Printed in the Republic of Korea

ANALYTICAL SCIENCE & TECHNOLOGY

Vol. 39 No. 4, 243-255, 2026

https://doi.org/10.5806/AST.2026.39.4.243

Optimization and validation of a GC–MS method for the determination of fragrance allergens in cosmetic products

Yewon Lee★, Sunghee Han, Sam-Ju Jung, Jinkyung Yu, Si-Yeon Jo, Bokyung Jung, Hyunjung Kim, and Jusung Park

Seoul Metropolitan Government Research Institute of Public Health and Environment, Yangjae-dong 202-3, Seoul 137130, Republic of Korea

(Received June 5, 2026; Revised July 9, 2026; Accepted July 10, 2026)

Abstract: Fragrance allergens in cosmetics are major triggers for allergic contact dermatitis, highlighting the need for accurate labeling and effective regulatory monitoring. This study aimed to validate and optimize the Ministry of Food and Drug Safety guideline GC-MS analytical method for the quantitative determination of 23 fragrance allergens and to assess labeling compliance in 106 commercial cosmetic products, including perfumes, body mists, creams, and body washes. Method optimization revealed that the concentration of the internal standard (ISTD) significantly affected calibration linearity. Adjusting the concentration of 2,3-dichlorotoluene from 100 μg/g to 2 μg/g, corresponding to the analyte calibration range (0.5–20 μg/mL), improved the average coefficient of determination (R^2) from 0.790 to 0.994. The optimized method showed excellent linearity ($R^2 \geq 0.987$), high sensitivity (LOD: 0.05–0.81 μg/mL), and generally acceptable accuracy (84.7–109.6%). Based on the label declaration and GC-MS analysis, limonene, linalool, and citronellol were the most prevalent fragrance allergens, each identified in over 50 % of the tested products. Benzyl salicylate showed the highest mean concentration in perfumes (8,418.6 μg/g). Notably, one body mist product contained coumarin at 510.9 μg/g (0.0511 %) without label declaration, indicating non-compliance with labeling requirements. In conclusion, the optimized GC-MS method provides a robust and reliable analytical tool for regulatory surveillance and cosmetic quality control. These findings provide important empirical evidence to support cosmetic safety management and the prevention of fragrance allergen-related health risks.

Key words: fragrance allergen, GC-MS, cosmetic products

1. Introduction

Cosmetics are essential in daily life, and fragrances significantly enhance product appeal and the user experience. Beyond aesthetic contributions, fragrances serve functional purposes such as masking inherent raw material odors and providing psychological benefits, including relaxation and mood enhancement.[1,2] However, the usage of fragrances in cosmetics poses certain health and safety concerns. Fragrances are

★ Corresponding author
Phone : +82-(0)2-570-3128 Fax: +82-(0)2-570-3129
E-mail : yw0322@naver.com

This is an open access article distributed under the terms of the Creative Commons Attribution Non-Commercial License (http://creativecommons.org/licenses/by-nc/3.0) which permits unrestricted non-commercial use, distribution, and reproduction in any medium, provided the original work is properly cited.

broadly classified as natural or synthetic. While synthetic fragrances offer a diverse olfactory spectrum and cost-effectiveness, certain ingredients function as allergens, increasing the risk of allergic contact dermatitis (ACD) in sensitive individuals.[1,3] Furthermore, fragrance mix I allergens have been reported to induce ACD in a substantial proportion of consumers, particularly women with facial or hand eczema.[3] To enhance consumer safety, the European Commission requires the labeling of specific fragrance allergens when they exceed established concentrations.[4] Similarly, the Ministry of Food and Drug Safety (MFDS) of Korea has made it essential to label 25 allergy-causing ingredients in cosmetics including fragrances, beginning in 2020, emphasizing international cooperation in safety regulations.[5] Guidelines have been established for gas chromatography-mass spectrometry (GC-MS) analysis of 23 fragrance allergens and liquid chromatography-mass spectrometry (LC-MS) analysis of two fragrance allergens. Regulatory requirements mandate the labeling of these ingredients when concentrations exceed 0.01 % in wash-off products or 0.001 % in leave-on products.[5] Despite regulatory requirements, differences between labeled and real fragrance allergen content have been reported. Some fragrance-free cosmetics have been found to include fragrance ingredients, including allergens such as Lyral.[6,7] These findings highlight the importance of comprehensive analytical monitoring to ensure product safety and prevent adverse reactions such as allergic contact dermatitis. To ensure safety, the MFDS updated the Cosmetic Analysis Method Compendium in 2024, providing protocols for the quantitative analysis of fragrance allergens using GC-MS.[5] GC-MS is widely recognized for its sensitivity and specificity in the analysis of complex fragrance mixtures, enabling accurate detection and quantification of allergenic compounds and supporting regulatory compliance.[8,9] Although the MFDS (2024)[5] compendium provides a vital regulatory baseline, directly applying its generic parameters, such as standard internal standard ISTD concentrations, to sensitive GC-MS systems can cause non-linear detector responses. Consequently, optimizing these official guidelines is a necessary prerequisite to ensure accurate analysis of diverse commercial cosmetics. Accordingly, this study aimed to critically evaluate and optimize the MFDS (2024)[5] GC-MS analytical method—with a specific focus on refining instrumental parameters and ISTD concentrations to ensure strict quantitative linearity—and to apply the validated method to commercial cosmetic products to evaluate allergen content and labeling compliance. Although atranol and chloroatranol (from oakmoss and tree moss extracts) are recognized fragrance allergens, they were excluded from this study as they require LC-MS analysis. The findings of this study provide empirical data to support regulatory enforcement, improve cosmetic safety management, enhance consumer transparency, and reduce health risks associated with fragrance allergens.

2. Experimental

2.1. Chemicals and reagents

Twenty-three fragrance allergens standards (amyl cinnamaldehyde, benzyl alcohol, cinnamyl alcohol, citral, eugenol, hydroxycitronellal, isoeugenol, amyl cinnamyl alcohol, benzyl salicylate, cinnamic aldehyde, coumarin, geraniol, anisyl alcohol, benzyl cinnamate, farnesol, butylphenyl methylpropional, linalool, benzyl benzoate, citronellol, hexyl cinnamaldehyde, limonene, methyl 2-octynoate, and α-isomethyl ionone), and 2,3-dichlorotoluene for ISTD were purchased from Sigma-Aldrich (St. Louis, MO, USA, *Table* 1). Individual stock solutions of the 23 fragrance allergens were prepared by accurately weighing 10 mg of each standard and dissolving it in 10 mL of methanol (Thermo Fisher Scientific, Waltham, MA, USA). The stock solutions were subsequently diluted with methanol to prepare working standard solutions at concentrations of 0.5, 1, 2.5, 5, 10, and 20 μg/mL.

