Volatilomics Profiling of Counterfeit Perfume by Gas Chromatography Hyphenated to Mass Spectrometry and Fourier-Transformed Infrared Spectroscopy

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Abstract: *To prevent deleterious effects on consumers and potential health damage caused by counterfeit perfumes, this study aims to distinguish the original perfume from its suspected counterfeit products. Fingerprint and volatilomics profiling was performed using attenuated total reflection-Fourier infrared spectroscopy (ATR-FTIR) and gas chromatography hyphenated to mass spectrometry (GC-MS). Headspace (HS)-GC-MS was optimized to analyze perfume samples containing water. In the presence of water, our optimized HS-GC-MS method shows linalool's consistent signal intensity, providing an alternative analytical method for water-based perfume formulation. The GC-MS chemical characterization revealed 45 compounds detected in the original sample but only four compounds were detected in the counterfeit products: linalool, citronellol, methyl jasmonate, acetic acid, and propanol. This suggests a clear difference in the formulation of counterfeit products. Counterfeit products also cheat by using a lower amount of ingredients. Relative quantification shows that linalool in counterfeit products was as low as only 5.1% of the amount in the original product. In addition, cheaper and hazardous materials like methanol and 6,7-dihydrogeraniol were detected in counterfeit products. The combination of ATR-FTIR, GC-MS, and HS-GC-MS demonstrated fast authentication of counterfeit perfumes for routine quality control purposes and the possibility of water-based perfume analysis.*

Keywords: *headspace gas chromatography; mass spectrometry; volatilomics; cosmetic analysis*

■ INTRODUCTION

Perfume (*eau de perfume*) is a mixture of odorly compounds that enable to gain a long-lasting, agreeable, and desirable scent. In general, a perfume consists of top notes (typically citrus with green notes to give initial impact and freshness), middle notes (typically spicy, leather, or floral, to give the main character of a product), and base notes (typically amber or musk, to give substantivity), dissolved in a solvent (alcohol, water, or matrix) [1]. Perfume is used regularly to increase mood and confidence, to give aphrodisiac reasons, or to meet social expectations for always smelling pleasantly fresh [2-3]. To achieve a signature scent, a high-quality luxury perfume is formulated using natural fragrances such as essential oils derived from various plants and musky components extracted from animal sources [4-6]. Synthetic aromatics are often added to the formulation as an alternative for rare natural fragrance sources, to add novel scents that are not found in nature, to minimize problems with poor crop quality, or to reduce the production cost [7].

A combination of high demand, expensive natural fragrances, and difficult access to rare ingredients leads to the booming of adulterated or counterfeit perfume products [8]. A perfume is usually adulterated by diluting the original product, mixing it with cheaper materials, using low-quality ingredients, adding different materials, or even adding harmful compounds [9]. These methods cause economic loss, deleterious effects to consumers, and potential allergy or health damage

[2]. Therefore, chemical characterization of perfume products is important for authentication purposes, production quality control, and consumer protection. Since perfume mostly consists of volatile compounds, it can be characterized based on its volatile profiles [10].

Several analytical methods have been reported for the analysis of perfume ingredients, such as liquid chromatography (LC), Fourier-transformed infrared spectroscopy (FTIR), and gas chromatography (GC). LC separates and analyzes compounds based on their hydrophobicity and has been a method of choice in many analytical applications as it is well-developed, reliable, and robust. However, LC requires a liquid sample to be carried by a liquid mobile phase to the analytical column, making it indirectly suitable for volatile compounds analysis [11]. FTIR offers fingerprint analysis but fails to provide complete structural information and identification of each compound [12-13]. GC offers a most convenient method for the analysis of volatile compounds [14-16]. GC method has been applied widely for essential oils analysis from various plants and flowers as well as fragrances and perfumery analysis [17-21]. However, conventional GC is water incompatible, disturbing column selectivity, if perfume formulated using a water-based solvent is analyzed [21]. Although previous studies have developed water-compatible GC by modifying columns in the stationary phase where the compound separation takes place [22-23], such a column is costly and not readily available on the market.

Headspace GC (HS-GC) offers the possibility to analyze volatile compounds even in the presence of water in the sample [24-26]. In HS-GC, the sample is heated and agitated in a closed vial to allow an equilibrium state between the gas phase and the sample before the introduction to the column, preventing the transfer of non-volatile compounds into the GC-MS system, thus resulting in cleaner peaks and less signal noise [27]. Apart from that, HS-GC provides direct sample analysis without prior sample preparation, such as extraction, making it suitable for analyzing volatile compounds from either liquid or solid samples [28]. This method has been well-applied in the food and beverage industry [29-30], forensic science [31], and personal care industry [32-33].

Despite the superiority of HS-GC over conventional GC, this technique often suffers from peak splitting and broadening due to the large sample volume produced in the gas phase and the presence of moisture [34]. Therefore, optimization is essential to overcome limitations and ensure optimal analytical conditions. As for the detection method, mass spectrometry (MS) can be coupled to both GC and HS-GC to achieve higher sensitivity and possible chemical structure elucidation [35]. In this study, FTIR was first performed to screen for fingerprints of suspected counterfeit perfumes. GC-MS and HS-GC-MS for volatile compound identification were then examined and compared. Lastly, HS-GC-MS was optimized for better sensitivity and selectivity, even with the presence of water in the sample. We demonstrate the possibility of a fast, simple, and reliable method for routine quality control purposes by combining FTIR and HS-GC-MS.

■ EXPERIMENTAL SECTION

Materials

An original luxury brand perfume labeled *eau de perfume* purchased from its official store was used as the original sample. This original sample is a mixture of top notes (Green Notes and Orange), middle notes (Jasmine Sambac, Honeysuckle, Tuberose), and base notes (Sandalwood and Orris Root). Eight of its suspected counterfeit products assigned as C1 to C8 were obtained from various local stores or online marketplaces in Indonesia. Analytical grade ethanol (99.8%) and water were purchased from Merck KGaA (Darmstadt, Germany).

