryophyllene	Clove

to have seven chemotypes. We do not address authentication of chemotypes in this review.

2.2. Regulations

The diversity of chemical functions encountered in essential oils offers a variety of properties, and subsequently a variety of uses. Sometimes, these compounds can also have undesirable properties, such as allergenicity or toxicity, resulting in safety and security concerns. For this reason, standards and specifications have been established by national authorities and international organizations to limit and to control the use of essential oils. To achieve this, monographs contain specifications that define the qualitative and quantitative characteristics of a substance in order to ensure optimum quality compatible with the requirements of public health. These monographs are produced by international organizations [e.g., International Standards Organization (ISO), Ph. Eur., Codex Alimentarius Commission, Food Chemicals Codex, Flavor and Extract Manufacturers Association (FEMA), or Research Institute for Fragrance Material (RIFM)]. Some other national authorities issuing recommendations are British Standards Institution (BSI), AFNOR Standards (France), Essential Oil Association of USA, US Pharmacopoeia (USP), Indian Standards, and German DIN Standard (Deutsch Arzneibuch) [13,16]. The use of essential oils is also governed by specific regulations for application areas [e.g. European Union Cosmetics Regulation (CE 1223/2009) and European Food Safety Authority (EFSA)]. There are also non-governmental organizations supported by industrial companies that study and gather chemical, technical, and toxicological information about the ingredients used in perfumery [e.g., International Fragrance Association (IFRA), which publishes recommended practices of use, usually followed by professionals [17]].

2.3. Characterization

Essential oils are complex matrices that need to be analyzed by different techniques to ensure quality, consumer safety and fair trade. Thus, there is a wide range of instrumental techniques available (e.g., physical, organoleptic, chemical, chromatographic, and spectroscopic analysis) (Fig. 1) [16,18–20]. Olfactory analysis could be envisaged, but is typically performed by a trained evaluator. It is often carried out by comparison with a standard sample. Physical measurements required in most monographs are: density, refractive index and optical rotating power. The density of an essential oil is the ratio between its volumic mass and the volumic mass of a reference compound (water). The refractive index is the ratio between the sine of the angle of incidence and the sine of the angle of refraction of a luminous ray of a predetermined wavelength in the essential oil maintained at a constant temperature. The optical rotation of an essential oil is the angle of rotation of the plane of polarization of light radiation at a wavelength of 589 ± 0.3 nm when it passes through a thickness of 100 mm of essential oil in well-defined temperature conditions [15,19]. Physical analysis and organoleptic analysis are simple, cheap, fast techniques for identifying gross falsifications, but do not identify more subtle adulterations.

With respect to chemical analysis, analyses are mostly carried out by titration to determine water content, ester and iodine values, carbonyl index, alcohol content and total free alcohol content, phenol content, or peroxide content [15]. These techniques are simple, fast, and cheap, and they solve simple problems.

The control of essential oils could also involve chromatographic techniques, such as gas chromatography (GC) and spectroscopic analysis, to provide more accurate information on the chemical composition of the extract and to quantify the compounds of interest *via* universal or specific detectors [1,21,22].

2.4. The problem of authentication

Essential oils are used all around the world, but the problem of adulteration can slow or jeopardize the development of international trade [23]. Prices typically range from few to thousands euros (US\$) and vary from one year to another. The prices correlate with the importance of use of essential oils, and have resulted in adulteration for dishonest profits [24,25]. Adulteration of essential oils can be due to several factors. In some cases, falsification can be defined by the addition of: cheaper synthetic material; cheap volatiles from other natural sources [24]; or, vegetable oils to increase the weight. Adulterations can also involve partial or total substitution of part of the original plant by other plants [26], or the addition of non-volatile products.

All these adulteration methods can degrade the quality and, in adding one or more synthetic compounds, adulteration can lead to safety issues or non-compliance with the natural grade. Consequently, authentication is an important topic for consumer protection and the quality of essential oil production [27]. Adulteration of essential oils can also have an effect on the regulatory aspect, as an essential oil may no longer comply with specifications of standardization. Most of the time, adulterants are added at a low level (5–8%) to avoid detection by common analytical methods [28].

3. Known cases of authentication issues

Control methods and standardization of essential oils are intended to attest compliance with monographs or standards of quality, but non-compliance results do not necessarily reveal adulteration. For example, aging, processing or storage can induce a racemization of chiral compounds or polymerization reactions of terpenoids, and can take the optical activity values out of specification without there being adulteration [29].

Some cases of adulterations are already known (e.g., adding a non-volatile ingredient, synthetic or natural compounds, or a cheaper essential oil) [22].

3.1. Addition of other products: oil and solvents

Essential oils have significant volumes and turnover, so they are sometimes subject to dilution by adding a non-volatile ingredient to reduce the cost (e.g., adding vegetable or mineral oils because of their relatively low cost, their easy availability, their density being close to that of essential oils, and a greasy texture similar to that of essential oils) [2,7,22]. This kind of adulteration only results in dilution, which reduces the scent of the essential oil [30].

A study on lemongrass oil identified kerosene or coconut oil as adulterants [31,32]. Another example of this kind of adulteration is sandalwood oil diluted with polyethylene glycol [32]. Other solvents that could be used are triacetin, triethyl citrate or benzyl alcohol, ethyl alcohol, and, in the case of aromatherapy, vegetable oils, such as almond oil [33].

3.2. Addition of specific compounds: synthetic and natural

Standardization of essential oils is defined by values with low and/or high limits for the content of selected compounds. Commercial essential oils need to comply with such standards [16]. For this reason, cases of adding a compound, synthetic and nature-identical or natural, can be found. By definition, natural compounds are obtained directly from natural sources by enzymatic, microbial, or physical procedures [13,28]. Those specific types of adulteration can have different motivations. One reason could be to enhance the quality of the essential oil, in terms of compound contents. This kind of adulteration can be done to increase the benefit of essential oils and to meet the needs of industry [34] (e.g., adding