2.2. Sample collection

Five types of cosmetic products (perfume, body mist, hand cream, body cream, and body wash) were purchased from cosmetic stores in Seoul, South Korea (*Table* 2). Approximately 1.0 g of each sample was accurately weighed (±0.01 g), mixed with 10 mL of

Table 1. Fragrance allergen standards used in this study

Fragrance allergen	CAS number	Purity (%)
Amyl cinnamaldehyde	122-40-7	99.0
Benzyl alcohol	100-51-6	100
Cinnamyl alcohol	104-54-1	99.5
Citral	5392-40-5	99.5
Eugenol	97-53-0	99.8
Hydroxycitronellal	107-75-5	99.1
Isoeugenol	97-54-1	98.8
Amyl cinnamyl alcohol	101-85-9	98.6
Benzyl salicylate	118-58-1	99.8
Cinnamic aldehyde	14371-10-9	99.1
Coumarin	91-64-5	100
Geraniol	106-24-1	99
Anisyl alcohol	105-13-5	99.9
Benzyl cinnamate	103-41-3	98.9
Farnesol	4602-84-0	98.5
Butylphenyl methylpropional	80-54-6	97.9
Linalool	78-70-6	99.7
Benzyl benzoate	120-51-4	100
Citronellol	106-22-9	96.6
Hexyl cinnamaldehyde	101-86-0	99.8
Limonene	5989-27-5	99.2
Methyl 2-Octynoate	111-12-6	99.7
α-isomethylionone	127-51-5	94.1
2,3-Dichlorotoluene (IS)	32768-54-0	99.7

methanol, and sonicated in an ultrasonic bath (Branson, Danbury, CT, USA) for 30 min at room temperature. Subsequently, 2 mL of the ISTD solution was added, and the mixture was diluted to a final volume of 20 mL with methanol. The resulting solution was filtered through a 0.45 μm membrane filter (Chemco Scientific, Osaka, Japan) to obtain the test solution.

2.3. Optimization of fragrance allergen analysis using GC-MS

Fragrance allergens were identified and quantified using a Thermo Fisher Scientific ISQ7000 GC-MS system. Chromatographic separation was performed on a DB-17MS column (30 m × 250 μm, 0.25 μm film thickness). Helium (99.999 % purity) was used as the carrier gas at a constant column flow rate of 1.0 mL min^{-1}. The GC oven temperature program was as follows initial temperature of 40 °C held for 3 min, increased to 100 °C at 5 °C/min and held for 12 min, then increased to 250 °C at 10 °C/min and held for 15 min, followed by an increase to 300 °C at 25 °C/min and held for 5 min. The total run time was 35 min. The injector was operated in splitless mode at 250 °C with an injection volume of 1.0 μL. The transfer line and ion source temperatures were maintained at 260 °C and 230 °C, respectively (*Table* 3). The initial optimization utilized the full-scan mode (*m/z* 30–300), while validation and quantification were performed in the selected ion monitoring (SIM) mode.

Table 2. Information on cosmetic samples analyzed in this study

Type	Formula	Number of samples
Perfume	Aliquot	22
Body mist	Aliquot	20
Hand cream	Cream	23
Body cream	Cream	20
Body wash	Gel	21
Total		106

2.4. Method validation

Method validation was performed according to the guidelines for analytical procedures described in ICH Q2.[10] The limit of detection (LOD), limit of quantitation (LOQ), and coefficients of determination (R^2) values were calculated for all 23 fragrance

Table 3. GC–MS operating conditions for fragrance allergen analysis

Parameter	Analytical condition
Column	DB-17MS (30 m × 250 μm, 0.25 μm film thickness)
Injection temperature	250°C
Oven program	40°C (3 min) → 100°C at 5°C/min (12 min) → 250°C at 10°C/min (15 min) → 300°C at 25°C/min (5 min)
Transfer line temperature	260°C
Ion source temperature	230°C

allergens, and validation regarding accuracy and precision was performed for the ten major fragrance allergens (limonene, linalool, citronellol, citral, geraniol, hexyl cinnamaldehyde, hydroxycitronellal, coumarin, benzyl benzoate, and benzyl salicylate). Five replicate measurements were conducted for each of the six standard solutions of a mixture containing 23 fragrance allergens at different concentrations (0.5, 1, 2.5, 5, 10, and 20 μg/mL). Calibration curves and R^2 were obtained using linear regression analysis. LOD and LOQ were calculated based on the slope of the calibration curve (S) and the standard deviation of the response (σ). The LOD and LOQ were calculated as 3.3σ/S and 10σ/S, respectively. To assess the accuracy and precision of the method, two concentrations (35 and 50 μg/mL) of a mixture containing the ten major fragrance allergens were spiked into cosmetic matrices free of fragrance allergens. The spiked sample was pretreated as described in section 2.2 (Sample Collection) and diluted to a final volume of 20 mL. Thus, the spiked levels of 35 and 50 μg/g in the samples corresponded to approximately 1.75 and 2.5 μg/mL in the GC-MS analysis. The recovery was calculated as the ratio of the measured concentration to the spiked concentration, and precision was expressed as the relative standard deviation (%RSD) based on three replicate analyses.

