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Short communication

Determination of salicylate- and benzophenone-type sunscreen agents in cosmetic products by gas chromatography–mass spectrometry

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Abstract

A novel simple method to detect salicylate- and benzophenone-type sunscreen agents in cosmetic products by gas chromatography–mass spectrometry (GC–MS) has been developed. Seven sunscreen agents (two salicylate-type and five benzophenone-type) were used for this study. Sunscreen agents and cosmetic product solutions were prepared by dissolving in dimethylformamide, and silylated with bis-trimethylsilyltrifluoroacetamide–trichloromethylsilane (BSTFA). Silylated sunscreen agents were separated on a cross-linked methyl silicone gum column. The identification of each sunscreen agent was accomplished by retention time and mass spectrum library search with a computer, and the quantitation was made in the selected-ion monitoring (SIM) mode of GC–MS. Silylation increased the detection limits of all sunscreen agents about 20–170-fold. Linearity was maintained over the range 1–300 μg/ml for each sunscreen agent. Each cosmetic product (i.e. sun lotion, sun cream and sun cream foundation) was found to contain amounts of the sunscreen agents. This method was sensitive and gave 95.2–104.1% recovery of each sunscreen agent from these cosmetic products. From these results, we concluded that silylation with BSTFA followed by GC–MS analysis allows the simple, convenient and exact determination of sunscreen agents from cosmetic products.

1. Introduction

Sunscreen agents in cosmetics are used to protect the skin from aging and sunburn and to prevent discoloration or fading of cosmetic products due to sunlight. A variety of sunscreen agents have been developed and used in cosmetic products, especially skin care (e.g., lotion, cream) and make-up products (e.g., foundation, twin cake).

To detect the sunscreen agents in cosmetic products, thin-layer chromatography (TLC) [1], high-performance liquid chromatography (HPLC) [1–5], and gas–liquid chromatography (GC) [1,6,7] have been used. Confirmation of sunscreen agents by these methods has been done on the basis of retention time, and spectral characteristics of sunscreen agents on UV spectrophotometers.

Recently, a gas chromatography–mass spectrometry (GC–MS) method for the identification of sunscreen agents was reported [7]. The GC–MS method in selected-ion monitoring (SIM) mode allowed the accurate determination and

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confirmation of sunscreen agents among many ingredients of the cosmetic products.

We propose a new simple method based on GC–MS for the detection of two salicylate- and five benzophenone-type sunscreen agents [2-ethylhexylsalicylate (octylsalicylate), 3,3,5-trimethylcyclohexylsalicylate (homosalate), 2,4-dihydroxybenzophenone (benzophenone-1), 2,2′,4,4′-tetrahydroxybenzophenone (benzophenone-2), 2-hydroxy-4-methoxybenzophenone (benzophenone-3), 2,2′-dihydroxy-4,4′-dimethoxybenzophenone (benzophenone-6), and 2,2′-dihydroxy-4-methoxybenzophenone (benzophenone-8)] in cosmetic products.

Since most of the benzophenone-type sunscreen agents have low sensitivity and volatility for gas chromatography, derivatization such as silylation has been used to overcome these drawbacks. According to Cumpelik [6], a silylation method using HMDS (hexamethyldisilazane) and TMS-Cl (trichloromethylsilane) requires the complete removal of water from all solvents and samples. We adapted a simple silylation method using BSTFA which was used by Valdez [8] and Molever [9].

2. Experimental

2.1. Reagents and materials

Benzylbenzoate, 2,4-dihydroxybenzophenone (benzophenone-1), dimethylformamide (DMF) and bis-trimethylsilyltrifluoroacetamide–1% trichloromethylsilane (BSTFA) were purchased from Sigma (USA). All reagents were analytical grade and used without further purification. Commercially available sunscreen agents used in this study are listed in Table 1.

2.2. Instruments and conditions

Analysis of sunscreen agents was performed on a Model HP 5890 Series II gas chromatograph (Hewlett-Packard, USA) interfaced with a Model HP 5971A mass selective detector, and a Model HP 7673A automatic sampler. Electron impact (EI) mass spectra were recorded at an ionization potential of 70 eV. The mass spectrometer was scanned from m/z 35 to 550 rate of 1.1 scan per second. Fused-silica capillary column (HP-1, Hewlett-Packard), 25 m × 0.20 mm I.D. was used which had been coated with methyl silicone gum (cross-linked) of 0.33 μm film thickness.