Instrumentation

FTIR Thermo Nicolet iS10 ATR Diamond (Thermo Fisher Scientific, Waltham, MA, USA) was equipped with a DTGS detector for fast fingerprint characterization. Thermo Scientific Trace 1310 GC (Thermo Fisher Scientific, Waltham, MA, USA) coupled to a Thermo Scientific ISQ LT single quadrupole mass spectrometer detector with electron ionization source (EI) (Thermo Fisher Scientific, Waltham, MA, USA) was used for further volatile compounds characterization.

This GC-MS system was equipped with a static headspace and a Thermo Scientific TriPlus RSH autosampler (Thermo Fisher Scientific, Waltham, MA, USA).

Procedure

Compounds characterization with ATR-FTIR

Attenuated total reflection-FTIR Spectroscopy (ATR-FTIR) spectra of the original sample and all its suspected counterfeit products were obtained using FTIR Thermo Nicolet iS10 ATR Diamond equipped with DTGS detector. The measurement of each sample was done in three replicates. A 20 μL sample was deposited in the ATR diamond cell dropwise and measured simultaneously until the scans were finished to avoid sample evaporation. The ATR-FTIR spectra were obtained in the range between 600 and 4000 cm^{-1}, with a resolution of 4 cm^{-1} and 32 scans per spectrum. The background spectrum of the empty ATR cell was obtained under the same instrumental conditions after cleaning the ATR crystal with ethanol 95% and before each sample measurement [12].

Volatile compounds characterization with GC-MS and HS-GC-MS

Samples were analyzed and coupled to a single quadrupole mass spectrometer detector (GC-MS) with an EI source. The method used in this study followed the basic principle of HS explained by Sithersingh and Snow [30]. The chromatographic separation was performed using an HP-5MS UI column (30 m × 0.25 mm: 0.25 μm). Helium was used as carrier gas with a flow rate of 1 mL/min. For conventional GC-MS analysis, injection volume was set to 1 μL, and the syringe temperature was 200 °C. For HS-GC-MS analysis, a 100 μL sample was put into a 20 mL HS vial, the HS agitator temperature was set to 120 °C with 5 min incubation time, and an injection volume of 1,000 μL gas phase, unless stated otherwise for method optimization purposes. The gradient for both GC-MS and HS-GC-MS started at 45 °C for 3 min and gradually increased to 200 °C at 10 °C/min rate for 3 min, resulting in a total runtime of 22 min. The ionization mode was EI in positive mode with 230 °C ion source temperature. The full mass scan was done from 25 amu to 350 amu with 0.2 s scan time.

Method optimization of HS-GC-MS

The original sample, containing linalool, was used as a model sample to optimize the HS-GC-MS method. Optimization of the sample introduction system in HS-GC-MS was performed by varying one independent parameter at a time while the remaining parameters were kept constant [36]. The parameters checked were headspace temperature (90–120 °C), incubation time (5–30 min), initial sample volume in 20 mL HS vial (5, 10, 20, 30, 50, and 100 μL), and water amount in the sample (10, 30, 50, 70, and 90%). A total of 21 single-factor experiments were carried out to determine the effect of selected parameters on the signal intensity of linalool's total ion chromatogram (TIC).

Data processing for GC-MS and HS-GC-MS

The National Institute of Standards and Technology (NIST 14) database and library available as a bundle with the Chromeleon software in the GC-MS instrument was used for the identification of compounds from the GC-MS and HS-GC-MS experiments by spectra matching identification. The similarity between unknown spectra from the experimental data and the spectra library was presented as a match factor (SI score). A higher SI score means higher similarity, thus a higher probability of correct identification. SI score of > 900 is labeled as an excellent match, 800–900 is a good match, 700–800 is a fair match, and 600–700 is a poor match. In this study, only compounds with SI scores of > 700 were considered as confidently identified and presented in this article.

■ RESULTS AND DISCUSSION

ATR-FTIR Spectra of Original Sample and Its Suspected Counterfeit Products

A quick test using FTIR from 600 to 4000 cm^{-1} was performed to see general spectra patterns among samples by looking at bands of major functional groups. In FTIR, the spectra quality and signal-to-noise ratio can be enhanced by increasing the scan number to 64 or even 128 scans. However, in the ATR module, the IR signal is attenuated significantly at the element-sample boundary by the absorption characteristics of the surface layer.

Therefore, scans beyond 32 do not dramatically improve the spectra quality [37].

In our study, we focused on identifying the differences between original and counterfeit samples through the IR spectra fingerprint, and a scan number of 32 was enough for this purpose, indicating the absence of the need to emphasize on a higher number of scans to achieve better quality spectra. In addition, scan number 32 instead of 64 or higher reduced the time required to acquire the spectrum, which is desirable to obtain a faster method, especially when dealing with easily evaporating compounds in perfume samples. Fig. 1 shows the ATR-FTIR spectra of all nine perfumes zoomed at 600 to 2400 cm^{-1}. The presence of the characteristic vibration bands of the main components of each sample can be seen, and they appear to have high similarity among samples. Only sample 2 shows different peak patterns at 800–900 cm^{-1}. Strong bands on 1045 and 1087 cm^{-1} were spotted in all samples associated with C–O stretching, while weak bands seen on 1724 cm^{-1} for all samples possibly correspond to the carbonyl group (C=O). For samples 1, 4, 5, and 6, bands at 1045 and 1087 cm^{-1} shifted to lower wavenumber, which tells the presence of the same functional group but different neighboring substituent functional group [13]. In other words, those bands might come from different compounds, but they

have C–O in their functional groups. Spectra of samples 3, 7, and 8 show a similar pattern to the spectra of the original sample. In the spectra of the original sample and samples 3, 7, and 8, the absorption peak of C$_{sp2}$–H bending vibration of the aromatic ring was observed around 879 and 802 cm^{-1}. The spectra of samples 1, 4, 5, and 6 clearly show the absence of those two bands. This absence can be attributed to the absence of aromatic ring compounds in samples 1, 4, 5, and 6.