3. Results and Discussion

3.1. Optimization of fragrance allergen analysis in cosmetic products

This study evaluated the MFDS (2024)[5] GC–MS analytical method for determining 23 fragrance allergens in cosmetic products. The MFDS method applied an excessive ISTD concentration (100 μg/mL), which was approximately 50 to 2000 times higher than the analyte concentrations. Consequently, the average R^2 across the 23 fragrance allergens was inadequate at 0.790 (range: 0.561–0.865; *Fig.* 1). To investigate the effect of the ISTD on linearity, calibration curves were re-evaluated without ISTD correction, resulting in a substantial increase in the average R^2 value to 0.990 (*Fig.* 2). This improvement demonstrates the pronounced impact of ISTD concentration on method performance. According to ICH guidelines (2023),[10] excessively high ISTD concentrations may induce ion suppression and competitive ionization effects in the mass spectrometer, leading to nonlinear detector responses that distort the response ratio and compromise calibration linearity. when ISTD concentrations are disproportionately elevated, the ionization chamber becomes saturated, reducing ionization efficiency of target analytes through competitive ionization processes and distorting the linear relationship between analyte concentration and detector response. In mass spectrometry, a severe concentration imbalance —such as an excessively high concentration of an ISTD—induces competitive ionization, where co-eluting compounds compete for limited ionization resources (e.g., energy and charge), ultimately distorting the quantitative linearity.[11] Furthermore, specifically in GC-MS systems, when the injected concentration of an analyte or ISTD exceeds the upper threshold of the instrument, it triggers space-charge effects within the ion source and causes physical saturation of the electron multiplier, leading to a complete loss of quantitative linearity.[12] Therefore, ISTD concentration should be maintained within a range comparable to that of the target analytes. Accordingly, the ISTD concentration was adjusted to 2 μg/mL to match the analyte calibration range (0.5–20 μg/mL), corresponding approximately to the third calibration level (2.5 μg/mL). After optimization, the average R^2 value improved to 0.994, demonstrating appropriate linearity. All other analytical conditions were applied according to the MFDS (2024).[5] Additionally, previous study[13] reported methanol as the most effective pretreatment solvent for detecting 28 fragrance allergens in cosmetic products, producing the highest peak response compared with other solvents. These findings support the suitability of methanol as a pretreatment solvent for fragrance allergen analysis.

3.2. Method validation for fragrance allergens

The optimized method exhibited high linearity over the concentration range of 0.5–20 μg/mL, with the R^2 exceeding 0.987 for all 23 fragrance allergens

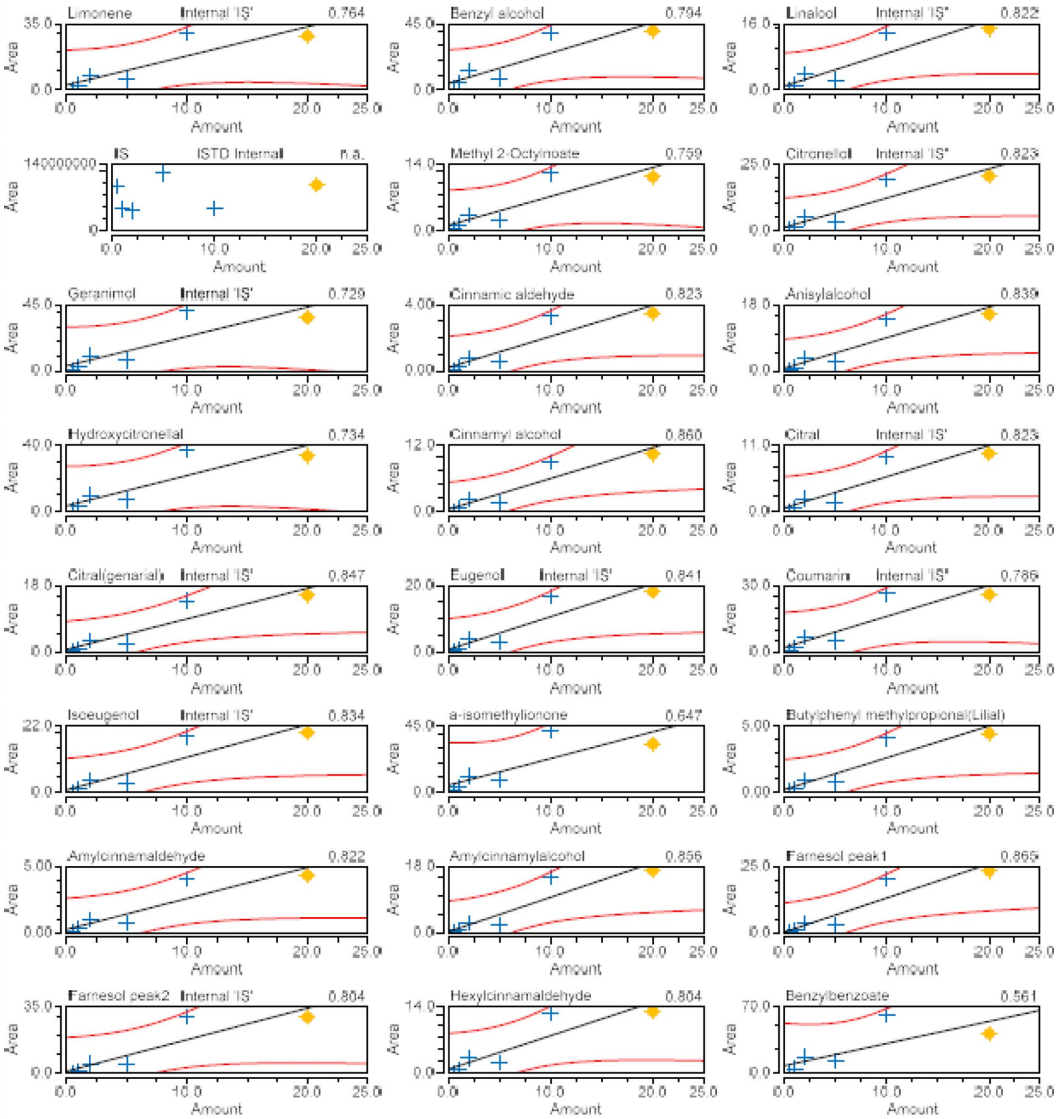

Fig. 1. Calibration plots of allergens using the internal standard method.

(*Table* 4). The LOD and LOQ for the 23 fragrance allergens ranged from 0.05 to 0.81 μg/mL and from 0.16 to 2.46 μg/mL, respectively (*Table* 4). The recovery rate ranged from 84.7 % to 107.0 % at the low spiking level (35 μg/mL) and from 93.0 % to 109.6 % at the high spiking level (50 μg/mL; *Table* 5). All calculated recovery values and precision results satisfied the acceptable criteria specified in the Codex guidelines[14].

