

Detecting Essential Oil Adulteration

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Abstract

An upsurge in worldwide essential oil sales seems to have intensified corrupt practices by unscrupulous cost-cutters and adulterators with varying levels of expertise. From outright misrepresentation of botanical species to the addition of cheaper oils to create additional profit for the oil producer, adulteration is unfortunately a common place occurrence in essential oil trade.

The most adulterated essential oils fall into two categories: high-value oils like sandalwood and rose and the best-selling oils such as lavender, peppermint, citrus oils, wintergreen, oregano, and thyme. While some adulterations can be detected simply by routine GC-MS testing, with technology such as GC-IRMS and SNIF-NMR, analysts are able to spot adulteration with synthetic compounds or the natural compounds and/or oil fractions taken from cheaper essential oils. Today's cutting-edge technology for essential oil adulteration detection encompasses many analytical techniques from HPLC and fast GC to GC × GC, IRMS to MS, ¹H, and ¹³C NMR.

This paper is a review of 30 studies dating up to May 2014 that detail the analytical procedures used to uncover essential oil adulteration in order to ensure that essential oils are authentic and genuine.

Introduction

Nearly two millennia ago, Pliny the Elder wrote, "It is the natural propensity of man to falsify and corrupt everything." His words referred to such practices as the then-common adulteration of wine with gypsum, pitch, lime, rosin, wood ashes, salt, sulphur, artificial pigments, etc [1]. While wine fraud is still with us, the more common food adulteration is the topic of over 60,000 studies on PubMed, where this contamination is termed Economically Motivated Adulteration (EMA) [2].

Riding a popular natural health trend, the aromatherapy market in the United States enjoyed retail sales of nearly \$32 million in 2012, a 17.7% increase over 2011 totals [3]. The United States is home to a large direct-sale essential oil industry as well. More impressive gains were posted for world trade in essential oils: sales rose from just over U.S. \$706 million in 1990 to slightly over U.S. \$1.7 billion in 2005 [4].

Unfortunately, this burgeoning market has encouraged the adulteration of essential oils. A brief Medline search revealed 30 studies dealing with this topic. A study conducted at the University of Messina in Italy reports that "Unscrupulous producers have begun to fraudulently increase profits while keeping down raw material costs mainly through the addition of cheaper oils or oil constituents" [5]. While Pliny was undoubtedly at the forefront of first-century chemistry, his simple balsam purity test—"Moreover a drop of pure balsam thickens in warm water, settling to the bottom of the vessel, whereas when adulterated it floats on the top like oil" [6], would hardly pass muster today.

Some oil adulterations are easily red-flagged with routine testing; e.g., adulterated cinnamon bark (*Cinnamomum verum*) essential oil that has been diluted with cheaper cinnamon leaf oil can be detected because leaf oil has a higher content of eugenol, which is handily ascertained with GC analysis. Other adulterations require more advanced technology. A 1997 study in the Journal of Essential Oil Research states that "as the latest progress in origin specific analysis of essential oils and flavors, an integral authenticity evaluation, including isotopic data, enantiomeric distributions, as well as quantification of compounds analyzed, has been established" [7].

However, a worldwide consensus for essential oil constituent standards has not yet been established. The International Organization for Standardization (ISO) and Association Française de Normalisation (AFNOR) have set constituent levels for certain essential oils. However, hundreds of oils lack international standards, creating uncertainty. International standards are critical for essential oil trade and commerce.

Meeting Essential Oil Standards

For the oils that do have ISO standards, natural variations resulting from climate, geography, and altitude must be considered.

Peppermint (*Mentha piperita*) oil is the perfect example. The U.S. produces nearly 80% of global peppermint essential oil, most of which is grown specifically for flavoring gum, candy, food, toothpaste, mouthwash, pharmaceuticals, and confectionaries. It is estimated that less than 1% of the U.S.-grown peppermint essential oil is available to the aromatherapy/alternative health care industry. This makes India the largest supplier of peppermint essential oil for aromatherapy markets and introduces geographically unique oil when analyzing for possible adulteration. Because of geographical differences, ISO standards are different for U.S.-grown peppermint and the peppermint grown in India.

India also produces cornmint (*Mentha arvensis*), a less-expensive mint plant that is frequently used as a peppermint adulterant. This can be avoided by carefully considering analytical analyses. Cornmint is higher in menthol, while peppermint contains unique marker compounds that identify it as genuine. Menthofuran is found in peppermint in levels from 0.4 to 14.6%, while this compound is either not detected or is detected only in levels up to 0.01% in cornmint. The biomarker viridifloral is found in peppermint up to 0.9%, while it is not detected in cornmint.

Enantiomeric Analyses

Mosandl reports that "the systematic evaluation of natural enantiomeric ratios has been proven to be a valuable criterion for

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differentiating natural compounds from those of synthetic origin" and that "under good manufacturing practice (GMP) the chirality evaluation of linalool has been proven to be a reliable indicator in the authenticity assessment of bergamot, sweet orange, or lavender oils" [8]. Chanotiya et al. employed enantiomeric composition studies as indicators of origin authenticity and quality of essential oils of Indian origin: *Citrus sinensis*, basil, bergamot, rose, geranium, *Lippia alba*, *Zingiber roseum*, lemongrass, and oregano [9].