Although they are similar, a quick analysis from the ATR-FTIR spectra concluded that those nine samples differed. It showed that ATR-FTIR spectroscopy can be used for the rapid quality control and adulteration check of commercial perfumes without using either sample preparation or analyte separation. However, this method is limited to general spectra fingerprint recognition with a general conclusion on the main functional groups of compounds in the sample and lacks comprehensive identification and characterization in each sample. The limitation of ATR-FTIR was more noticeable when manually looking at samples 3, 7, 8, and the original sample whose ATR-FTIR spectra were very similar. Utilizing the chemometric method for analyzing the ATR-FTIR fingerprint of samples 3, 7, 8, and original may provide more information related to the composition of
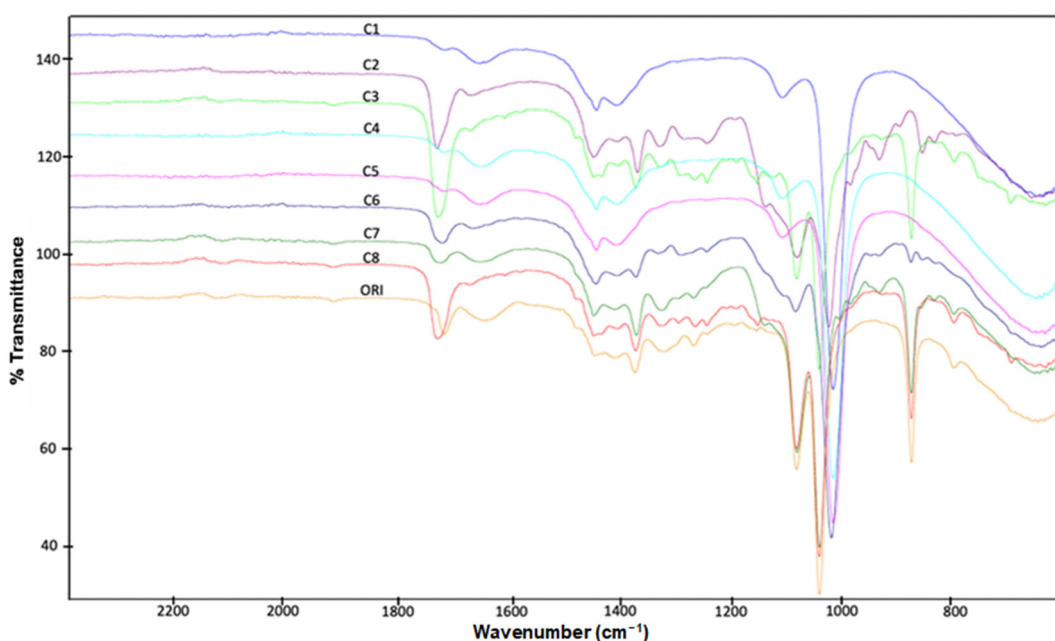

Fig 1. ATR-FTIR spectra of the original sample and its suspected counterfeit products (C1–C8)

major compounds present in the sample and the degree of differences between samples [38]. However, it will still be unable to provide information regarding the exact identity of complete compounds in each sample, especially the minor components. On the other hand, the use of GC-MS or HS-GC-MS clearly identifies the compounds in the sample (see Table 1). This is possible due to the availability of fragments ions generated during MS analysis that provide more confident characterization.

GC-MS vs HS-GC-MS for Characterization of Volatile Compounds

The limitation of ATR-FTIR for comprehensive compounds identification and characterization can be tackled by performing GC-MS analysis. In this study, volatile compounds of all samples were analyzed and characterized using both conventional GC-MS and HS-GC-MS methods. Fig. 2 shows the TIC of the original sample analyzed with both methods. It can be seen clearly that conventional GC-MS shows higher peak intensity and higher number of detected peaks, especially peaks eluted after 15 min. This can be explained by the fact that all compounds in the sample were injected into the conventional GC system in liquid form. In contrast, only compounds evaporated below the agitator temperature were injected in HS-GC. However, the peaks in the HS-GC-MS appeared cleaner and sharper, with better signals for noise. This is possible due to limited or no transfer of non-volatile compounds into the system. In conventional GC, non-volatile compounds such as water and sample matrix introduced to the system with the sample may interfere with the analysis. Liquid non-volatile compounds will deposit in the GC column, resulting in peak spitting and retention time shifts [21]. Spectra matching identification was performed to identify peaks by comparing the unknown peaks to those peaks in the library, as can be seen in Fig. 3. Compilation of compounds identified in conventional GC-MS and HS-GC-MS were listed in Table 1 for the original sample and its counterfeit products.
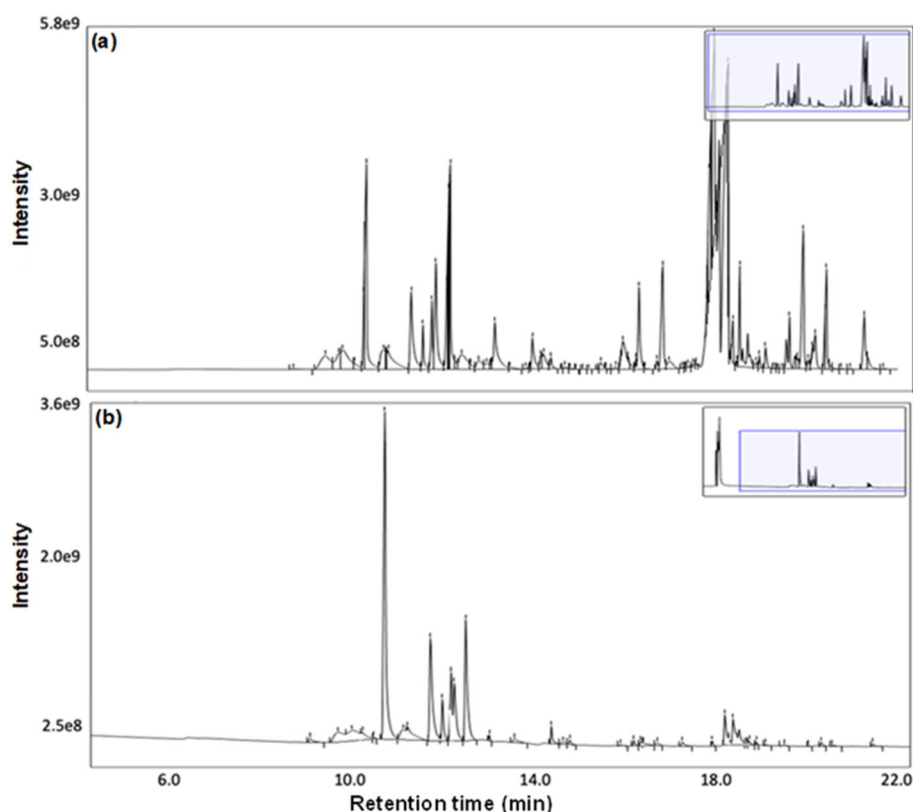