3.3. Application of the optimized GC–MS method for fragrance allergen analysis in cosmetic products

Analysis of 106 cosmetic products using the validated GC-MS method revealed distinct fragrance allergen concentration profiles. Perfumes exhibited the broadest and highest concentration range (N.D. -15,476.6 μg/g), followed by body mists (N.D. -7,602.2 μg/g) and hand creams (N.D.-5,948.0 μg/g). In contrast, body washes (N.D.-4,598.0 μg/g) and

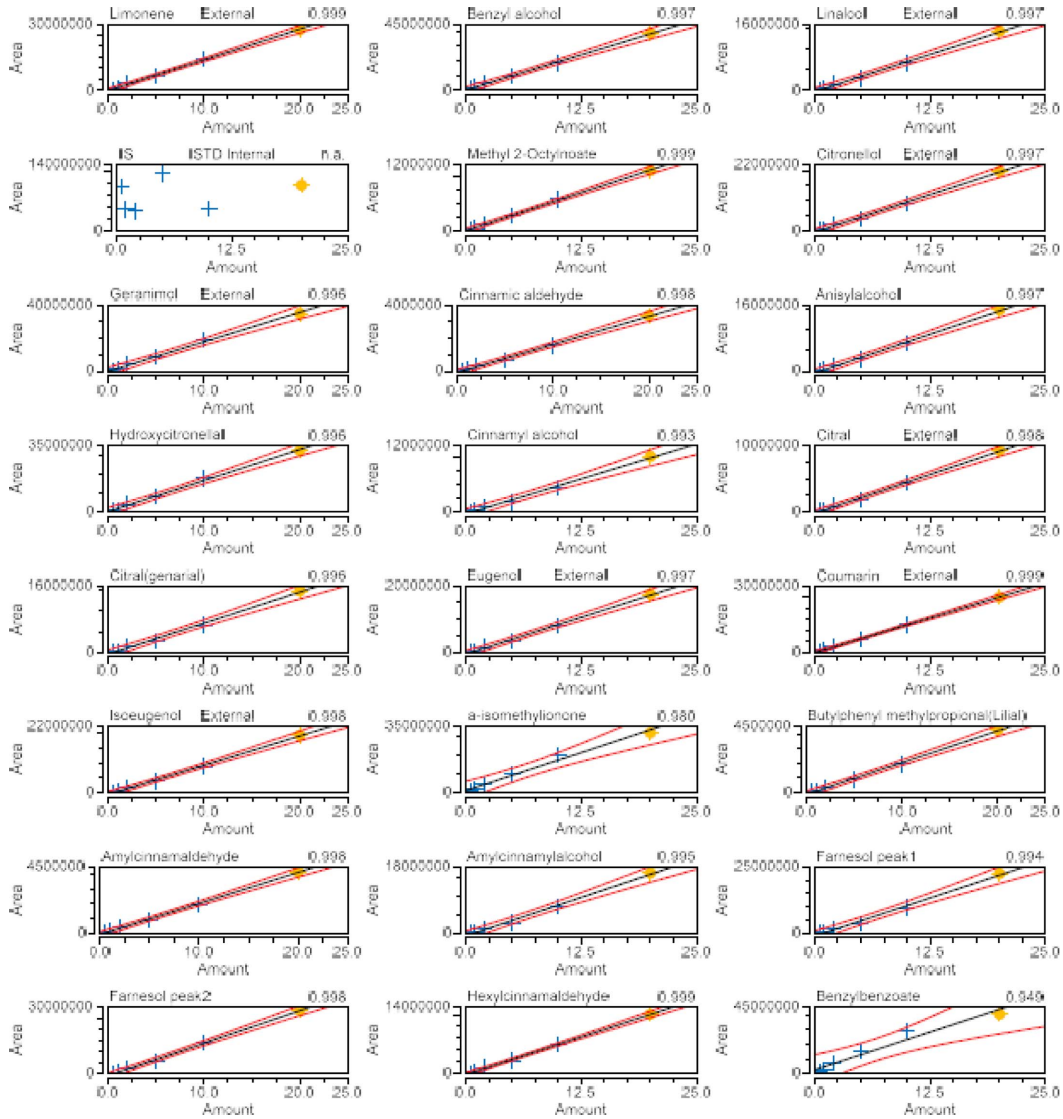

Fig. 2. Calibration plots of allergens using the external standard method.

body creams (N.D.-3,726.2 μg/g) showed comparatively lower concentrations (Tables 6–8). By detection frequency, linalool was the most prevalent fragrance allergen across most product categories. The allergen exhibiting the highest mean concentration varied according to product category: benzyl salicylate in perfumes (8,418.6 ± 5,340.3 μg/g) and body washes (814.6 ± 1,236.2 μg/g); butylphenyl methylpropional in body mists (2,402.9 ± 3,591.5 μg/g) and hand creams (2,096.8 ± 2,165.5 μg/g); and benzyl alcohol in body creams (936.1 ± 1,366.4 μg/g). Salicylates such as benzyl salicylate are known to reduce vapor pressure within fragrance mixtures and function as fragrance fixatives. Therefore, their relatively high concentrations in perfumes, and to a lesser extent in body mists and body washes, are consistent with the purpose of prolonging scent longevity.[15] However, a previous study reported that exposure to 8 % benzyl salicylate induced allergic reactions in sensitive individuals; therefore, high concentrations should be

Table 4. Correlation coefficients (R^2), limits of detection (LOD), and limits of quantification (LOQ) of fragrance allergens analyzed by GC–MS

Allergen	RT (min)	R^2	Calibration range (μg/mL)	LOD[1)] (μg/mL)	LOQ[2)] (μg/mL)
Limonene	13.002	0.999	0.49–19.80	0.33	1.01
Benzyl alcohol	13.140	0.999	0.49–19.80	0.27	0.84
Linalool	15.201	0.999	0.49–19.80	0.29	0.88
Methyl 2-octynoate	17.652	0.997	0.48–19.40	0.12	0.37
Citronellol	18.217	0.998	0.48–19.32	0.12	0.37
Geraniol	18.674	0.999	0.49–19.70	0.74	2.25
Cinnamic aldehyde	19.097	0.990	0.49–19.82	0.51	1.54
Anisyl alcohol	19.277	0.995	0.49–19.60	0.05	0.16
Hydroxycitronellal	19.317	0.998	0.47–18.80	0.11	0.34
Cinnamyl alcohol	19.684	0.995	0.48–19.20	0.10	0.30
Citral	20.100	0.995	0.49–19.60	0.50	1.52
Eugenol	20.430	0.991	0.49–19.60	0.10	0.32
Coumarin	21.727	0.997	0.49–19.80	0.11	0.34
Isoeugenol	21.838	0.987	0.49–19.60	0.28	0.87
a-isomethylionone	22.214	0.999	0.45–18.00	0.08	0.25
Butylphenyl methylpropional	22.900	0.994	0.48–19.20	0.14	0.43
Amyl cinnamaldehyde	24.357	0.994	0.49–19.80	0.29	0.88
Amyl cinnamyl alcohol	24.789	0.991	0.49–19.60	0.12	0.38
Farnesol	25.122	0.992	0.49–19.80	0.22	0.66
Hexyl cinnamaldehyde	25.491	0.999	0.49–19.70	0.08	0.29
Benzyl benzoate	25.769	0.995	0.49–19.80	0.61	1.87
Benzyl salicylate	26.882	0.989	0.49–19.70	0.57	1.74
Benzyl cinnamate	29.080	0.991	0.49–19.78	0.81	2.46