Both the injection and the transfer line temperature were 280°C. The oven temperature was held at 170°C for 3 min, then increased at a rate of 5°C/min to a final temperature of 280°C, and kept there for 5 min. The carrier gas was helium at a column head pressure of 8 p.s.i. (1 p.s.i. = 6894.76 Pa), and the split ratio was 20:1. Using an automatic sampler, 1 μl-aliquots of the prepared standard and sample solutions were analysed under the operation conditions described above.

Quantitation was made based on peak area

Table 1
List of sunscreen agents studied

Chemical name	Synonym	Supplier
2-Ethylhexylsalicylate	Octylsalicylate	Vandyk
3,3,5-Trimethylcyclohexylsalicylate	Homosalate	Merck
2-Hydroxy-4-methoxybenzophenone	Benzophenone-3	BASF
2,4-Dihydroxybenzophenone	Benzophenone-1	Sigma
2,2′-Dihydroxy-4-methoxybenzophenone	Benzophenone-8	Sigma
2,2′-Dihydroxy-4,4′-dimethoxybenzophenone	Benzophenone-6	Vandyk
2,2′,4,4′-Tetrahydroxybenzophenone	Benzophenone-2	Vandyk

Table 2
Retention times and detection limits of sunscreen agents before and after silylation

Peak no.	Sunscreen agent	Before silylation		After silylation	
		t_R (min)	Detection limit (μg/ml)[b]	t_R (min)	Detection limit limit (μg/ml)[b]
1	Benzylbenzoate (I.S.)[a]	5.60	0.3	5.59	0.30
2	Octylsalicylate	6.18	2.0	7.69	0.03
3	Homosalate	6.81, 7.08	2.0	8.09, 8.53	0.03
4	Benzophenone-3	8.40	2.0	9.05	0.03
5	Benzophenone-1	9.21	5.0	9.83	0.03
6	Benzophenone-8	9.74	7.0	10.75	0.03
7	Benzophenone-6	12.52	7.0	12.57	0.10
8	Benzophenone-2	N.D.[c]	N.D.	13.69	0.30

[a] I.S. = Internal standard.
[b] Detection limits were measured in GC–MSD-SIM mode.
[c] N.D. = Not detected.

with GC–MS in SIM mode using benzylbenzoate as an internal standard.

2.3. Standard solutions

Standard stock solutions were prepared by dissolving the appropriate amount of sunscreen agent in DMF. A set of working standard solutions were made by diluting aliquots of the stock solutions with DMF to 100 ml in volumetric flasks containing 5 ml internal standard solution. Then, each 200-μl aliquot of the mixed solutions was transferred to an automatic sampler vial and 400 μl of BSTFA were added. The concentration of each compound for the calibration curves is in the range of 1–300 μg/ml.

2.4. Sample solutions

About 5 g of cosmetic product was weighed into a 100-ml beaker, dissolved in about 40 ml of DMF by sonication and transferred into a 100-ml volumetric flask. The beaker was rinsed three times with 10-ml portions of DMF. The solution was diluted with DMF to 100 ml in volumetric flasks containing 5 ml internal standard solution. An aliquot of the solution was filtered through a 0.45-μm membrane filter. Then, each 200 μl

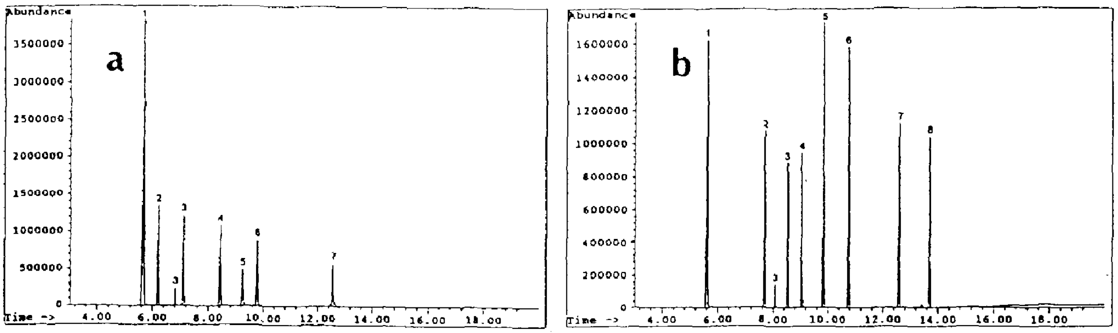

Fig. 1. Total-ion chromatogram of sunscreen agents (a) before and (b) after silylation.