Fig 2. TIC of the original sample was analyzed with conventional GC-MS (a) and HS-GC-MS (b), using the same gradient elution of 45 to 200 °C at a 10 °C/min rate

Table 1. Volatile compounds identified in the original sample and its eight suspected counterfeit products

No.	SI hint*	Compound (identified in original sample)	Perfumery information	C1	C2	C3	C4	C5	C6	C7	C8
1	882	Ethanol**	solvent	-	-	√	-	-	-	√	√
2	903	1,1'-Oxybis-2-propanol	solvent for enhancing a fragrance formulation	√	√	√	√	√	√	√	√
3	743	2,6-Dimethyl-7-octen-2-ol	common fine fragrance ingredient	-	-	-	-	-	-	-	-
4	752	cis-Linalool oxide	gives additional lift to floral accords	-	-	√	√	√	-	√	√
5	943	Linalool**	a floral and spicy terpene alcohol, from flowers such as lavender and citrus	√	√	√	√	√	√	√	√
6	888	Phenylethyl alcohol	gives medium odor impact (rose notes)	√	-	√	√	√	√	-	√
7	835	3,7-Dimethyl-1,6-nonadien-3-ol	a fragrance ingredient	√	√	√	-	-	√	√	√
8	962	Phenylmethyl acetate	floral top note smells of flowers and civet	√	√	√	√	√	√	√	√
9	832	1-(1-Oxobutyl)-1,2-dihydropyridine	detected in essential oil of black pepper	√	-	√	√	√	√	√	-
10	834	Citronellol**	natural acyclic monoterpenoid found in citronella oils	√	√	√	√	√	√	√	√
11	863	Geraniol**	a monoterpenoid found in citronella oil, rose oil, and palmarosa oil	-	-	√	√	√	√	√	√
12	901	Linalyl acetate	the acetate ester of linalool	-	-	√	-	-	√	√	-
13	816	4-(1-Methylethyl)-trans-cyclohexanemethanol	has a fresh, soft, and clean floral odor reminiscent of white petals and blossoms	-	-	-	-	-	√	√	√
14	870	4-(1-Methylethyl)-cis-cyclohexanemethanol	has a fresh, soft, and clean floral odor reminiscent of white petals and blossoms	√	-	√	-	√	√	√	√
15	792	Geranyl vinyl ether	diffusive ethereal fruity green	√	-	√	-	-	-	√	-
16	839	7-Hydroxy-3,7-dimethyl-octanal	gives citrus and melon undertones	√	-	-	-	√	√	√	√
17	740	8-Hydroxymenthol	menthol	√	-	-	√	√	-	-	-
18	756	Citronellyl butyrate	adds freshness to rose and geranium compositions	-	-	-	-	-	-	-	-
19	890	Eugenol**	used to create a spicy, clove-like scent	√	-	√	-	√	√	-	√
20	929	Farnesol**	nature-inspired sesquiterpene alcohol	-	-	-	-	-	-	-	√
21	733	1,2-Dihydrolinalool	synthetic aroma ingredient with fresh floral, citrusy, woody, and slightly fruity	-	-	-	-	-	-	-	-
22	859	Geranyl acetate	acetate ester of geraniol	-	-	√	-	-	√	√	√
23	725	Isobornyl thiocyanoacetate	from *Illicium verum*	-	-	-	-	-	-	-	-
24	773	(*R*)-Lavandulyl acetate	acetate ester of lavandulol	-	√	√	-	-	√	-	-
25	810	Jasmone	jasmine bases and floral compositions	-	-	-	-	-	-	-	-
26	821	3-(4-Isopropylphenyl)-2-methylpropionaldehyde	has powerful green notes	-	-	-	-	-	√	-	-
27	801	3,4-Methylenedioxyphenyl acetone	gives sweet, spicy of balsamic fragrance	-	-	-	-	-	-	-	-
28	773	Butylated hydroxytoluene	used as antioxidant in perfumery	-	-	-	-	-	√	-	-
29	913	trans-fl-Ionone	found in essential oils, including rose oil	-	-	-	-	-	-	-	-
30	730	7-epi-cis-Sesquisabinene hydrate	found in aster flowers	-	-	-	-	-	-	-	-
31	801	Isoshyobunone	a natural	-	-	-	-	-	-	-	-
32	929	Nerolidol	sesquiterpene alcohol	-	-	-	-	-	-	-	-
33	702	6-epi-Shyobunol	commonly found in *Zingiber officinale*	-	-	-	-	-	-	-	-
34	769	Methyl jasmonate	for a powerful jasmine flowery note	√	√	√	√	√	√	√	√
35	726	8-Propoxy-cedrane	woody and cedarlike odor	√	√	√	√	-	-	-	-
36	895	Naphtho[2,1-b]furan	amber	-	-	-	-	-	-	-	-
37	703	Ambrox	adds musky and woody tone	√	√	-	-	-	-	-	-
38	916	Isopropyl myristate	a moisturizer, ameliorate the skin absorption	√	-	-	-	-	√	-	√
39	855	5-Cyclohexadecen-1-one	synthetic musk for powdery volume	-	-	-	-	-	-	-	√
40	949	2-Hydroxy-cyclopentadecanone	medium odor strength (powdery, musk)	√	-	-	√	√	-	-	√
41	874	Galaxolide	gives clean sweet musky woody odor	-	-	-	-	-	-	-	-
42	939	Phenylmethyl 2-hydroxybenzoate	used as a solvent for nitro-musk	-	-	-	-	-	-	-	-
43	734	Ethyl 2-cyano-3-methyl-5-phenyl-2-pentenoate	commonly found in fragrance palette	-	-	-	-	-	-	-	-
44	943	Ambrettolide	used as musky perfume base	-	-	-	-	-	-	-	-
45	829	1,2-15,16-Diepoxyhexadecane	found in essential oil from various plants	-	-	-	-	-	-	-	-