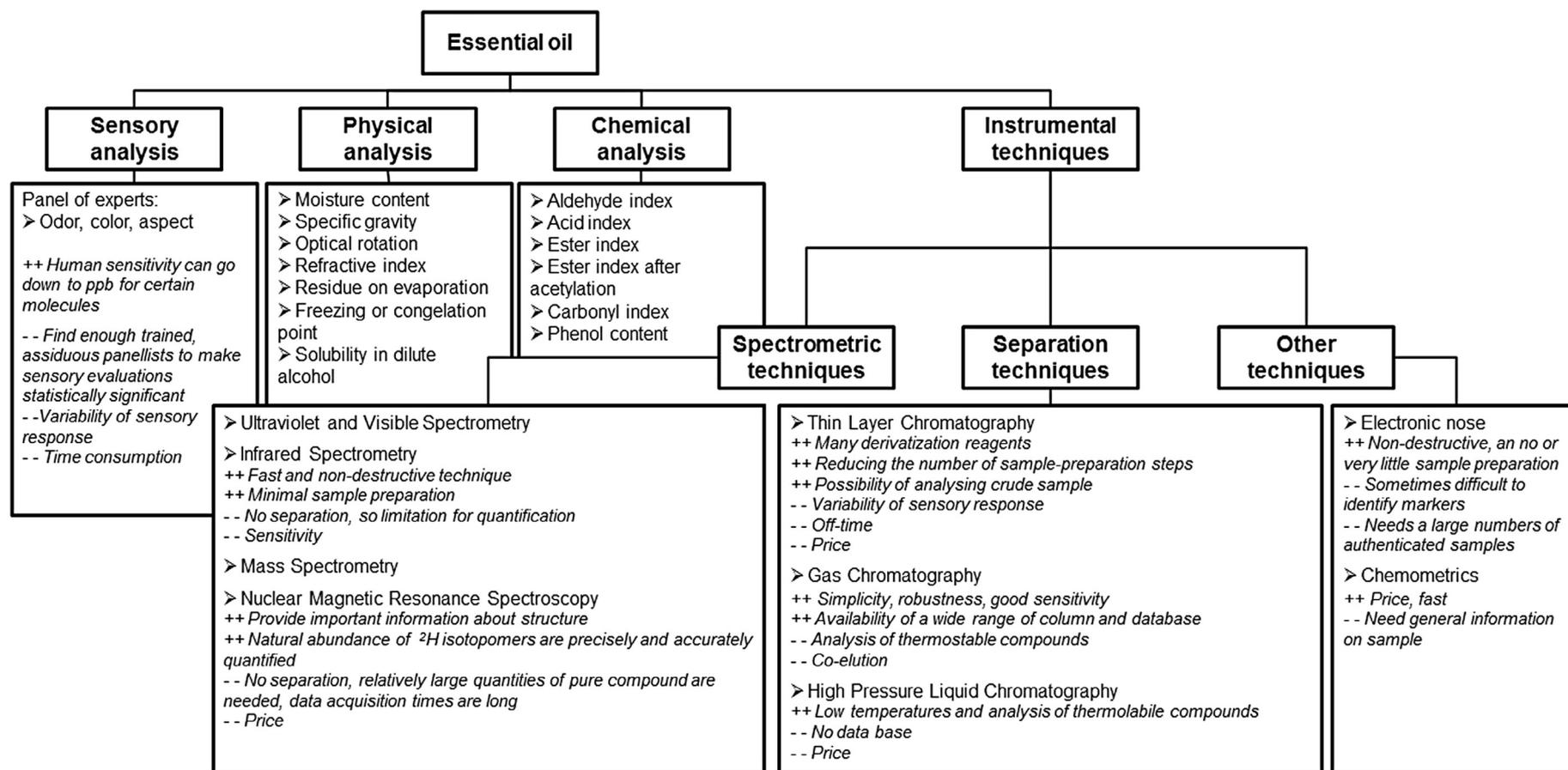


Fig. 1. Advantages and disadvantages of quality assessment techniques (+: Advantages; -: Disadvantages).

citral to lemon (*Citrus lemon* L.) essential oil [35], benzyl benzoate to balsam of Peru (*Myroxylon balsamum* (L.) Harms) [26], or synthetic irone to iris oil [36].

The price of the iris essential oil varies greatly depending on the percentage of irone. For example, the price of an iris oil containing 8% irone is 6200 €/kg, while with 10% irone it increases to 9750 €/kg, and could even reach 101,000 €/kg for pure irone. The price difference can be really large, which is a good reason for adulterating iris oil, particularly because a mixture of isomers of synthetic α -irone and β -irone cost only around 25 €/mL. Another reason could be to improve the olfactory quality of the essential oil, as is the case for bergamot oil (*Citrus aurantium* L. spp. *Bergamia*) or lavender oil (*Lavandula angustifolia* Mill.) for which the addition of linalyl acetate or linalool was reported, or vetiver oil (*Vetiveria zizanioides* (L) Nash) with the addition of a mixture of terpenyl cyclohexanols, in order to increase the sandalwood note [22,24]. Essential oils are sometimes used for medicinal properties [37] so they can be altered by the adding other oils containing the bioactive compound(s) of interest {e.g., chamomile oil (*Chamomilla recutita*, syn. *Matricaria chamomilla*), which is used for its content of α -bisabolol, and could be altered with synthetic bisabolol [24,38]}.

3.3. Addition of another essential oil

The addition of another essential oil can be motivated by olfactory and/or economic reasons. To do this, the addition can be an essential oil of lower quality but with similar olfactory notes [35,39]. This is especially the case when there is a significant price difference between the two oils. One of the most known examples is the adulteration of essential oils from citrus by sweet orange essential oil, which is the cheapest citrus oil. Another typical example is lavender essential oil (*Lavandula angustifolia* Mill.), whose price can reach 130 €/kg, and which could be mixed with the essential oil of other species of genus *Lavandula*, whose prices are around 20 €/kg [24]. Lemon-balm essential oil (*Melissa officinalis* L.), a highly valued raw material (~5000 €/kg), produced in low yields and featuring pronounced medicinal interest, could be mixed with cheap citronella oil (*Cymbopogon winterianus* Jowitt ex Bor) [40].

Adulteration can also occur by mixing different essentials oils obtained by the extraction of different parts of the same plant. Cinnamon bark essential oil can be adulterated by leaf cinnamon essential oil to reduce the presence of allergens, such as cinnamaldehyde. The leaf oil, while possessing the same olfactory notes, although less “gourmand”, has indeed reduced cinnamaldehyde contents. This type of fraud can reduce the allergenic effect but also increase the volume, and hence the profit [41]. Concerning all types of citrus oils, another well-known falsification is the addition of orange essential oil (*Citrus aurantium* var. *sinensis* L.) [42]. Another case concerning citrus oil is neroli oil made from flowers (*Citrus aurantium* L. spp. *Amara* L. var. *pumilia*), frequently mixed with cheaper petitgrain oil made from leaves [24].

3.4. Other cases

Another example of fraud worth mentioning is the case of wintergreen essential oil that can be completely substituted by methyl salicylate [43]. A gross case of adulteration could be the use of synthetic oil, consisting in a mixture of synthetic compounds resembling the formulae of the natural essential oil, in lieu of the valuable natural material. Also, bergamot oil or geranium oils can be obtained by mixing monoterpenes and distilled oils of different origins, linalyl acetate and other citrus oils [33,44].

In summary, the diversity of the adulteration strategies relates to the large, diverse collection of essential oils used in manufacture of valuable products, making each case different from the others.

4. Techniques of authentication

Two main approaches to the determination of adulteration are possible: monitoring the global fingerprint of the product, or searching for one or more specific markers in the product. To carry out these controls, modern analytical techniques are typically used [7], but simple tests are also available, set up long before the advent of powerful analytical devices. These methods proved useful and were widely used, but showed deficiencies over time. For example, the iodine test can be used to characterize the oxidation of the product, considered an indication of adulteration by vegetable oils [45]. Another test can be performed using a saponification reaction with aqueous potassium hydroxide; and, the formation of crystals indicates a potential fraud by addition of esters [46].