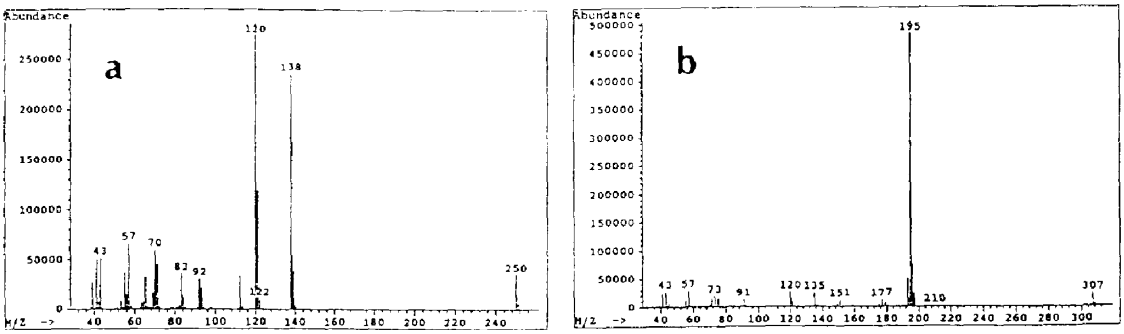

Fig. 2. EI mass spectra of (a) octylsalicylate and (b) silylated octylsalicylate.

aliquot was transferred to an automatic sampler vial and 400 μl of BSTFA were added.

2.5. Internal standard solutions

About 2.0 g of benzylbenzoate was weighed into a 50-ml volumetric flask and diluted to the volume with DMF.

3. Results and discussion

The retention times and the detection limits for the investigated sunscreen agents before and after silylation are shown in Table 2. The total-ion chromatograms (TIC) obtained with the proposed GC–MS method are shown in Fig. 1a (before silylation) and Fig. 1b (after silylation). After silylation, all studied sunscreen agents showed remarkable increases (20–170 times) in the sensitivities and the detection limits. Benzophenone-2 was detected with a high sensitivity and a good detection limit in Fig. 1b (peak 8), but not in Fig. 1a. The seven sunscreen agents were found to be well separated after silylation.

The electron impact (EI) mass spectra of the sunscreen agents are shown in Fig. 2–8. Octylsalicylate and homosalate showed intense peaks at m/z 195 due to the 2-dimethylsilyloxybenzoic acid moiety. All the benzophenone-type sunscreen agents showed strong $[M-CH3]^+$ ion peaks as base ions. The base and characteristic mass ion peaks of the sunscreen agents after silylation are listed in Table 3.

Sometimes, the peaks of the sunscreen agents in practical GC analysis overlap with those of other ingredients in cosmetic products. In this case, the GC–MS information obtained from monitoring the characteristic molecular and major ions helped to detect the presence of particular sunscreen agents, and to determine the exact amounts of sunscreen agents in cosmetic products. In this study, the selected-ion

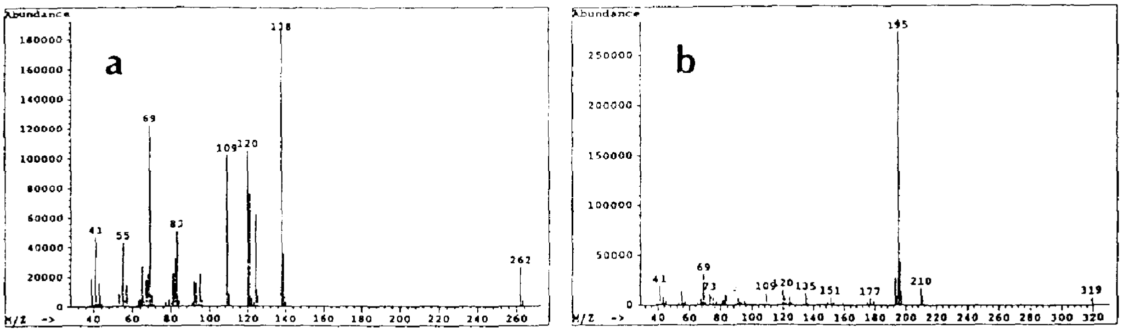

Fig. 3. EI mass spectra of (a) homosalate and (b) silylated homosalate.