*NIST database search scoring function, in which score closer to 1000 indicates higher matching to database spectra, thus higher confidence in identification, only compounds with score higher than 700 were included in this table. **Ingredients mentioned in the packaging information of the original sample
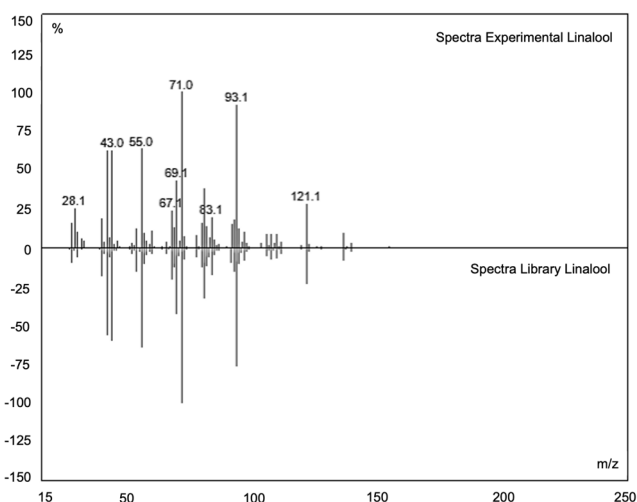
Fig 3. Example of spectra matching identification of linalool in the experiment and NIST 14 library

Evaluation of Counterfeit Perfumes Based on Their Volatile Compounds

Nine samples were tested, including one original sample and eight of its suspected counterfeit products (three samples (C1, C4, and C5) claiming to be original with packaging and information exactly the same as the original sample, while samples C2, C3, C6, C7, and C8 claiming to be decanted from the original perfume bottle or inspired by the original sample but prepared by local perfume artist). Counterfeit perfume can be sold cheaper than the original and generate higher profit. The price point of the counterfeit products used in this study ranges from 10 to 50 USD per 100 mL or more than 3–15 times cheaper than the original sample (155 USD per 100 mL). This price is possible due to the minimum quality and quantity of its ingredients. Adulteration of a perfume is usually done by diluting the original product, mixing it with cheaper materials, using low-quality ingredients, adding different materials, or even adding harmful compounds. Chemical characterization of compounds in all samples can be seen in Table 1. From a total of 45 compounds identified in the original sample with SI score > 700, only four compounds, namely, linalool, citronellol, methyl jasmonate, acetic acid, and propanol, were detected in counterfeit products. Most counterfeit products did not identify main perfume components such as eugenol, farnesol, cedrane, ambrox, and geraniol. This result clearly indicates that counterfeit products have completely different ingredients.

Although linalool was identified in all counterfeit products with an SI score of > 900, the relative amount of linalool in the counterfeit products is very low. This study used fragment ion of linalool in *m/z* of 71.1 to generate the extracted ion chromatogram (XIC). The area of the XIC was then used to compare the quantity of linalool in all samples relatively. Fig. 4 clearly shows a significant difference in linalool content in the original sample and its counterfeit products. Samples C5, for example, claim that it is an original product, but the linalool content is only 5.13%. Four counterfeit products tested in this study were revealed to contain less than 20%
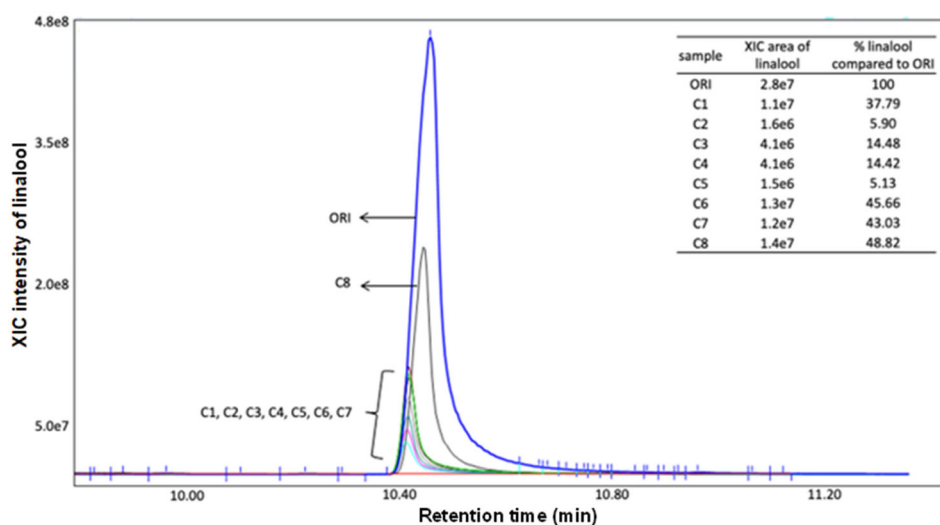

sample	XIC area of linalool	% linalool compared to ORI
ORI	2.8e7	100
C1	1.1e7	37.79
C2	1.6e6	5.90
C3	4.1e6	14.48
C4	4.1e6	14.42
C5	1.5e6	5.13
C6	1.3e7	45.66
C7	1.2e7	43.03
C8	1.4e7	48.82

Fig 4. XIC intensity of linalool of the original sample and its suspected counterfeit products

linalool compared to the original, and the other four samples contained less than 50% linalool of the original.

As perfume is usually sprayed in sensitive areas like the neck, wrist, and behind the ears, perfume may penetrate the skin. Mild solvent should be used in perfume formulation. However, this study found that 5 of 8 counterfeit products (C1, C2, C4, C5, and C6) used methanol as solvent, while the original sample and C3, C7, C8 used ethanol. Methanol has long been known to have adverse effects ranging from skin inflammation, headache, nausea, and cerebral vasculopathy to liver cancer [39-40]. Apart from methanol, a compound named 3,7-dimethyl-2-octen-1-ol known as 6,7-dihydrogeraniol, was also detected in the counterfeit products with SI hit > 850. According to the recommendation of the Scientific Committee on Cosmetic Products and Non-Food Products intended for Consumers (SCCNFP), this compound must not be used in fragrance ingredients due to the absence of reports on the use of this material as a fragrance ingredient and

inadequate evaluation of potential adverse effects resulting from its use in fragrances [41]. In fact, many common fragrance chemicals possess a negative impact if used above a certain level [42]. Their use in original registered products is controlled, while in counterfeit perfumes, it is impossible for the consumers to know. Therefore, it is better to avoid using counterfeit presumes at all costs.