4.1. Tests recommended by the authorities

Control of the conformity of an essential oil starts with a series of tests according to the recommendations of certification and regulatory authorities (e.g., ISO, and Pharmacopoeia) to ensure identity, quality, safety and efficiency of the extract [47].

The first step is sensory analysis, which is, by definition, examination of the organoleptic properties of a product by the sense organs. This type of analysis can be performed by a sensory-analysis panel that evaluates the essential oil, or, as indicated by ISO recommendations, by a group of assessors selected to form the sensory-analysis panel that will be a true “measuring instrument” [48]. However, this necessary step has the disadvantage of involving trained panelists in time-consuming operations [49]. There are indeed two types of experts: the “expert assessor” and “specialized expert assessor”. The former is an assessor selected with a high degree of sensory sensitivity and experience of sensory methodology, able to make consistent, repeatable sensory assessments of various products. The latter is a subject who has additional experience as a specialist in the product and/or process and/or marketing, and able to perform sensory analysis of the product and to evaluate or predict effects of variations (e.g., raw materials, recipes, processing, storage, and ageing). Selection of individuals for the sensory-analysis panel must be performed with care and requires guidelines for selection, training and monitoring of assessors [48]. Once the assessors are selected, a standard methodology following ISO recommendations must be applied. Sensory analysis has the advantage of avoiding costly investments in analytical instruments, but requires time and assiduity of the assessors for training and evaluation [49]. The result of the sensory-analysis panel can be as simple as just indicating compliance or non-compliance of the essential oil, or more complicated with statistical analysis and comparison with an essential oil used as reference [48].

The second step comprises a series of physical and chemical analyses. The physico-chemical properties are determined by standardized methods, such as measuring the ester, acid or carbonyl index, or the refraction, density, optical rotation, freezing or boiling points, or quantification of ethanol or moisture [8]. Quality control (QC) and assessment of essential oils can be performed based on these techniques, and possible adulteration can be detected [50]. Some essential oils, such as citrus oils, which contain predominantly (+)-limonene, will have a lower specific gravity and a lower optical rotation on adding turpentine because α -pinene, its major component, has a lower boiling point and a lower optical rotation [22]. On adding synthetic anethole in star anise (*Illicium verum* L.) essential oil, a change in the optical rotation could be observed and used as evidence of fraud. For peppermint oil, adding turpentine is characterized by a freezing point lower than 10.5°C [41].

However, these simple, effective methods are insufficient for more subtle adulteration. It is then necessary to use more powerful analytical techniques: separation techniques [GC, liquid chromatography

(LC), high-performance thin-layer chromatography (HPTLC) and spectroscopic techniques (vibrational techniques, and nuclear magnetic resonance)]. Adulteration with ethanol, edible oils, or liquid paraffin can be detected by TLC, GC or infrared (IR) spectroscopy. [41] GC analysis is the last step recommended in some monographs, as it is a key technique in the analysis of essential oils. The analysis of qualitative and quantitative composition by GC provides a chromatogram sufficiently fine to highlight defects in quality. In this regard, comparisons use the chromatographic profile obtained by GC equipped with a flame-ionization detector (FID), which provides a large range of linearity and has relatively simple maintenance requirements. GC is effective for the QC of an essential oil, by comparing the chromatogram of the product with a standard meeting the chosen specifications. The required steps are, first, to identify the appearance or the disappearance of peaks on the chromatogram and, second, to compare the relative percentage area to determine whether their differences are significant for the product being analyzed, although this technique gives only an approximation of the real quantity of a component present in the sample tested.

Various perfumery materials were characterized qualitatively and quantitatively by GC coupled to mass spectrometry (GC-MS) in order to characterize and to detect adulteration accurately [51]. For sandalwood oil, GC-MS analysis reliably evaluated the santalol content as a valuable marker in detecting adulteration by the addition of synthetic material, such as Sandalore [52], Verdox, Santaliff, Vertofix Coeur, or Ebanol [53].

4.2. Analytical techniques commonly used for the detection of adulteration

4.2.1. Chiral GC analysis

Chiral GC is a practical, powerful technique for the authentication of essential oils and is becoming crucial for the detection of adulterants [33,34,54–56]. Plants produce metabolites in many instances as chiral molecules, and enantiomers can differ from one species to another within the same genus. Although presenting the same physicochemical properties, except for their optical activity, enantiomers can exhibit divergent biological activities, one enantiomer being harmless while the other is toxic, so appropriate, efficient chemical analyses are essential [57]. For example, (*R*)-limonene is responsible for the odor of oranges while (*S*)-limonene accounts for the odor of lemon. (*S*)-carvone is the key odorant of the essential oil of caraway (smell of cumin), and (*R*)-carvone is in the essential oil of spearmint (smell of spearmint). In others cases, one or more stereoisomers could be less active or even odorless, such as (*R*)-linalool, which has a powerful flowery note, while (*S*)-linalool is less intense, or (*2S,4R*)-*cis*-rose oxide, which has a powerful rosy scent, while (*2R,4S*)-*cis*-rose oxide is odorless [29].

Compounds from essential oils are, in most cases when applicable, chiral compounds occurring in specific enantiomer ratios, often specific to the essential oil (e.g., α -pinene, β -pinene and limonene, making these compounds good markers of the origin and subsequently of adulteration by mixing these materials from different origins) (Table 3) [48]. Chiral analysis allows detection of adulteration of natural products with synthetic substitutes, usually in the racemic form, or bulking oils from other crops, by using values of enantiomeric purity and enantiomeric excess. Those values comprise a measured ratio of detected enantiomers expressed as a percentage, and by the relative difference of the separated enantiomers also expressed as a percentage [29,34,48,58].

One example is the case of rose and geranium essential oils with (*-*)-*trans* rose oxides, which are a specific indicators of genuine rose oils and can discriminate rose oils from geranium oils [29]. Chiral analyses also detect the addition of synthetic linalool and linalyl acetate in lavender oil [6,7,59]. Another case of chiral analysis is the analysis of limonene, which shows a high ee-value in favor

of (*R*)-limonene for bergamote, orange, mandarin, lemon, or lime oils, and a high ee-value in favor of (*S*)-limonene for lemongrass or citronella oils [29].

In this way, chiral analysis plays a critical role in essential oil analysis and has been among the most important analytical techniques in recent times. It is a cheap, sensitive technique, but it requires method development that can take some time especially because there is no universal chiral stationary phase [60]. In essential oils, some non-enzymatic reactions or racemization can occur during processing or storage, which can induce false-positive responses in chiral analysis [30].