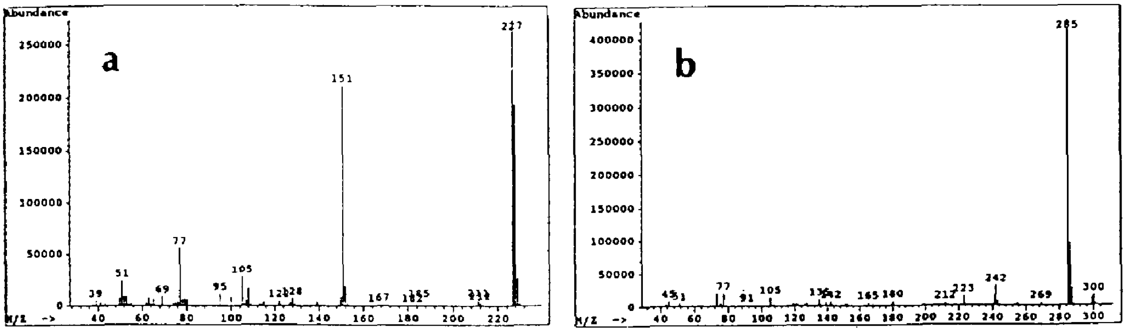

Fig. 4. EI mass spectra of (a) benzophenone-3 and (b) silylated benzophenone-3.

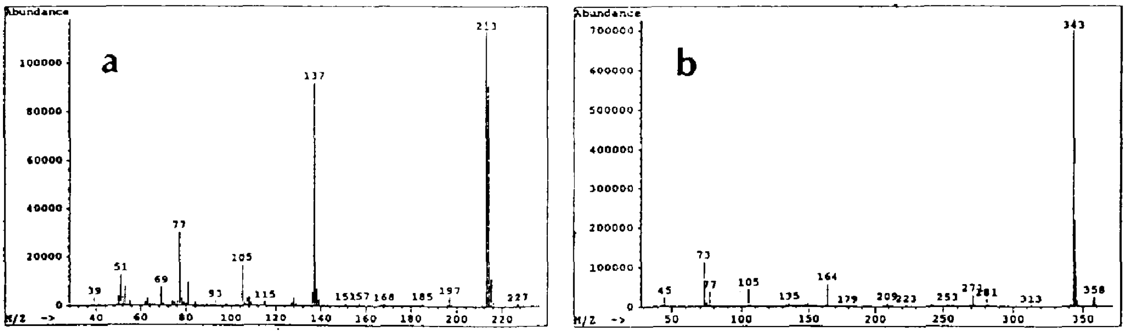

Fig. 5. EI mass spectra of (a) benzophenone-1 and (b) silylated benzophenone-1.

monitoring (SIM) mode of GC–MS was used as a selective detector for sunscreen agents

A calibration curve was constructed by plotting the peak areas against the concentration of the silylated standards injected in GC–MS-SIM mode. Correlation coefficients were in the range of 0.991–1.000, and linear relationship was maintained over the range of 1–300 μg/ml for each silylated sunscreen agent.

Recovery tests were carried out to evaluate the reproducibility and accuracy of the proposed method. A proprietary sun lotion, a sun cream, and a sun cream foundation were spiked with the amounts of agents reported in Table 4 and subjected to the described analytical procedure. Quantitation was made in GC–MS-SIM mode with internal standard, and selected mass ions for the SIM mode were the same as those listed

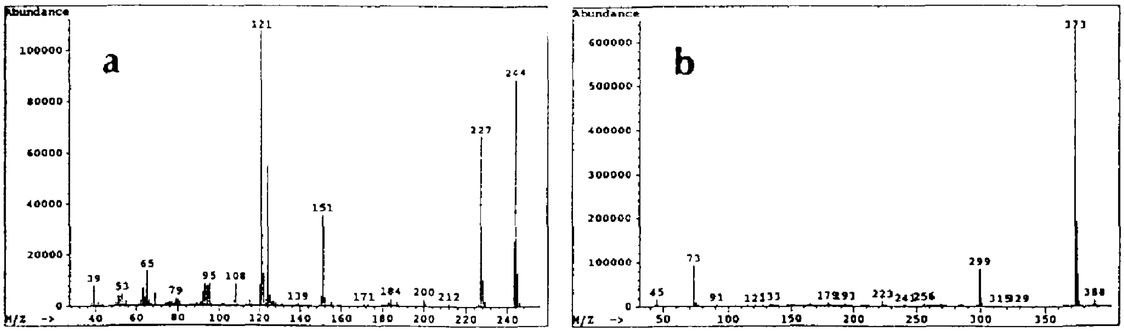

Fig. 6. EI mass spectra of (a) benzophenone-8 and (b) silylated benzophenone-8.