HS-GC-MS Method Optimization

Four different agitator temperature points (90–120 °C) were tested in HS-GC-MS, higher agitator temperature is known to lower the partition coefficient (K value) of the gas phase sample. In the same sample volume, a smaller K value will increase the sample concentration in the gas phase, resulting in increased signal intensity and, thus, increased TIC area of all samples. Fig. 5(a) shows the TIC area of the linalool that increased as the HS agitator temperature was set at a higher temperature. In the HS-GC-MS system, the sample
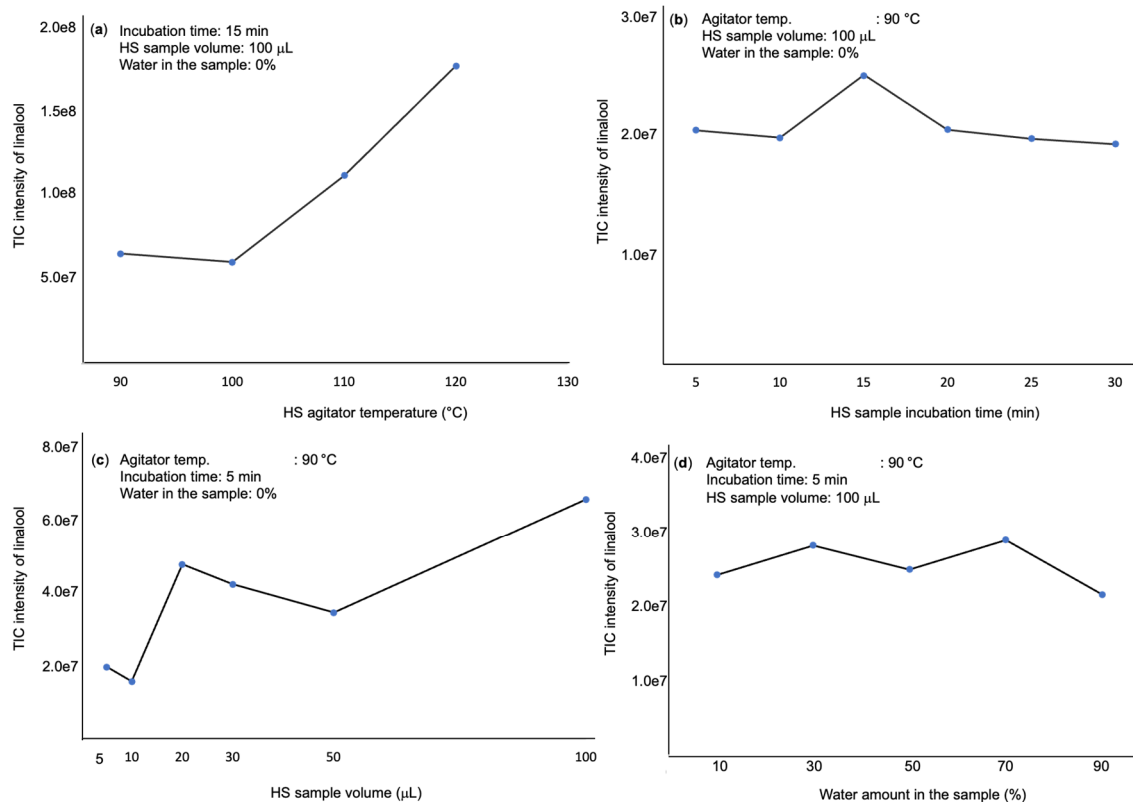

Fig 5. Effect of different HS-GC-MS parameters on TIC intensity of linalool in original sample such as (a) agitator temperature, (b) sample incubation time, (c) sample volume in 20 mL HS vial, and (d) water amount in the sample

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is heated for a period in a selected agitator temperature, thus the peak intensity might also be affected by sample incubation time. Incubation times from 5 to 30 min were tested for samples heated at 90 °C agitator temperature. No significant change in the signal intensity was observed with the longer incubation time (see Fig. 5(b)). The TIC intensity was highest at an incubation time of 15 min but then slightly decreased as the incubation time increased. For more efficient analysis, 5 min incubation time was chosen for all experiments in this study, while the agitator temperature was set to 120 °C. When the K value is small (due to high agitator temperature), the volume of gas and volume of liquid put in the sample vial might greatly affect signal intensity. It can be seen from Fig. 5(c) that increasing the sample volume in 20 mL HS vial from 5 to 100 μL increased the TIC area of the linalool.

In HS-GC, water evaporation can be avoided if the agitator temperature is kept below 100 °C. Therefore, only the volatile vapor is injected into the system. This would prevent disturbance in column selectivity. Fig. 5(d) shows the TIC intensity of linalool remains relatively unchanged as the water content in the sample increases. However, performing analysis in an agitator temperature less than 100 °C means missing the detection of compounds that evaporate at a higher temperature. Also, when the agitator temperature is too low, the TIC intensity is slightly lower than at higher temperature, making it unfavorable when analyzing low-abundance compounds. Nevertheless, HS-GC is ideal for identifying volatile compounds in water-based matrices/formulations samples. It can also help direct and fast analyze volatile compounds in solid matrixes without sample preparation, thus avoiding sample loss or evaporation during preparation [43].

■ CONCLUSION

With a combination of ATR-FTIR and GC-MS, this study showed successful quality control of counterfeit perfumes. ATR-FTIR gave rapid and straightforward authentication of perfume without analyte separation, while GC-MS and HS-GC-MS provided comprehensive chemical characterization of perfume compounds. In addition, HS-GC-MS is an ideal method for analyzing volatile compounds in water-based perfume, offering an alternative to conventional GC-MS. These three methods can be used directly for volatile compounds in perfume analysis without sample preparation.

■ CONFLICT OF INTEREST

The authors declare that there is no competing interest.