4.2.2. Isotope-ratio mass spectrometry

To certify the naturality of one or more components of an essential oil, another kind of analysis to be performed is isotope-ratio analysis using isotope-ratio MS (IRMS) or stable-isotope-ratio analysis (SIRA). Plants can be discriminated by their metabolic assimilation of atmospheric CO₂, in particular by reaction intermediates derived from incorporating carbon dioxide (molecules of three or four carbon atoms). Most plants go through 3-phosphoglycerate, an intermediate with three carbon atoms (C₃). The C₄ plants pass through a malate intermediate with four carbon atoms. Some plants are able to select the glycerate pathway or the malate pathway (CAM cycle) depending on their environment. These metabolites do not exhibit the same isotopic fractionation, and this difference therefore allows plants to be distinguished by their isotopic ratio [61,62]. The measurement of isotopic variations in natural compounds is based on the principle that the majority of chemical elements have different stable isotopes that result in distinct molecular weights [63]. For each element, one or more isotopes are present at different levels, with a specific distribution pattern. The stable-isotope ratios of carbon, hydrogen, oxygen, or nitrogen within the metabolites can allow the detection of accidental or deliberate addition of a synthetic product (predominantly of fossil origin), or even the discrimination of different geographical or botanical origins [16,24,25,34,44,64]. This evaluation of isotopic data has been established as the premium analysis of the origin and the naturality of flavors and fragrances [65].

IRMS is most of time coupled to combustion/pyrolyze (C/P-IRMS) for adulteration control. This technique can reliably differentiate natural from synthetic for mandarin essential oil regarding the C-isotope-ratio measurements for terpinen-4-ol, γ -terpinene, α -terpineol, and terpinolene. The authenticity of thyme and oregano essential oils can be based on the H-isotope-ratio measurements for carvacrol and thymol [25,39,55]. IRMS also detects addition of synthetic benzaldehyde in bitter almond oil [66].

IRMS is a very powerful technique, but it requires a significant financial investment and an experienced operator. Also, its use requires databases that take a relatively long time to build.

Table 3
Enantiomeric Ratio (%) of α -pinene, β -pinene and limonene [29]

	α -pinene		β -pinene		limonene	
	1S	1R	1S	1R	4S	4R
Oil of bergamot	72	28	94	6	14	86
Oil of bitter orange	8	92	97	3	1	99
Oil of grapefruit	-	100	34	66	tr	100
Oil of lemon	67	38	95	5	1	99
Oil of lime	76	24	97	3	2	98
Oil of orange	tr	100	46	54	tr	100
Oil of neroli	77	23	96	4	3	97
Oil of petitgrain	82	18	98	2	12	88
Oil of mandarin	43	57	3	97	tr	100
Oil of citronella	23	77	tr	tr	96	4
Oil of lemongrass	96	4	tr	tr	100	tr

tr = trace < 0.5%.

4.2.3. NMR spectroscopy

NMR spectroscopy provides information for the control of authenticity by determining stable-isotope ratios, affording a means for measuring isotopic patterns within natural and synthetic molecules for the purposes of differentiation [7,34,43,67,68]. Investigation of site-specific natural-isotope fractionation (SNIF-NMR), based on the measurement of deuterium/hydrogen (D/H) ratios at specific positions of a molecule, has enabled characterization of the nature of plant precursors [7,69]. Quantitative deuterium NMR measured significant variations of deuterium-isotope distribution, according to the origin of the molecule, and has discriminatory potential to characterise the enantiomeric purity of compounds, such as α -pinene, or methyl salicylate [43]. SNIF-NMR is also used to determine the addition of synthetic linalool in essential oils, or to detect the addition of chamomile oil of (-)- α -bisabolol extracted from plants of the genus *Vanillosmopsis* [16].

NMR is a powerful technique but its use needs the isolation of compounds, databases, an experienced operator and significant investment.

4.3. Additional techniques

4.3.1. (HP)TLC analysis

Even though GC-MS is the method of choice for the analysis of essential oils, (HP)TLC has become widely accepted by pharmacopoeias and regulatory agencies as a tool well suited to identification of essential oils and detection of adulteration [14,34,46,70]. (HP)TLC enables the mobile phase to progress by capillarity over a plate charged with a stationary phase along with compounds from a mixture. Different lengths of migration are observed for each compound, depending on mechanisms of partition between the mobile and stationary phases and adsorption phenomenon.

The most recent advances in this technique were mainly observed in the quality of stationary phases and the efficiency of detection techniques. High-performance stationary phases, characterized by smaller particle sizes with narrow size distribution, were developed. These increased the resolution and the reproducibility of TLC analysis. Similarly, new stationary phases, such as chiral phases, were developed and are now commercially available. The detection systems were also considerably improved (e.g., the setup of scanners for densitography for the range 190–900 nm [71]).

TLC can be coupled with powerful detection systems: MS, and IR and Raman spectroscopies [19]. (HP)TLC was quickly established as a method of choice for analysis and control (e.g., in the adulteration of ylang-ylang essential oil by sunflower oil) [72]. The Ph. Eur. provides a few TLC methods for identifying adulteration of essential oils, such as adulteration of anise oil by fennel oil, or Chinese Star anise oil by Japanese Star anise oil [70].

HPTLC can be automated and allows fast analysis of numerous samples (more or less complex) simultaneously, and is considered as a greener technique by reducing the amount of waste material (including volatile organic compounds) and energy costs.

Despite these advantages, HPTLC has some disadvantages as an off-line technique and requires initial investment for acquisition of the equipment.

4.3.2. Vibrational spectroscopy

Vibrational spectroscopy is a chemical-analysis technique focusing on covalent chemical bonds of molecular constituents within the sample. This technique is based on the interaction of light and matter and the resulting molecular vibrations. Raman spectroscopy provides information about spectrometric diffusion from the vibrational state of a molecule. IR spectroscopy is based on the modification of vibrational and rotational energies of chemical bonds. The IR spectrum ranging from microwave to visible wavelengths of the electromagnetic spectrum, or in mid-IR regions. For near-IR

reflectance (NIR), the nominal range of wavelengths used is 1100–2500 nm [57,73–76].

Combined with chemometric algorithms (metabolomics), those techniques are gaining importance in the fast QC of essential oils [1,23,77]. For example, using spectroscopy analysis discriminated between different eucalyptus essential oils [78]. IR and Raman can also be used for the detection of cottonseed oil and paraffin oil in different essential oils by the presence of absorption bands characteristic of ester and unsaturated ester ($1705\text{--}1720\text{ cm}^{-1}$), acetates ($1\ 245\text{ cm}^{-1}$) and carbonyl group ($1250\text{--}1170\text{ cm}^{-1}$) for cottonseed oil, and saturated and unsaturated hydrocarbons ($3\ 000\text{ cm}^{-1}$) for paraffin oil [41]. NIR spectroscopy is promising in QC, since large sets or single samples can be quickly analyzed in order to identify suspect samples without requiring further testing by more time-consuming, expensive methods [23].

4.3.3. Coupled and multidimensional chromatography

Essential oils are complex matrices and their chromatographic analyses on one dimension do not avoid co-elution issues. It is under these circumstances that multidimensional chromatographic techniques can solve the problem because they offer better separation capacities. Multidimensional separation is defined as an orthogonal two-step separation. The sample is transferred from separation system 1 (e.g., column 1 for GC) to separation system 2 (column 2) [60]. Two orthogonal columns are commonly used: usually a non-polar first column and a polar second column.