[1)]LOD: 3.3(σ/S) σ: standard deviation of the response, S: calibration curve
[2)]LOQ: 10(σ/S)

Table 5. Accuracy and precision of the GC–MS method for fragrance allergen analysis in cosmetic products

Allergen	35 μg/mL		50 μg/mL	
	Recovery (%)[1)]	RSD (%)[2)]	Recovery (%)	RSD (%)
Limonene	85.9	4.9	109.6	1.3
Linalool	106.1	4.6	97.2	1.1
Citronellol	107.0	2.7	100.5	3.8
Citral	101.3	1.3	94.8	5.0
Geraniol	101.3	1.9	101.6	3.2
Hexyl cinnamaldehyde	89.2	2.4	93.0	1.0
Hydroxycitronellal	84.7	2.9	102.8	0.5
Coumarin	101.1	5.6	98.0	3.1
Benzyl benzoate	105.1	4.1	102.6	0.7
Benzyl salicylate	104.0	1.9	102.4	5.4

[1)] Recovery: [(concentration of spiked sample - concentration of original sample) / standard concentration] × 100
[2)] RSD: (standard deviation / average) × 100

used with caution.[15] Butylphenyl methylpropional is widely used as a masking agent in cosmetic formulations to provide a floral lily-of-the-valley fragrance while reducing undesirable base odors.[14] Nevertheless, butylphenyl methylpropional has been identified as a dermal sensitizer associated with allergic contact

Table 6. Occurrence and concentrations of fragrance allergens in fragrance products (perfumes and mists)

Allergen	Perfumes		Body mists	
	Positive samples (n/N)[a)]	Mean (Range)[b)] (μg/g)	Positive samples (n/N)	Mean (Range) (μg/g)
Linalool	20/22	2634.8 (25.1~7677.2)	19/20	709.2 (8.0~2002.5)
Limonene	21/22	2941.4 (36.0~8838.0)	20/20	823.5 (3.0~5988.0)
Methyl 2-octynoate	0/22	N.D.	0/20	N.D.
Benzyl benzoate	7/22	164.6 (29.2~794.8)	8/20	699.9 (7.7~3002.7)
Benzyl salicylate	7/22	8418.6 (320.1~15476.6)	7/20	2249.3 (247.5~5417.2)
Benzyl cinnamate	0/22	N.D.	0/20	N.D.
Benzyl alcohol	6/22	445.5 (0.6~1696.6)	3/20	348.8 (71.8 ~744.5)
Butylphenyl methylpropional	1/22	0.9	4/20	2402.9 (0.3~7602.2)
Citral	18/22	1517.8 (12.4~5278.0)	13/20	146.9 (7.4~1575.4)
Citronellol	16/22	3161.9 (45.1~13006.5)	11/20	467.9 (88.9~1245.1)
Cinnamyl alcohol	1/22	72.8	1/20	560.5
Cinnamic aldehyde	1/22	0.6	2/20	177.3 (9.0~345.5)
Anisyl alcohol	1/22	28.9	0/20	N.D.
Amyl cinnamyl alcohol	0/22	N.D.	0/20	N.D.
Amyl cinnamaldehyde	1/22	439.1	2/20	379.9 (53.1~706.7)
Isoeugenol	2/22	187.7 (139.8~235.6)	2/20	25.2 (21.1~29.3)
α-isomethylionone	8/22	1405.6 (9.2~3178.1)	9/20	143.2 (6.2~284.6)
Eugenol	7/22	443.2 (72.2~ 2031.7)	5/20	99.6 (9.3~293.3)
Geraniol	16/22	946.4 (120.1~2725.8)	10/20	174.7 (6.4~563.5)
Coumarin	8/22	896.9 (152.3~2186.8)	7/20	253.9 (4.4~757.7)
Farnesol	2/22	780.4 (36.1~1524.8)	1/20	28.7
Hydroxycitronellal	8/22	1318.6 (64.1~4216.6)	11/20	245.4 (4.9~748.4)
Hexyl cinnamaldehyde	7/22	2169.2 (99.5~6917.0)	12/20	532.6 (4.0~1911.2)

a) N: total number of samples; n: number of positive samples
b) The range represents the minimum and maximum detected concentrations.

dermatitis in humans.[16] Benzyl alcohol is characterized by floral, rose-like, phenolic, and balsamic odor properties.[17] In addition to its fragrance function, benzyl alcohol is also known to exhibit antimicrobial activity and is used as a preservative in cosmetic formulations.[18]

Among the 22 perfume products, limonene was the most prevalent fragrance allergen, detected in 95.5 % (21/22) of the samples with a mean concentration of 2941.4 μg/g (N.D.-8838.0 μg/g; *Table* 6). Previous study[19] analyzed 107 perfume samples and reported a maximum limonene concentration of 17,352.34 mg/kg, which is consistent with the findings of the present study. Methyl 2-octynoate, benzyl cinnamate, and amyl cinnamyl alcohol were not detected in any perfume samples, whereas benzyl salicylate exhibited the highest mean concentration (8,418.6 μg/g). Among the 20 body mist products analyzed, total allergen concentrations ranged from N.D. to 7,602.2 μg/g (*Table* 6). Limonene was detected in all 20 samples (100 %), making it the most frequent detected allergen, with a mean concentration of 823.5 μg/g (3.0–5988.0 μg/g). Methyl 2-octynoate, benzyl cinnamate, anisyl alcohol, and amyl cinnamyl alcohol were not detected, whereas butylphenyl methylpropional showed the highest mean concentration (2,402.9 μg/g). Among the 23 hand cream samples, total allergen concentrations ranged from N.D. to 5,948.0 μg/g (*Table* 7). Linalool and limonene were the most frequently detected allergens, each identified in 21 samples, with mean concentrations of 476.9 μg/g and 640.5 μg/g, respectively. Butylphenyl methylpropional exhibited the highest mean concentration (2,096.8 μg/g), whereas benzyl cinnamate, cinnamaldehyde, anisyl alcohol, amyl

Table 7. Occurrence and concentrations of fragrance allergens in cream products (hand cream and body cream)