Researchers at Service Central d'Analyse in France tested for adulteration in the essential oils of lemon, lemongrass, citronella, *Litsea cubeba*, *Lippia citriodora*, and lemon balm (*Melissa officinalis*). They report: "Our results indicate the utility of combined chiral and isotope analysis and use of the statistical method PCA for analysis of composition for detecting the adulteration and for determining the botanic origin of essential oils" [10].

Orthogonal Methodology

Swiss researchers note in a May 2014 study, "Since a control of authenticity by standard analytical techniques can be bypassed using elaborated adulterated oils to pretend a higher quality, a combination of advanced orthogonal methods has been developed" [11]. One such method was employed by French researchers using 2H-ERETIC-NMR technology on 19 samples of methyl salicylate (natural/synthetic and commercial/extracted). They found that deuterium site-specific natural isotope abundance "allows discrimination between synthetic and natural samples". [12] Wintergreen remains one of the most commonly adulterated essential oils, with the ease of synthetic methyl salicylate substitution or dilution. In fact, synthetic methyl salicylate is also known as "oil of wintergreen."

Cold-pressed citrus oils are found in multiple products relating to human health. Because of their high cost, synthetic chemicals and cheaper essential oils are common adulterants.

An Italian study using fast-GC/MS and HPLC analysis shows that a lemon essential oil was found to contain herniarin, isopimpinellin, and 5-heranyloxy-8-methoxypсорalen, normally present only in lime oil. This study concludes, "The experimental results shown in this study demonstrate that fast-GC/MS and HPLC remain one of the most effective means to detect these illegal modifications" [13]. HPLC and GCxGC were the technologies used to determine genuineness of two citrus oils, bergamot and sweet orange, in a recent Italian study [14].

A study conducted at Shiraz University of Medical Sciences in Iran reports that many of 19 tested samples of rose water did not contain rose essential oil but instead had the cheaper essential oil of palmarosa (*Cymbopogon martinii*), as determined by unusual δ (13)C values using GC/IRMS analysis. It states, "The increase in market demand has led to production of inferior products for hydrosol that contain synthetic essences or essential oils of other plants. Dibutyl phthalate was also detected in most samples" [15]. The latter plasticizing chemical is known as a reproductive and developmental toxicant and endocrine disrupter.

Hervé Casabianca on Thyme Adulteration

In a communication [16] from Hervé Casabianca, French expert in natural product analysis, he reiterates that using classical analysis, a person is not able to differentiate a natural from a synthetic flavoring molecule. He explained that by using IRMS, we can easily compare natural versus synthetic thymol because natural thymol must be deuterium depleted and ^{18}O enriched. Casabianca's research using deuterium/hydrogen ratio analysis of the essential oil constituent's

thymol, carvacrol, gamma-terpinene, and p-cymene is published in the Journal of Chromatography A [17].

Rose and Sandalwood Adulteration

We close with research on adulteration of high-value essential oils.

Rose oil (*Rosa damascena*) sells for as much as U.S. \$240 for a 5-milliliter bottle. It is, therefore, no surprise that university scientists from Italy used GC/C/IRMS in combination with GC/MS and GC/FID analysis on 19 commercial samples and found unusual δ (13)C values in most of the oils, indicating that a natural, cheaper palmarosa oil (*Cymbopogon martinii*) had been added [18].

Vankar reports the rose oil adulterator "now has to his disposal a number of natural isolates of lower-priced oils. The most important of these are geraniol and rhodinol (*l*-citronellol). If added in moderate quantities, these compounds cannot be detected in rose oil by mere routine analysis" [19]. Chanotiya, as previously mentioned, used enantioselective capillary gas chromatograph-flame ionization and mass spectrometry to determine the authenticity and quality of Indian essential oils, including rose [20]. Moein notes Iranian rose water samples were adulterated with less expensive essential oils (Pelargonium and Dianthus) and synthetic essences [21].

Because of shortages related to sustainability issues, sandalwood is an attractive target for adulteration. Distilled from the heartwood of the tree, sandalwood essential oil international standards require 90% total santalol content. Testing in 2004 revealed all tested samples failed to comply with the santalol content requirement, and only about half of the samples met the ISO standard [22]. Kuriakose et al. suggests that "NIR spectroscopy with chemometric techniques could be successfully used as a rapid, simple, instant and non-destructive method for the detection of adulterants, even 1% of the low-grade oils, in the high quality form of sandalwood oil" [23]. Updating the previous 2010 research in November 2013, Kuriakose et al. focused on "the application of near infrared spectroscopy to detect sample authenticity and quantify economic adulteration of sandalwood oils. Several pre-treatments are investigated for calibration and prediction using partial square regression (PLSR)" [24].

Summary

In summation, illegal essential oil adulteration and contamination scandals now require sophisticated and highly technical methods to authenticate the oils. Analytical chemistry must be employed in all its forms to thwart the escalating, economic adulteration of these valued therapeutic agents.

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