Two main approaches are adopted in GC analysis of complex volatile fractions of plant matrices: so-called heart-cut GC-GC and the two-dimensional comprehensive GC (GCxGC) [79]. In heart-cut GC-GC, analytes or individual segments eluting from a first column (^1D , first dimension) are on-line and directly transferred to the second column (^2D , second dimension) for further separations, using a valve or Deans switch device [80]. With a comprehensive GCxGC system, the entire sample passes through the two capillaries connected in series with a transfer device [81].

Multidimensional GC (MDGC) finds application in environmental analysis, oil-refining and petrochemical industry, and natural extracts [79,82,83]. MS coupled to MDGC (MDGC-MS), or GC-time-of-flight MS (GC-TOF-MS) are analytical techniques available for the control of essential oil, but the use of TOF-MS is not very affordable and requires trained users [34,55]. For sandalwood essential oil, MDGC-MS or MDGC-FID enabled the high-resolution separation of santalol isomers, and provided elements of proof of the genuine quality of the sandalwood oil [53]. Besides the question of co-elution of one or more metabolites of the sample, GCxGC gives access to more detailed, comprehensive overview of the chemical composition, thereby increasing the number of possible markers, or the reliability of fingerprinting. Multidimensional chromatographic techniques coupled or not to an MS detector have greatly enhanced separation power, which has simplified sample preparation in target analysis. GCxGC has the disadvantage of needing a slow temperature-program rate in the first dimension, and a detector with a high frequency. The data processing is not easy and the instrument is not very affordable.

The combination of chiral analysis with MDGC (enantio-MDGC) is an option for analysis of essential oils with a high degree of molecular complexity [34]. Enantioselective GC coupled on-line with IRMS was recently used in origin-specific analysis of flavor and fragrance compounds. Analyses focused on the $^{13}\text{C}/^{12}\text{C}$ ratio of the detected enantiomers [65].

4.4. Emerging techniques

Some existing techniques are already used in natural extracts but for different purposes.

4.4.1. Application of chemometrics

The fingerprint of an essential oil can be defined as a characteristic profile reflecting the complex chemical composition of the sample, and can be obtained by many analytical techniques. In essential oils, there are a lot of unknown components often present only in trace amounts. Even if chromatographic instruments have shown a great improvement in terms of separation over the years, selection of just a few components should not be considered for evaluating the quality and the authenticity of samples of essential oils. Consequently, to obtain reliable fingerprints that represent chemically characteristic components is not an easy task.

Chemometrics, such as multivariate analysis, and chemical-pattern-recognition methods with principal component analysis and soft-independent modelling of class analogy, is now greatly appreciated for providing reasonable characterization of essential oils. Chemometrics is defined by The International Chemometrics Society as: “the chemical discipline that uses mathematical and statistical methods:

- 1 to design or to select optimal measurement procedures and experiments; and,
- 2 to provide maximum chemical information by analyzing chemical data”.

Nowadays, chemometrics is applied in many fields, such as analytical chemistry, including separation methods, such as chromatography (LC, GC, TLC), electrophoresis, and spectroscopic methods, such as Raman, Fourier transform IR spectroscopy (FTIR), NIR, mid-NIR [19,84–87]. Indeed, reprocessing data by using chemometrics obtains more information about samples.

Several application areas already benefit from the advantages provided by chemometrics, such as metabolomics, which is a chemometric approach used for phenotyping and biomarker research [88]. In essential oil authenticity, chemometrics is playing an increasingly important role. Indeed, more and more articles are published on integrating the chemometric approach in studying essential oils.

The combination of GC-MS with chemometric tools, such as multivariate curve resolution (MCR), overcomes the problems of background, baseline offset and overlapping/embedded peaks [89,90]. In vibrational spectroscopy combined with chemometrics, modeling in essential oil studies, several articles mentioned that this combination could be an alternative for the quality assessment of essential oils (e.g., lavender oil) [91]. Another technique based on a statistical model is “electronic-nose technology”, which is defined as “an instrument including a set of electronic chemical sensors with a cross selectivity, and a fitted pattern-recognition system capable of recognizing simple or complex odors” [19].

More techniques are being developed in response to specific requests from regulation bodies concerning authentication of essential oils. A study on the QC of bergamot oils showed the efficiency of electronic-nose systems with subsequent discriminant factorial analysis treatment of data [92].

This technique gives good results but requires the availability of a large number of well-defined samples to build the model, and the authenticity of the samples used must be certain.

4.4.2. HPLC

High-performance LC (HPLC) is not widely used in essential oils, but is rather a method of choice for analyzing less volatile or non-volatile constituents. HPLC highlights non-volatile markers of adulteration, such as synthetic compounds or vegetable oils [87]. This technique was used to detect a mixture of essential oils (e.g., adding orange oil in lemon oil) [93,94].

4.4.3. Other techniques

Other techniques have seen their applications evolve towards adulteration control. For example, differential scanning calorimetry (DSC), which is mainly used in the field of polymers, is by definition “the measurement of the change of the difference in the heat flow rate to the sample and to a reference sample while they are subjected to a controlled temperature program” [95]. It is based on measuring the consequences of applying temperature-programmed scans that can cause some structural modifications or decompositions [7]. Its use has changed and has been tested in QC because of its applicability in assessing the purity of samples. This use has been applied to some essential oils, such as orange, lemongrass and basil oils. They show predominant substances in their composition (respectively around 90% limonene, 66% citral and 84% methyl chavicol), and, in this way, have specific DSC profiles. In such cases, DSC can provide fingerprints with a relatively good degree of accuracy [96].

Authentication can also be based on thermal diffusivity, such as photoacoustic spectroscopy (PS), which is mainly used for gas analysis. Since the advent of more efficient lasers, its application areas have expanded. For example, in essential oils, PS was used to measure the thermal diffusivity in discriminating between different extraction processes for a study on concentrated citrus oils [97].

All these methods offer interesting perspectives, but there are few data, in the literature, on their use in essential oils and their adulteration.

5. The main problems and recommended analytical methods

Recent advances in knowledge and the chemical analysis of essential oils allowed a summary of the main authentication problems of essential oils to be established and the analytical methods recommended (Table 4).

6. Conclusion

Adulteration, particularly adulteration in essential oils, is a topic of growing interest. Despite this, only a few hundred articles refer to this major issue with economic consequences that challenge the analytical chemist. Essential oils are sometimes adulterated due to their cost, their increasing usage, and, for some of them, their scarcity, which contrasts with the ever-increasing demand.

Different methods are used to detect adulteration. Apart from tests recommended by pharmacopoeias and regulations (e.g., organoleptic examination, and physico-chemical analyses), GC, GC-MS, enantioselective, and IRMS analyses have made the major contribution towards detecting adulteration of essential oils. Other techniques, less frequently used to identify adulteration, are vibrational. The ability of (HP)TLC to provide fingerprints makes it accepted by the pharmacopoeias and regulations, and it is increasingly used to detect adulteration of essential oils. Some techniques are gaining in importance in authenticating essential oils, such as the use of coupled techniques, GCxGC, or new phases in GC, HPLC, or HPTLC. Recent advances in analytical techniques, particularly in chromatography systems, coupled to MS and NMR, the automation of sample preparations, and the computerization of data systems make chemometric approaches very promising.