Allergen	Hand cream		Body cream	
	Positive samples (n/N)[a)]	Mean (Range)[b)] (μg/g)	Positive samples (n/N)	Mean (Range) (μg/g)
Linalool	21/23	476.9 (8.4~2608.5)	12/20	127.0 (1.6~307.0)
Limonene	21/23	640.5 (1.8~5948.0)	11/20	216.0 (5.2~1539.6)
Methyl 2-octynoate	1/23	4.8	2/20	5.7 (4.0~7.3)
Benzyl benzoate	6/23	141.3 (7.0~536.6)	4/20	123.4 (6.8~408.3)
Benzyl salicylate	5/23	1104.7 (186.3~2319.8)	3/20	451.0 (71.5~1079.6)
Benzyl cinnamate	0/23	N.D.	0/20	N.D.
Benzyl alcohol	5/23	249.2 (0.9~1153.3)	7/20	936.1 (7.7~3726.2)
Butylphenyl methylpropional	3/23	2096.8 (719.2~4592.8)	0/20	N.D.
Citral	19/23	19.1 (5.9~58.7)	12/20	29.1 (6.3~134.9)
Citronellol	15/23	223.2 (14.7~749.5)	11/20	150.2 (9.2~619.7)
Cinnamyl alcohol	2/23	95.8 (9.4~182.1)	1/20	48.8
Cinnamic aldehyde	0/23	N.D.	0/20	N.D.
Anisyl alcohol	0/23	N.D.	0/20	N.D.
Amyl cinnamyl alcohol	0/23	N.D.	0/20	N.D.
Amyl cinnamaldehyde	2/23	26.1 (4.3~47.8)	2/20	65.7 (1.3~130.1)
Isoeugenol	0/23	N.D.	0/20	N.D.
α-isomethylionone	9/23	232.2 (14.6~411.0)	5/20	192.3 (37.0~422.5)
Eugenol	7/23	106.8 (24.8~216.7)	1/20	131.4
Geraniol	15/23	197.5 (4.5~761.1)	10/20	108.8 (7.5~246.6)
Coumarin	8/23	65.0 (19.1~165.0)	4/20	134.6 (24.6~213.9)
Farnesol	2/23	6.8 (6.0~7.6)	2/20	69.4 (7.0~131.9)
Hydroxycitronellal	10/23	208.6 (6.9~765.0)	7/20	132.1 (6.1~509.1)
Hexyl cinnamaldehyde	12/23	448.6 (4.8~1759.1)	8/20	150.0 (3.6~402.3)

a) N: total number of samples; n: number of positive samples
b) The range represents the minimum and maximum detected concentrations.

cinnamyl alcohol, and isoeugenol were not detected. Body cream products (n = 20) exhibited relatively lower allergen concentrations ranging from N.D. to 3,726.2 μg/g (*Table* 7). Linalool and citral were the most frequent detected allergens, each identified in 12 samples, with mean concentrations of 127.0 μg/g and 17.5 μg/g, respectively. Benzyl alcohol exhibited the highest mean concentration (936.1 μg/g), while benzyl cinnamate, cinnamaldehyde, anisyl alcohol, amyl cinnamyl alcohol, and isoeugenol were not detected. This result indicates a generally lower allergen concentration profile compared with other cosmetic categories, despite the prolonged skin contact associated with body cream use. Among the 21 body wash products, total allergen concentrations ranged from N.D. to 4,598.0 μg/g (*Table* 8). Linalool was detected in all 21 body wash samples, with a mean concentration of 523.5 μg/g, whereas benzyl salicylate exhibited the highest mean concentration (814.6 μg/g). Benzyl cinnamate, butylphenyl methylpropional, cinnamic aldehyde, anisyl alcohol, and amyl cinnamyl alcohol were not detected in all body wash samples. Across all product categories, limonene was emerged as the most prevalent allergen, while the allergen exhibiting the highest mean concentration varied significantly by product type: benzyl salicylate (perfumes and body washes), butylphenyl methylpropional (body mists and hand creams), and benzyl alcohol (body creams).

3.4. Labeling compliance assessment

To assess regulatory compliance, measured allergen concentrations were systematically compared with product label declarations and applicable regulatory

Table 8. Occurrence and concentrations of fragrance allergens in wash-off cosmetic products

Allergen	Positive samples (n/N)[a)]	Mean (Range)[b)] (μg/g)
Linalool	21/21	523.5 (2.0~3573.1)
Limonene	15/21	516.5 (28.3~4598.0)
Methyl-2-octynoate	1/21	36.1
Benzyl benzoate	7/21	229.3 (16.9~981.3)
Benzyl salicylate	8/21	814.6 (36.9~3391.6)
Benzyl cinnamate	0/21	N.D.
Benzyl alcohol	3/21	28.9 (16.4~37.3)
Butylphenyl methylpropional	0/21	N.D.
Citral	7/21	108.8 (8.5~307.0)
Citronellol	17/21	159.1 (4.6~460.8)
Cinnamyl alcohol	1/21	18.7
Cinnamic aldehyde	0/21	N.D.
Anisyl alcohol	0/21	N.D.
Amyl cinnamyl alcohol	0/21	N.D.
Amyl cinnamaldehyde	4/21	4.4 (2.7~6.8)
Isoeugenol	4/21	46.2 (26.7~89.6)
α-isomethylionone	7/21	172.3 (42.0~273.7)
Eugenol	9/21	18.7 (10.7~60.0)
Geraniol	12/21	228.0 (6.7~964.8)
Coumarin	13/21	150.3 (7.3~1246.9)
Farnesol	4/21	23.4 (6.9~52.2)
Hydroxycitronellal	8/21	142.3 (11.7~266.3)
Hexyl cinnamaldehyde	8/21	385.2 (218.5~567.8)

a) N: total number of samples; n: number of positive samples
b) The range represents the minimum and maximum detected concentrations.