■ AUTHOR CONTRIBUTIONS

Siti Nurul Hidayah designed and performed the experiments. Siti Nurul Hidayah and Artania Adnin Tri Suma performed data analysis. Siti Nurul Hidayah, Artania Adnin Tri Suma, and Endang Lukitaningsih wrote the manuscript. All authors agree on the final version of this manuscript.

■ REFERENCES

[1] Rodrigues, A.E., Nogueira, I., and Faria, R.P.V., 2021, Perfume and flavor engineering: A chemical engineering perspective, *Molecules*, 26 (11), 3095.

[2] Kumar, M., Devi, A., Sharma, M., Kaur, P., and Mandal, U.K., 2021, Review on perfume and present status of its associated allergens, *J. Cosmet. Dermatol.*, 20 (2), 391–399.

[3] Sowndhararajan, K., and Kim, S., 2016, Influence of fragrances on human psychophysiological activity: With special reference to human electroencephalographic response, *Sci. Pharm.*, 84 (4), 724–751.

[4] Abedi, G., Talebpour, Z., and Jamechenarboo, F., 2018, The survey of analytical methods for sample preparation and analysis of fragrances in cosmetics and personal care products, *TrAC, Trends Anal. Chem.*, 102, 41–59.

[5] Burger, P., Plainfossé, H., Brochet, X., Chemat, F., and Fernandez, X., 2019, Extraction of natural fragrance ingredients: History overview and future trends, *Chem. Biodiversity*, 16 (10), e1900424.

[6] Brown, A., Mettetal, A., and Hettiarachchi, D., 2022, "Sandalwood—Perfumery" in *Materials Horizons: from Nature to Nanomaterials*, Eds. Arunkumar, A.N., Joshi, G., Warrier, R.R., and Karaba, N.N., Springer Nature, Singapore, 449–461.

[7] Lecourt, M., and Antoniotti, S., 2020, Chemistry, sustainability and naturality of perfumery biotech ingredients, *ChemSusChem*, 13 (21), 5600–5610.

[8] Chaudhry, P., and Zimmerman, A., 2013, "The Global Growth of Counterfeit Trade" in *Protecting Your Intellectual Property Rights: Understanding the Role of Management, Governments, Consumers and Pirates*, Springer, New York, US, 7–31.

[9] Pierson, M., Fernandez, X., and Antoniotti, S., 2021, Type and magnitude of non-compliance and adulteration in neroli, mandarin and bergamot essential oils purchased on-line: potential consumer vulnerability, *Sci. Rep.*, 11 (1), 11096.

[10] Lubes, G., and Goodarzi, M., 2017, Analysis of volatile compounds by advanced analytical techniques and multivariate chemometrics, *Chem. Rev.*, 117 (9), 6399–6422.

[11] Kempińska-Kupczyk, D., and Kot-Wasik, A., 2019, The potential of LC–MS technique in direct analysis of perfume content, *Monatsh. Chem.*, 150 (9), 1617–1623.

[12] Bounaas, K., Bouzidi, N., Daghbouche, Y., Garrigues, S., de la Guardia, M., and El Hattab, M., 2018, Essential oil counterfeit identification through middle infrared spectroscopy, *Microchem. J.*, 139, 347–356.

[13] Cebi, N., 2021, Quantification of the geranium essential oil, palmarosa essential oil and phenylethyl alcohol in *Rosa damascena* essential oil using ATR-FTIR spectroscopy combined with chemometrics, *Foods*, 10 (8), 1848.

[14] Lebanov, L., Tedone, L., Ghiasvand, A., and Paull, B., 2020, Characterisation of complex perfume and essential oil blends using multivariate curve resolution-alternating least squares algorithms on average mass spectrum from GC-MS, *Talanta*, 219, 121208.

[15] Xiao, Z., Luo, J., Niu, Y., and Wu, M., 2018, Characterization of key aroma compounds from different rose essential oils using gas chromatography-mass spectrometry, gas chromatography–olfactometry and partial least squares regression, *Nat. Prod. Res.*, 32 (13), 1567–1572.

[16] Feng, Y., Cheng, X., Lu, Y., Wang, H., Chen, D., Luo, C., Liu, H., Gao, S., Lei, T., Huang, C., and Yu, X., 2022, Gas chromatography-mass spectrometry analysis of floral fragrance-related compounds in scented rose (*Rosa hybrida*) varieties and a subsequent evaluation on the basis of the analytical hierarchy process, *Plant Physiol. Biochem.*, 185, 368–377.

[17] Gasparini, G., Semaoui, S., Augugliaro, J., Boschung, A., Berthier, D., Seyfried, M., and Begnaud, F., 2020, Quantification of residual perfume by Py-GC-MS in fragrance encapsulate polymeric materials intended for biodegradation tests, *Molecules*, 25 (3), 718.

[18] Cebi, N., Arici, M., and Sagdic, O., 2021, The famous Turkish rose essential oil: Characterization and authenticity monitoring by FTIR, Raman and GC–MS techniques combined with chemometrics, *Food Chem.*, 354, 129495.

[19] Wei, L., Wei, S., Hu, D., Feng, L., Liu, Y., Liu, H., and Liao, W., 2022, Comprehensive flavor analysis of volatile components during the vase period of cut lily (*Lilium* spp. 'Manissa') flowers by HS-SPME/GC–MS combined with E-nose technology, *Front. Plant Sci.*, 13, 822956.

[20] Popova, V., Ivanova, T., Stoyanova, A., Nikolova, V., Hristeva, T., and Zheljazkov, V.D., 2020, GC-MS Composition and olfactory profile of concretes from the flowers of four *Nicotiana* species, *Molecules*, 25 (11), 2617.

[21] Rangarajan, R., and Ghosh, P., 2011, Role of water contamination within the GC column of a GasBench II peripheral on the reproducibility of $^{18}O/^{16}O$ ratios in water samples, *Isot. Environ. Health Stud.*, 47 (4), 498–511.

[22] Mazzucotelli, M., Minteguiaga, M.A., Sgorbini, B., Sidisky, L., Marengo, A., Rubiolo, P., Bicchi, C., and Cagliero, C., 2020, Ionic liquids as water-compatible GC stationary phases for the analysis of

fragrances and essential oils: Quantitative GC–MS analysis of officially-regulated allergens in perfumes, *J. Chromatogr. A*, 1610, 460567.