Along with progress in chemical analysis, adulteration methods are also improving, and solving these problems requires a case-by-case approach, since there is no general method.

The ingenuity of fraudsters is a reflection of the interest in natural ingredients. The methods of adulteration, more and more technical, involve development of appropriate methods of analysis, which becomes a perpetual problem for the chemical analyst.

The cost of implementation is extremely varied, from relatively cheap to very expensive, so a balanced evaluation of analytical performance has to take into account cost, efficiency and speed.

Table 4
Table of the main problems of authenticating essential oils and their associated analytical methods

Latin name	Kind of adulteration	Analytical methods and target of the analysis	Ref.
Bergamot (<i>Citrus aurantium</i> L. spp. <i>Bergamia</i>)	<ul style="list-style-type: none"> Addition of linalool 	<ul style="list-style-type: none"> Enantioselective GC (Only the <i>R</i>-enantiomer is present) SNIF- NMR (linalool) Electronic nose system 	[24,41] [69] [92]
Buchu (<i>Agathosma betulina</i> (P.J. Bergius) Pillans)	<ul style="list-style-type: none"> Discrimination of natural cold-pressed bergamot oil from those deterpenated and bergapten-free Addition of linalyl acetate Addition of synthetic compounds 	<ul style="list-style-type: none"> HRGC-P-IRMS, or SNIF NMR (Linalyl acetate) Enantio-MDGC ((1<i>S</i>, 4<i>R</i>)-menthone, isomenthone, (1<i>S</i>)-pulegone, k(1<i>S</i>, 4<i>R</i>)-cis-3-oxo-p-menthane-8-thiol, (1<i>S</i>, 4<i>R</i>)-trans-3-oxo-p-menthane-8-thiol, (1<i>S</i>, 4<i>R</i>)-cis-3-oxo-p-menthane-8-thiol acetate, (1<i>S</i>, 4<i>R</i>)-trans-3-oxo-p-menthane-8-thiol acetate are specific indicators of genuine of buchu leaf oil) Enantioselective GC (α-bisabolol is present only as a single stereoisomer, so the three other stereoisomers prove adulteration) SNIF-NMR ((-)-α-bisabolol) 	[41,55,98] [29]
Chamomile (<i>Chamomilla recutita</i> (L.) Rauscher)	<ul style="list-style-type: none"> Addition of α-bisabolol from cheaper oil such as candeia oil (<i>Vanillosmopsis erythropappa</i> L.) Addition of α-bisabolol from cheaper oil such as candeia oil (<i>Vanillosmopsis erythropappa</i> L.) Addition of cinnamaldehyde in China bark essential oil 	<ul style="list-style-type: none"> Enantioselective GC ((+)-trans-sabinene: 1% in <i>M. piperita</i>, around 0% in <i>M. arvensis</i>) Enantioselective GC ((<i>S</i>)(-)-citronellol, (2<i>S</i>,4<i>R</i>)(-)-cis, (-)-trans rose oxides are specific indicators of genuine rose oils, (2<i>S</i>,5<i>S</i>)-trans linalol oxides, (2<i>S</i>,5<i>R</i>)-cis linalool, and (<i>S</i>)-linalyl acetate are identified as unnatural enantiomers) GC/IR/MS ($\delta^{13}\text{C}$ of geraniol) EA/IRMS, or GC/C/IRMS ($\delta^{13}\text{C}$ of geraniol) 	[24] [16]
Cinnamon (<i>Cinnamomum cassia</i> Nees ex Blume)	<ul style="list-style-type: none"> Addition of cinnamaldehyde in China bark essential oil 	<ul style="list-style-type: none"> GC-MS (Presence of impurities such as phenyl pentadienal, benzyl alcohol and eugenol in synthetic cinnamaldehyde) HPLC/PLS-DA (Seven major bioactive: coumarin, 2-hydroxyl cinnamaldehyde, cinnamyl alcohol, cinnamic acid, eugenol, cinnamaldehyde, 2-methoxy cinnamaldehyde) 	[41] [99]
Cinnamon (<i>Cinnamomum zeylanicum</i> Blume)	<ul style="list-style-type: none"> Addition of twig oil in bark essential oil 	<ul style="list-style-type: none"> Polarimeter, densitometer (Specific gravity and optical rotation are reduced) HPTLC (Presence of black zone (Rf = 0.47)) HPTLC (Presence of black zone (Rf = 0.19)) HRGC-P-IRMS (Linalool) Enantioselective GC ((+)-trans-sabinene: 1% in <i>M. piperita</i>, around 0% in <i>M. arvensis</i>) Enantioselective GC ((<i>S</i>)(-)-citronellol, (2<i>S</i>,4<i>R</i>)(-)-cis, (-)-trans rose oxides are specific indicators of genuine rose oils, (2<i>S</i>,5<i>S</i>)-trans linalol oxides, (2<i>S</i>,5<i>R</i>)-cis linalool, and (<i>S</i>)-linalyl acetate are identified as unnatural enantiomers) GC/IR/MS ($\delta^{13}\text{C}$ of geraniol) EA/IRMS, or GC/C/IRMS ($\delta^{13}\text{C}$ of geraniol) 	[22] [100] [100] [41,55] [24]
Citrus oil	<ul style="list-style-type: none"> Addition of turpentine 	<ul style="list-style-type: none"> EA/IRMS, or GC/C/IRMS ($\delta^{13}\text{C}$ of geranyl acetate) 	[28]
Clary sage (<i>Salvia sclarea</i> L.)	<ul style="list-style-type: none"> Addition of sage oil (<i>Salvia officinalis</i> L.) Addition of Spanish sage oil (<i>Salvia lavandulifolia</i> L.) Addition of linalool Addition of de <i>Mentha X piperita</i> L. oil 	<ul style="list-style-type: none"> EA/IRMS, or GC/C/IRMS ($\delta^{13}\text{C}$ of linalool) FT-Raman spectra, or ATR-IR (β-citronellol, 1,8-cineole, citronellal) 	[28] [78]