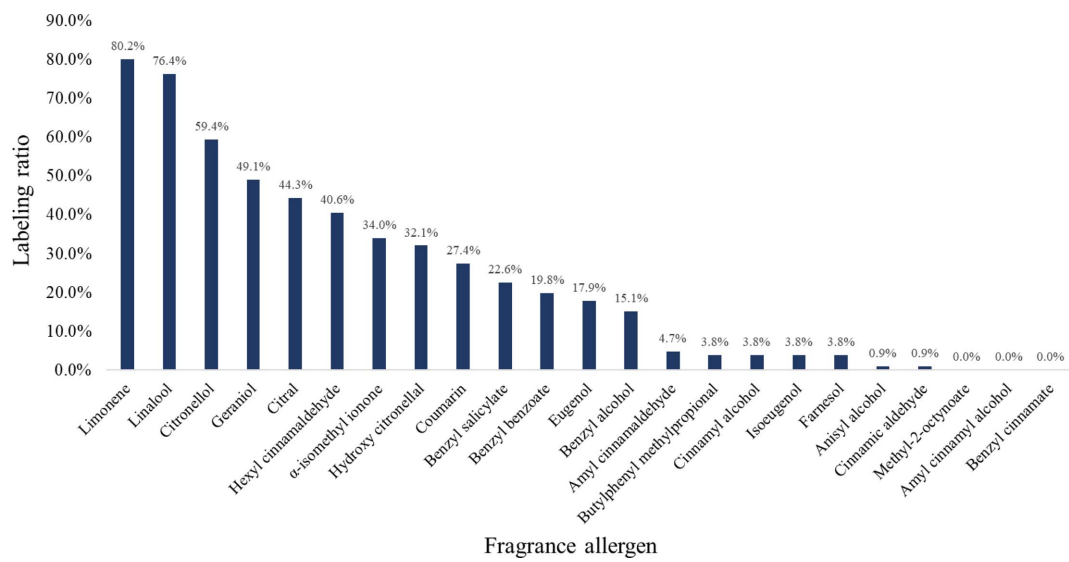

Fig. 3. Frequency of fragrance allergens labeling in cosmetic products.

thresholds (0.01 % for wash-off products; 0.001 % for leave-on products). Label analysis of the 106 cosmetic products revealed that all contained one or more fragrance allergens. Limonene was the most frequently listed fragrance appearing in 85 products (80.2 %; *Fig.* 3). Linalool and citronellol were listed in 81 products (76.4 %) and 63 products (59.4 %), respectively, indicating that these allergens were present in more than half of the tested products (*Fig.* 3). While the labeling patterns showed overall similarity to the GC-MS detection results, some differences were observed (*Table* 9). GC-MS analysis revealed that linalool was detected in 93 products (87.7 %), compared with 81 products (76.4 %) listed on labels (*Table* 9). Analysis of 12 products revealed concentrations of 1.6–8.4 μg/g in leave-on products and 2.0–96.2 μg/g in wash-off products, with all detected levels below the regulatory labeling requirements. Similarly, limonene was detected in 88 products (83.0 %), whereas only 85 products (80.2 %) declared its presence. Three products, all classified as leave-on formulations, showed concentrations of 5.2–7.8 μg/g, remaining below the labeling threshold. Citronellol was detected in 70 products (66.0 %) by GC-MS, versus 63 products (59.4 %) listed on labels (*Table* 9). Differences between label declarations and GC-MS detection could be attributed to the regulatory labeling threshold. Since products with fragrance allergens below the threshold are permitted to list components collectively as "fragrance", some allergens detected by GC-MS analysis were not individually declared on product labels.

Perfumes exhibited the greatest variety of fragrance allergens, with one sample containing 15 distinct allergens. All products contained one or more fragrance allergens; however, products labeled only as 'fragrance' necessarily contained allergens below the regulatory labeling thresholds. A critical labeling violation was

Table 9. Comparison of label declaration and GC-MS detection of fragrance allergens in cosmetic products

Allergen	Label declaration n/N[a)] (%)	GC-MS detection n/N (%)
Linalool	81/106 (76.4%)	93/106 (87.7%)
Limonene	85/106 (80.2%)	88/106 (83.0%)
Methyl-2-octynoate	0/106 (0.0%)	6/106 (5.7%)
Benzyl benzoate	21/106 (19.8%)	38/106 (35.8%)
Benzyl salicylate	24/106 (22.6%)	30/106 (28.3%)
Benzyl cinnamate	0/106 (0.0%)	0/106 (0.0%)
Benzyl alcohol	16/106 (15.1%)	24/106 (22.6%)
Butylphenyl methylpropional	4/106 (3.8%)	8/106 (7.5%)
Citral	47/106 (44.3%)	69/106 (65.1%)
Citronellol	63/106 (59.4%)	70/106 (66.0%)
Cinnamyl alcohol	4/106 (3.8%)	6/106 (5.7%)
Cinnamic aldehyde	1/106 (0.9%)	3/106 (2.8%)
Anisyl alcohol	1/106 (0.9%)	1/106 (0.9%)
Amyl cinnamyl alcohol	0/106 (0.0%)	0/106 (0.0%)
Amyl cinnamaldehyde	5/106 (4.7%)	11/106 (10.4%)
Isoeugenol	4/106 (3.8%)	8/106 (7.5%)
α-isomethylionone	36/106 (34.0%)	38/106 (35.8%)
Eugenol	19/106 (17.9%)	29/106 (27.4%)
Geraniol	52/106 (49.1%)	63/106 (59.4%)
Coumarin	29/106 (27.4%)	40/106 (37.7%)
Farnesol	4/106 (3.8%)	11/106 (10.4%)
Hydroxycitronellal	34/106 (32.1%)	44/106 (41.5%)
Hexyl cinnamaldehyde	43/106 (40.6%)	47/106 (44.3%)

a) N: total number of samples; n: number of positive samples

identified in one body mist product: coumarin was detected at 510.9 μg/g (0.0511 %), which exceeds the labeling threshold and warrants mandatory ingredient disclosure. Coumarin is widely used as a fragrance ingredient; however, European safety assessments have identified a threshold above which dermal exposure may induce skin sensitization, thereby necessitating mandatory labeling at regulated concentration levels.[20] According to a previous study,[6] the most frequently listed fragrance allergens in 35 leave-on products were linalool (91.4 %), limonene (85.7 %), citronellol (71.4 %), whereas in 16 rinse-off products, limonene (68.8 %), linalool (62.5 %), and citronellol (37.5 %) were most commonly detected. These findings showed a similar pattern to the results obtained in the present study. Limonene and linalool were well known as top-note fragrance compounds because of their high volatility and relatively low molecular weights, allowing fragrances to disperse rapidly.[21] While limonene and linalool are considered relatively mild allergens, their oxidation metabolites —particularly hydroperoxides—have been documented to induce severe allergic contact dermatitis upon oxidative degradation and dermal exposure.[22]

3.5. Limitations

This study has two primary limitations that warrant discussion. First, the method addresses only 23 of 25 MFDS-regulated fragrance allergens, as atranol and chloroatranol—constituents of moss extracts—require LC-MS analysis. Second, recovery validation was conducted for only 10 of the 23 target allergens due to certified reference standard availability. Although these 10 analytes represent frequent fragrance allergens, validation of all 23 allergens remains incomplete. Future work should incorporate LC-MS analysis for thermally unstable allergens and expand recovery testing to all target allergens, thereby enhancing the method's regulatory applicability and comprehensiveness.