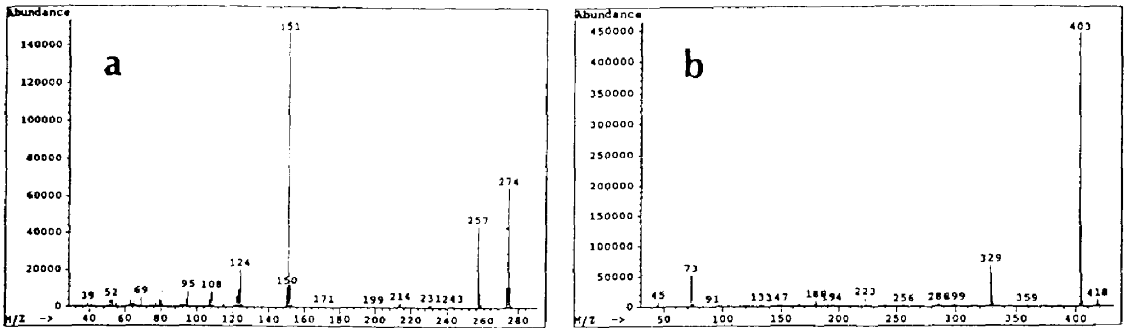

Fig. 7. EI mass spectra of (a) benzophenone-6 and (b) silylated benzophenone-6.

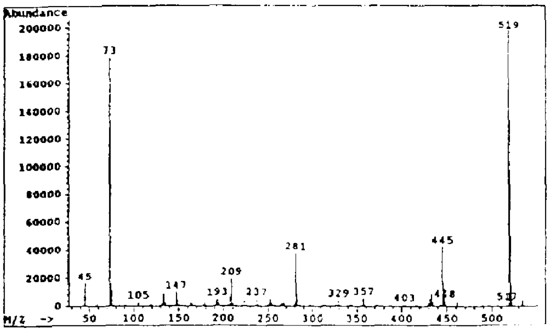

Fig. 8. EI mass spectrum of benzophenone-2.

in Table 3. Excellent recovery with precision was observed, as shown in Table 4. From the total-ion chromatogram (Fig. 9a, 10a and 11a) and selected-ion chromatogram (Fig. 9b, 10b and 11b) of sun lotion, sun cream and sun cream foundation, it was seen that GC–MS-SIM could be used as a selective detector for sunscreen agents. Therefore, in GC–MS-SIM mode, it was possible to exclude the unwanted peaks of ingredients in cosmetic products and determine the amounts of sunscreen agents with accuracy.

4. Conclusion

A novel method was developed for the determination of sunscreen agents in cosmetic products by GC–MS. Simple silylation with BSTFA followed by GC–MS analysis allowed a remarkable increase in the sensitivity and the detection limit as well as the accurate determi-

Table 3
The characteristic mass ions of sunscreen agents after silylation

Peak no.	Sunscreen agent	*m/z*	*m/z*
1	Benzylbenzoate (I.S.)	105 $[M - C_7H_7O]^+$	212 $[M]^+$
2	Octylsalicylate	195 $[M - C_9H_{19}]^+$	307 $[M - CH_3]^+$
3	Homosalate	195 $[M - C_{10}H_{19}]^+$	319 $[M - CH_3]^+$
4	Benzophenone-3	285 $[M - CH_3]^+$	300 $[M]^+$
5	Benzophenone-1	343 $[M - CH_3]^+$	358 $[M]^+$
6	Benzophenone-8	373 $[M - CH_3]^+$	388 $[M]^+$
7	Benzophenone-6	403 $[M - CH_3]^+$	418 $[M]^+$
8	Benzophenone-2	445 $[M - C_4H_{13}Si]^+$	519 $[M - CH_3]^+$

Table 4
Recoveries of sunscreen agents from cosmetic samples

Peak no.	Sunscreen agent	Amount added (%, w/w)	Recovery ± S.D.(%) [a]		
			Lotion	Cream	Cream foundation
2	Octylsalicylate	3.0	97.0 ± 0.9	98.8 ± 0.7	99.7 ± 0.6
3	Homosalate	3.0	96.5 ± 1.3	97.2 ± 1.1	97.6 ± 0.8
4	Benzophenone-3	3.0	98.3 ± 0.8	98.1 ± 1.6	98.8 ± 1.1
5	Benzophenone-1	3.0	98.0 ± 0.9	97.7 ± 1.2	100.6 ± 1.8
6	Benzophenone-8	3.0	97.6 ± 1.9	98.7 ± 1.3	99.9 ± 0.5
7	Benzophenone-6	3.0	98.8 ± 1.1	98.0 ± 0.8	99.5 ± 0.8
8	Benzophenone-2	3.0	101.6 ± 3.1	100.8 ± 1.4	101.3 ± 2.8

[a] Each value is the average of five determinations.