Coriander (<i>Coriandrum sativum</i> L.)	<ul style="list-style-type: none"> Addition of linalool 	<ul style="list-style-type: none"> Chemometric treatment with MIR & NIR (Citronellol, geraniol, linalool, citronellyl formate, isomenthone, geranyl formate, guaia-6,9-diene) Enantioselective-GC (Egyptian geranium oil contain 10-epi-eudesmol which is absent in geranium Bourbon) Enantioselective-GC (Citronellol, the (-) enantiomer in geranium, (+) enantiomer in citronella oil) Enantioselective-GC Put a drop of the sample an blotting paper, pure essential oils would evaporate completely Chemometric treatment by MID-IR spectroscopy (The main 13 hydrocarbons and oxygenated compounds) HRGC-P-IRMS (Linalool) Enantioselective-GC ((<i>R</i>)(-)-linalol 94%, Detection of dihydrolinalool and dehydrolinalool) Enantioselective-GC (linalool and linalyl acetate) SNIF NMR (Linalool, linalyl acetate) HRGC-P-IRMS (Linalool, linalyl acetate) Quantitative GC analysis (Presence of high amounts of 1,8-cineol and camphor) 	[101] [16,33] [33] [33] [33] [85]
Cornmint (<i>Mentha arvensis</i> L.)	<ul style="list-style-type: none"> Addition of de <i>Mentha X piperita</i> L. oil 	<ul style="list-style-type: none"> EA/IRMS, or GC/C/IRMS ($\delta^{13}\text{C}$ of geranyl acetate) 	[28]
Damask rose (<i>Rosa damascena</i> Aut. Ou Mill.)	<ul style="list-style-type: none"> Addition of citronellol 	<ul style="list-style-type: none"> EA/IRMS, or GC/C/IRMS ($\delta^{13}\text{C}$ of linalool) FT-Raman spectra, or ATR-IR (β-citronellol, 1,8-cineole, citronellal) 	[28] [78]
	<ul style="list-style-type: none"> Addition of palmarosa oil (<i>Cymbopogon martini</i> (Roxb.) Will. Watson) Addition of geraniol from <i>Cymbopogon martini</i> (Roxb.) Will. Watson, or from <i>Cymbopogon nardus</i> (L.) Rendle Addition of geranyl acetate from <i>Cymbopogon citratus</i> (DC.) Stapf or from <i>Cymbopogon martini</i> (Roxb.) Will. Watson Addition of linalool from <i>Ocimum basilicum</i> L. Discrimination of eucalyptus oil from Australia with Chinese eucalyptus oil Mixture of chemotypes 	<ul style="list-style-type: none"> EA/IRMS, or GC/C/IRMS ($\delta^{13}\text{C}$ of geranyl acetate) 	[28] [28,41]
Eucalyptus (<i>Eucalyptus globulus</i>)	<ul style="list-style-type: none"> Discrimination of eucalyptus oil from Australia with Chinese eucalyptus oil 	<ul style="list-style-type: none"> EA/IRMS, or GC/C/IRMS ($\delta^{13}\text{C}$ of linalool) FT-Raman spectra, or ATR-IR (β-citronellol, 1,8-cineole, citronellal) 	[28] [78]
Geranium (<i>Pelargonium graveolens</i> L'Her. Ex Aiton)	<ul style="list-style-type: none"> Mixture of chemotypes Addition of Egyptian geranium oil in geranium Bourbon Addition of citronella oil from Ceylon and java (<i>Cymbopogon winterianus</i>) in Bourbon oil Addition of fraction of palmarosa oil in Bourbon oil Addition of almond oil in Bourbon oil 	<ul style="list-style-type: none"> Chemometric treatment with MIR & NIR (Citronellol, geraniol, linalool, citronellyl formate, isomenthone, geranyl formate, guaia-6,9-diene) Enantioselective-GC (Egyptian geranium oil contain 10-epi-eudesmol which is absent in geranium Bourbon) Enantioselective-GC (Citronellol, the (-) enantiomer in geranium, (+) enantiomer in citronella oil) Enantioselective-GC Put a drop of the sample an blotting paper, pure essential oils would evaporate completely Chemometric treatment by MID-IR spectroscopy (The main 13 hydrocarbons and oxygenated compounds) HRGC-P-IRMS (Linalool) Enantioselective-GC ((<i>R</i>)(-)-linalol 94%, Detection of dihydrolinalool and dehydrolinalool) Enantioselective-GC (linalool and linalyl acetate) SNIF NMR (Linalool, linalyl acetate) HRGC-P-IRMS (Linalool, linalyl acetate) Quantitative GC analysis (Presence of high amounts of 1,8-cineol and camphor) 	[101] [16,33] [33] [33] [33] [85]
Lavandin (<i>Lavandula angustifolia</i> P. Mill. \times <i>Lavandula latifolia</i> (L.f.) Medikus)	<ul style="list-style-type: none"> Discrimination of origin 	<ul style="list-style-type: none"> EA/IRMS, or GC/C/IRMS ($\delta^{13}\text{C}$ of linalool) FT-Raman spectra, or ATR-IR (β-citronellol, 1,8-cineole, citronellal) 	[28] [78]
lavender (<i>Lavandula angustifolia</i> Miller)	<ul style="list-style-type: none"> Addition of linalool Addition of synthetic linalool and linalyl acetate 	<ul style="list-style-type: none"> EA/IRMS, or GC/C/IRMS ($\delta^{13}\text{C}$ of linalool) FT-Raman spectra, or ATR-IR (β-citronellol, 1,8-cineole, citronellal) 	[28] [78]
	<ul style="list-style-type: none"> Addition of lavender oil (<i>Lavandula angustifolia</i> Mill. X <i>L. latifolia</i> Medik.) Addition of grapefruit oil 	<ul style="list-style-type: none"> EA/IRMS, or GC/C/IRMS ($\delta^{13}\text{C}$ of linalool) FT-Raman spectra, or ATR-IR (β-citronellol, 1,8-cineole, citronellal) 	[28] [78]
	<ul style="list-style-type: none"> Addition of lavender oil (<i>Lavandula angustifolia</i> Mill. X <i>L. latifolia</i> Medik.) Addition of grapefruit oil 	<ul style="list-style-type: none"> EA/IRMS, or GC/C/IRMS ($\delta^{13}\text{C}$ of linalool) FT-Raman spectra, or ATR-IR (β-citronellol, 1,8-cineole, citronellal) 	[28] [78]
	<ul style="list-style-type: none"> Addition of lavender oil (<i>Lavandula angustifolia</i> Mill. X <i>L. latifolia</i> Medik.) Addition of grapefruit oil 	<ul style="list-style-type: none"> EA/IRMS, or GC/C/IRMS ($\delta^{13}\text{C}$ of linalool) FT-Raman spectra, or ATR-IR (β-citronellol, 1,8-cineole, citronellal) 	[28] [78]