4. Conclusions

This study validated and optimized an MFDS-guided GC-MS method for quantifying 23 fragrance allergens in cosmetic products. The key optimization —aligning the ISTD concentration (2 μg/mL) with the analyte concentration range—eliminated signal interference and substantially improved the average R^2 from 0.790 to 0.994. Application of the optimized method to 106 commercial cosmetic products identified limonene, linalool, and citronellol as the most prevalent fragrance allergens. Although most products complied with current labeling regulations, one body mist exhibited a labeling violation with undeclared coumarin exceeding the regulatory threshold (0.01 % for wash-off products and 0.001 % for leave-on products). In conclusion, the optimized GC-MS method provides robust analytical support for regulatory surveillance and underscores the critical importance of continuous monitoring of fragrance allergens to reduce consumer exposure risks, ensure labeling compliance, and prevent allergic sensitization.

Acknowledgements

This study was supported by the Seoul Metropolitan Government Research Institute of Public Health and Environment.

References

1. J. D. Johansen, *American Journal of Clinical Dermatology*, **4**(11), 789-798 (2003). https://doi.org/10.2165/00128071-200304110-00006
2. C. Spence, *Frontiers in Psychology*, **11**, 598859 (2020). https://doi.org/10.3389/fpsyg.2020.598859
3. T. Oktaviani, S. Widhiati, H. Kariosentono, M. E. Irawanto, and T. Oktavriana, *SKIN The Journal of Cutaneous Medicine*, **8**(6), 1908-1919 (2024). https://doi.org/10.25251/skin.8.6.1
4. European Commission. (2020). Scientific Committee on Consumer Safety (SCCS) Opinion on Fragrance allergens in cosmetic products. Available online : https://ec.europa.eu/health/scientific_committees/consumer_safety/docs/sccs_o_102.pdf (accessed 26-27 June 2012)
5. Ministry of Food and Drug Safety (MFDS), Republic of Korea. (2024). Cosmetic Analysis Method Compendium.

Available online: https://www.nifds.go.kr/brd/m_18/view.do?seq=12787 (accessed October 2024)
6. H. Lu, M. C. Fang, Y. Z. Chen, S. C. Huang, and D. Y. Wang, *Journal of Food and Drug Analysis*, **29**(4), 700 (2021). https://doi.org/10.38212/2224-6614.3373
7. B. Desmedt, M. Canfyn, M. Pype, S. Baudewyns, V. Hanot, P. Courselle, J. O. De Beer, V. Rogiers, K. De Paepe, and E. Deconinck, *Talanta*, **131**, 444-451 (2015). https://doi.org/10.1016/j.talanta.2014.08.006
8. H. Leijs, J. Broekhans, L. van Pelt, and C. Mussinan, *Journal of Agricultural and Food Chemistry*, **53**(14), 5487-5491 (2005). https://doi.org/10.1021/jf048081w
9. L. Mondello, D. Sciarrone, A. Casilli, P. Q. Tranchida, P. Dugo, and G. Dugo, *Journal of Separation Science*, **30**(12), 1905-1911 (2007). https://doi.org/10.1002/jssc.200600541
10. International Council for Harmonisation of Technical Requirements for Pharmaceuticals for Human Use (ICH). (2023). ICH harmonised guideline: Validation of analytical procedures Q2(R2) (Step 4 version). Available online: https://www.ich. org/page/quality-guidelines
11. A. Furey, M. Moriarty, V. Bane, B. Kinsella, and M. Lehane, *Talanta*, **115**, 104-122 (2013). https://doi.org/10.1016/j.talanta.2013.03.048
12. Hübschmann, H. J. Handbook of GC-MS: fundamentals and applications. John Wiley & Sons. (2025).
13. S. AL-Mussallam, A. T. Bawazir, R. S. Alshathri, O. Alharthi, and F. S. Aldawsari, *Cosmetics*, **10**(3), 91 (2023). https://doi.org/10.3390/cosmetics10030091
14. Codex. (2001). Harmonized IUPAC guidelines for the use of recovery information in analytical measurement. In: CAC/GL 37-2001. Available online: https://www.fao.org/input/download/standards/376/CXG_037e.pdf (Accessed June 23, 2026)
15. Scientific Committee on Consumer Safety (SCCS), (2019). SCCS/1591/17, SCCS OPINION ON the safety of Butylphenyl methylpropional (p-BMHCA) in cosmetic products-Submission II SCCS/1591/17-Final version. Available online: https://health.ec.europa.eu/publications/safety-butylphenyl-methylpropional-p-bmhca-cosmetic-products-submission-ii_en (accessed 10 May 2019).
16. A. Lapczynski, D. McGinty, L. Jones, S. Bhatia, C. S. Letizia, and A. M. Api., *Food and Chemical Toxicology*, **45**(1), S362-S380 (2007). https://doi.org/10.1016/j.fct.2007.09.036
17. C. de Groot. Chapter 3.16 Benzyl Alcohol. In: Monographs in Contact Allergy: Volume 2: Fragrances and Essential Oils. CRC Press; (2021) 81-92.
18. D. P. M. Canavez, G. de Oliveira Prado Corrêa, V. L. B. Isaac, D. C. Schuck, and M. Lorencini, *Journal of Applied Toxicology*, **41**(10), 1687-1699 (2021). https://doi.org/10.1002/jat.4156
19. S. Lim, S. M. Choi, K. B. Kim, K. Yoon, S. Kacew, H. S. Kim, and B. M. Lee, *Journal of Toxicology and Environmental Health Part A*, **81**(22), 1173-1185 (2018). https://doi.org/10.1080/15287394.2018.1543232
20. Scientific Committee on Consumer Products. (2006). Opinion on coumarin (sensitisation only) (SCCP/0935/05). European Commission. Available online: https://ec.europa.eu/health/ph_risk/committees/04_sccp/docs/sccp_o_061.pdf (accessed 20 June 2006)
21. J. B. Sharmeen, F. M. Mahomoodally, G. Zengin, and F. Maggi, *Molecules*, **26**(3), 666 (2021). https://doi.org/10.3390/molecules26030666
22. A. Ogueta, J. Brared Christensson, E. Giménez-Arnau, R. Brans, M. Wilkinson,, L. Stingeni, C. Foti, O. Aerts, C. Svedman, M. Gonçalo, and A. Giménez-Arnau, *Contact dermatitis*, **87**(1), 1-12 (2022). https://doi.org/10.1111/cod.14064