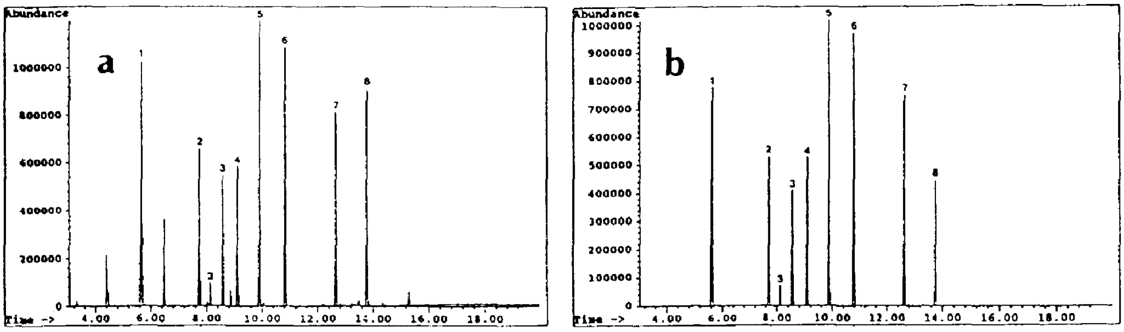

Fig. 9. (a) Total- and (b) selected-ion chromatogram of silylated sun lotion.

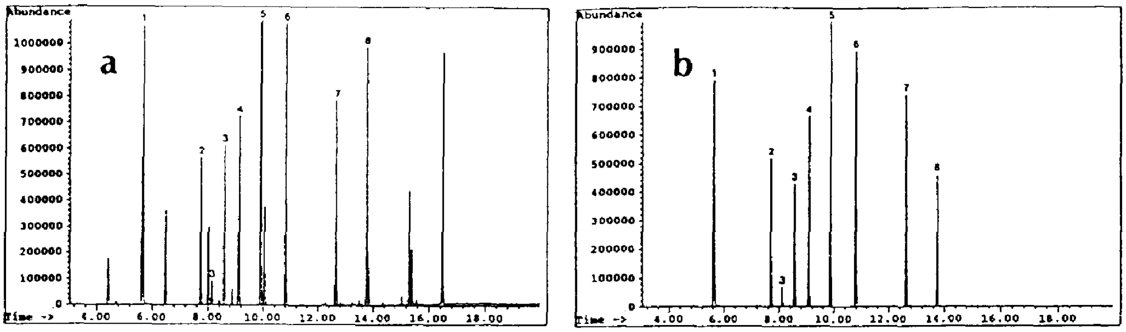

Fig. 10. (a) Total- and (b) selected-ion chromatogram of silylated sun cream.

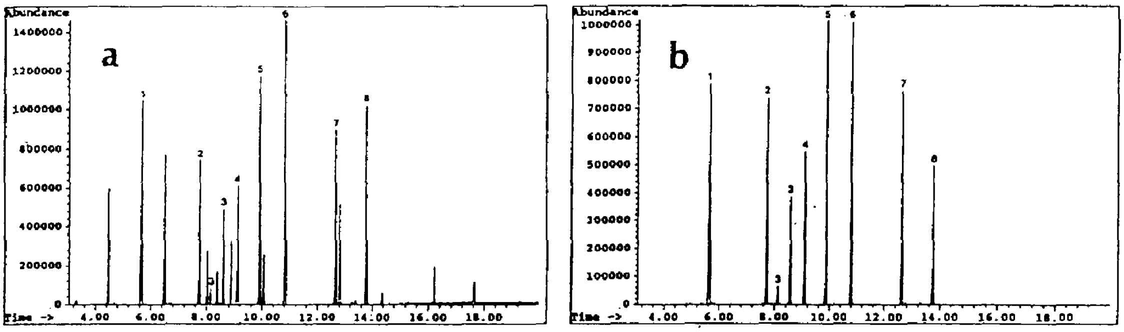

Fig. 11. (a) Total- and (b) selected-ion chromatogram of silylated sun cream foundation.

nation and confirmation of sunscreen agents in cosmetic products containing many ingredients.

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