(continued on next page)

Table 4 continued

Latin name	Kind of adulteration	Analytical methods and target of the analysis	Ref.
Lemon (<i>Citrus limon</i> L. Burm. F.)	<ul style="list-style-type: none"> Addition of sweet orange oil (<i>Citrus aurantium</i> var. <i>sinensis</i> L.) Addition of other origin (Ivory coast, USA, Argentina) in Italia Addition of synthetic (+)-(2R,4S)-cis-rose oxides, (+)-(2S,4S)-trans-rose oxides 	<ul style="list-style-type: none"> GC ultra-Fast (presence of δ-3-carene) HPLC (Presence of oxypeucedanine, oxypeucedanine oxide, byakangelcol) Enantio-MDGC ((+)-(2R,4S)-cis-rose oxides, (+)-(2S,4S)-trans-rose oxides) 	[42] [93] [29]
Lemon balm (<i>Melissa officinalis</i> L.)	<ul style="list-style-type: none"> Addition of synthetic (-)-(S)-citronellal, (+)-(R)-citronellal, or (-)-(S)-citronellol, (+)-(R)-citronellol Addition of lemon grass oil (<i>Cymbopogon citratus</i> (DC.) Stapf) or of citronella species oil (<i>Cymbopogon</i>) Addition of citronellal, or citral Addition of citronella essential oil (<i>Cymbopogon nardus</i> (L.) Rendle) Addition of coconut oil 	<ul style="list-style-type: none"> Enantio-MDGC ((-)-(S)-citronellal, (+)-(R)-citronellal, or (-)-(S)-citronellol, (+)-(R)-citronellol) IRMS (Lemon balm is a C3 plant and citronella is a C4 plant and C3 plants are much more depleted in their $\delta^{13}\text{C}_{\text{PDB}}$ levels than those from C4 source) Enantioselective-GC (Citronellal or citral) Enantioselective-GC (Citronellal) Physical analysis (Noting the changes in the physical constants and solubility in 70% alcohol) 	[29] [29] [35] [59] [31]
Lemongrass (<i>Cymbopogon citratus</i>)	<ul style="list-style-type: none"> Addition of synthetic citral 	<ul style="list-style-type: none"> Enantioselective-GC & IRMS (Citral) 	[35,41]
Lemony Litsea (<i>Litsea cubeba</i> (Lour.) Pers.)	<ul style="list-style-type: none"> Addition of terpineol 	<ul style="list-style-type: none"> IRMS ($\delta^{13}\text{C}$ of terpineol) 	[41,42]
Lime (<i>Citrus aurantifolia</i> (Christm.) Swingle)	<ul style="list-style-type: none"> Addition of terpinolene Addition of methyl-N-methyl anthranilate 	<ul style="list-style-type: none"> IRMS ($\delta^{13}\text{C}$ of terpinolene) GC-IRMS ($\delta^{13}\text{C}_{\text{PDB}}$, $\delta^{15}\text{N}_{\text{AIR}}$ values of methyl-N-methyl anthranilate) 	[41,42] [34,41]
Mandarin (<i>Citrus reticulata</i> Blanco)	<ul style="list-style-type: none"> Addition of sweet orange oil terpenes in cold-pressed oil 	<ul style="list-style-type: none"> GC-IRMS (The content of Δ-3-carene (present only in traces in mandarin oil), and the Δ-3-carene/camphene and Δ-3-carene/α-terpinene ratios) 	[25]
	<ul style="list-style-type: none"> Addition of distilled mandarin in cold-pressed oil 	<ul style="list-style-type: none"> GC-IRMS (Ratios between specific components, mainly terpinen-4-ol/citronellal, or terpinene-4-ol/decanal) 	[25]
Mint (<i>Mentha</i> L.)	<ul style="list-style-type: none"> Addition of synthetic methyl acetate 	<ul style="list-style-type: none"> HPTLC-enantio-GC coupling (Methyl acetate) 	[29]
Neroli (<i>Citrus aurantium</i> L. spp. <i>Amara</i> L. var. <i>pumilia</i>)	<ul style="list-style-type: none"> Addition of linalool 	<ul style="list-style-type: none"> HRGC-P-IRMS (Linalool) 	[55]
Niaouli (<i>Melaleuca quinquenervia</i> (Cav.) S. T. Blake)	<ul style="list-style-type: none"> Addition of tea tree (<i>Melaleuca alternifolia</i> Cheel) 	<ul style="list-style-type: none"> HPTLC (Presence of purple zone (Rf = 0.26)) 	[104]
Onion (<i>Allium cepa</i> L.)	<ul style="list-style-type: none"> Addition of cajeput oil (<i>Melaleuca leucadendra</i> L.) 	<ul style="list-style-type: none"> HPTLC (Presence of violet double zone (Rf = 0.23, Rf = 0.25)) 	[104]
Orange (<i>Citrus sinensis</i> Osbeck)	<ul style="list-style-type: none"> Addition of furanone Addition of turpentine oil in cold-pressed oil, or in flower oil 	<ul style="list-style-type: none"> GC-MS (Furanone, 2-n-hexyl-5-methyl-3(2H)furanone) UV spectrophotometry (Maximum absorption) 	[41] [20]
Patchouli (<i>Pogostemon cablin</i> Benth.)	<ul style="list-style-type: none"> Addition of cottonseed in cold-pressed oil, or in flower oil Addition of gurjum balsam Addition of <i>Mentha arvensis</i> L. essential oil 	<ul style="list-style-type: none"> UV spectrophotometry (Maximum absorption) GC-MS (The abnormal presence of α-gurjunene and alloaromadendrene) Enantioselective-GC (If level of (-)-isopulegol is around 1.2 to 2.0% it's indicative of <i>M. arvensis</i> L., average of <i>M. piperita</i> L. is 0.7%) 	[20] [16] [24,41]
Peppermint (<i>Mentha X piperita</i> L.)	<ul style="list-style-type: none"> Addition of racemic menthyl acetate Addition of mineral oil Addition of fraction Addition of synthetic borneol 	<ul style="list-style-type: none"> Enantioselective-GC ((-)-menthyl acetate present at -2–8%. Adulteration if (+)-menthyl acetate present) Physical, and chemical techniques (Turbidity when oil is added to 60–80% ethanolic solution) Enantio-MDGC ((1S)-(-)-borneol of high enantiomeric purity (>90%) is a reliable indicator of genuine of rosemary oils) Enantio-MDGC ((1S)-(-)-borneol of high enantiomeric purity (>90%) is a reliable indicator of genuine of rosemary oils) 	[24] [41] [29,41] [29]
Rosemary (<i>Rosmarinus officinalis</i> L.)	<ul style="list-style-type: none"> Addition of synthetic linalool 	<ul style="list-style-type: none"> ESI-MS, or HRGC-P-IRMS (Linalool) 	[55,105]
Rosewood (<i>Aniba rosaeodora</i> Ducke)	<ul style="list-style-type: none"> Addition of synthetic Sandalore 	<ul style="list-style-type: none"> GC-MS (Presence of Sandalore) 	[52]
Sandalwood (<i>Santalum album</i> L.)	<ul style="list-style-type: none"> Addition of castor oil or cedarwood oil Addition of Verdox, Santaliff, Vertofix Coeur, Ebanol Addition of polyethylene glycol Addition of anethole Addition of ajwain seeds oil (Trachyspermum amni L.) Addition of linalool Addition of vegetal oil 	<ul style="list-style-type: none"> GC-MS, GC-FID (Specification content of compounds) MDGC-qMS/FID (Presence of Verdox, Santaliff, Vertofix Coeur, Ebanol) TLC (Polyethylene glycol) ^2H NMR spectrometry (Anethole) GC-IRMS ($\delta^{13}\text{H}$ of thymol) HRGC-P-IRMS (Linalool) HPTLC (Presence of zone (Rf = 0.69)) 	[52] [53] [32] [41,106] [39] [55] [72]
Star anise (<i>Illicium verum</i> L.)			
Thyme (<i>Thymus vulgaris</i> L.)			

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