[23] Riboni, N., Fornari, F., Bianchi, F., and Careri, M., 2021, A simple and efficient solid-phase microextraction – gas chromatography – mass spectrometry method for the determination of fragrance materials at ultra-trace levels in water samples using multi-walled carbon nanotubes as innovative coating, *Talanta*, 224, 121891.

[24] Satpathy, G., 2013, Analysis of Volatile Organic Compounds in Water Using Static Headspace GC/MS, *Application Note*, Bruker Daltonik GmbH, Bremen, Germany.

[25] Huang, B., Yan, D., Fang, W., Wang, X., Liu, J., Zhang, D., Wang, Q., Ouyang, C., Han, Q., Jin, X., and Cao, A., 2020, Comparison of headspace solid-phase microextraction and solvent extraction method for the simultaneous analysis of various soil fumigants in soil or water by gas chromatography–mass spectrometry, *J. Sep. Sci.*, 43 (8), 1499–1513.

[26] González-Hernández, P., Pacheco-Fernández, I., Bernardo, F., Homem, V., Pasán, J., Ayala, J.H., Ratola, N., and Pino, V., 2021, Headspace solid-phase microextraction based on the metal-organic framework CIM-80(Al) coating to determine volatile methylsiloxanes and musk fragrances in water samples using gas chromatography and mass spectrometry, *Talanta*, 232, 122440.

[27] Lehner, A.F., and Buchweitz, J.P., 2022, Benefits and malefits of solvent vent mode in combination with tandem mass spectrometry for static headspace analysis of organic solvents by gas chromatography, *Chromatographia*, 85 (4), 315–331.

[28] Sithersingh, M.J., and Snow, N.H., 2021, "Headspace gas chromatography" in *Gas Chromatography*, Eds. Poole, C.F., Elsevier, Amsterdam, Netherland, 251–265.

[29] Rossi, L., Foschi, M., Biancolillo, A., Maggi, M.A., and D'Archivio, A.A., 2023, Optimization of HS-SPME-GC/MS analysis of wine volatiles supported by chemometrics for the aroma profiling of Trebbiano d'Abruzzo and Pecorino white wines produced in Abruzzo (Italy), *Molecules*, 28 (4), 1534.

[30] Chan, M., Sy, H., Finley, J., Robertson, J., and Brown, P.N., 2021, Determination of ethanol content in kombucha using headspace gas chromatography with mass spectrometry detection: Single-laboratory validation, *J. AOAC Int.*, 104 (1), 122–128.

[31] Taylor, L., Remeškevičius, V., Saskoy, L., Brodie, T., Mahmud, J., Moir, H., Brouner, J., Howe, C., Thatti, B., O'Connell, S., Trotter, G., and Rooney, B., 2020, Determination of ethanol in micro-volumes of blood by headspace gas chromatography: Statistical comparison between capillary and venous sampling sites, *Med., Sci. Law*, 61 (2), 86–96.

[32] Aspromonte, J., Giacoppo, G., Wolfs, K., and Adams, E., 2020, Headspace gas chromatography for the determination of volatile methylsiloxanes in personal care products, *Anal. Bioanal. Chem.*, 412 (11), 2537–2544.

[33] Chen, J., Yi, Z., Yin, J., Dong, S., Wang, L., and Li, Y., 2023, Determination of fragrance allergens in paper personal care products by headspace (HS) solid-phase microextraction (SPME) gas chromatography-mass spectrometry (GC-MS) with response surface methodology (RSM) optimization, *Anal. Lett.*, 56 (12), 1868–1883.

[34] Hartonen, K., Helin, A., Parshintsev, J., and Riekkola, M.L., 2019, Problems caused by moisture in gas chromatographic analysis of headspace SPME samples of short-chain amines, *Chromatographia*, 82 (1), 307–316.

[35] Remy, P.A., Pérès, C., Dugay, J., Corbi, E., David, N., and Vial, J., 2021, How high-resolution mass spectrometry can help for the accurate quantification of difficult fragrance allergens, *Flavour Fragrance J.*, 36 (2), 243–255.

[36] Batou, A., 2019, A sensitivity-based one-parameter-at-a-time model updating method, *Mech. Syst. Signal Process.*, 122, 247–255.

[37] Bell, J., Nel, P., and Stuart, B., 2019, Non-invasive identification of polymers in cultural heritage collections: Evaluation, optimisation and application

of portable FTIR (ATR and external reflectance) spectroscopy to three-dimensional polymer-based objects, *Heritage Sci.*, 7 (1), 95.

[38] Tarhan, İ., Çelikten, Ş., Kestek, H.M., Çelik, B., Öner, M., Kenar, A., and Kara, H., 2023, Development of a new and rapid FTIR method using chemometric modeling techniques for the determination of lavandin adulteration in lavender essential oil, *Vib. Spectrosc.*, 127, 103559.

[39] Mohammed, W.B., Tarabzouni, S., and Bohlega, S., 2022, Methanol-induced parkinsonism and cerebral vasculopathy due to perfume inhalation, *BMJ Neurol. Open*, 4 (1), e000221.

[40] Chan, A.P.L., and Chan, T.Y.K., 2018, Methanol as an unlisted ingredient in supposedly alcohol-based hand rub can pose serious health risk, *Int. J. Environ. Res. Public Health*, 15 (7), 1440.

[41] Scientific Committee on Cosmetic Products and Non-food Products Intended for Consumers, 2003, *The SCCNFP'S Notes of Guidance for Testing of Cosmetic Ingredients and Their Safety Evaluation*, 5th revision, Directorate-General for Health and Consumer Protection of the European Commission, Brussel, Belgium.

[42] Rádis-Baptista, G., 2023, Do synthetic fragrances in personal care and household products impact indoor air quality and pose health risks?, *J. Xenobiot.*, 13 (1), 121–131.

[43] Hwang, J.B., Lee, S., Yeum, J., Kim, M.K., Choi, J.C., Park, S.J., and Kim, J., 2019, HS-GC/MS method development and exposure assessment of volatile organic compounds from food packaging into food simulants, *Food Addit. Contam.: Part A*, 36 (10), 1574–1583.