

Note

Determination of sunscreen agents in cosmetic products by gas chromatography and gas chromatography–mass spectrometry

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Sunscreen agents are widely used to protect the skin against sunburn and to prevent the degradation of cosmetic products by sunlight, and a simple and reliable method for the determination and confirmation of sunscreen agents in cosmetic products is required in order to check whether the products were prepared in accordance with official regulations.

Several methods have been reported, including gas–liquid chromatography (GC)^{1–3} and high-performance liquid chromatography (HPLC)^{2–8}. Confirmation of sunscreen agents in these methods is usually done on the basis of retention times, and a method based on UV spectral characteristics of sunscreen agents was proposed by Gagliardi *et al.*⁵. However, a more definite identification of sunscreen agents by gas chromatography–mass spectrometry (GC–MS) has not been reported.

In a previous paper⁸, a simple method based on HPLC was proposed for the determination of six sunscreen agents {(2-hydroxy-4-methoxyphenyl)phenylmethanone (Oxybenzone), 2-ethoxyethyl 3-(4-methoxyphenyl)-2-propenoate (Cinoxate), 2-ethylhexyl 4-(dimethylamino)benzoate (Escalol 507), 2-ethylhexyl 3-(4-methoxyphenyl)-2-propanoate (Parsol MCX), 1-[4-(1-methylethyl)phenyl]-3-phenyl-1,3-propanedione (Eusolex 8020) and 1-[4-(1,1-dimethylethyl)phenyl]-3-(4-methoxyphenyl)-1,3-propanedione (Parsol 1789)} in cosmetic products. HPLC is useful for routine analysis but now difficult to use in combination with mass spectrometry in our laboratory. In this paper, we describe the application of GC to the determination of the six sunscreen agents and GC–MS to their confirmation using a DB-17 megabore capillary column.

EXPERIMENTAL

Reagents and materials

Oxybenzone, Cinoxate, Escalol 507, Parsol MCX, Eusolex 8020 and Parsol 1789 were used as reference standards as reported previously⁸. Water was deionized and distilled from glass apparatus. All other chemicals were of analytical-reagent grade.

Standard solutions

Stock standard solutions were prepared by dissolving the appropriate amount of sunscreen agent in tetrahydrofuran (THF). A set of working standard solutions were produced by diluting aliquots of the stock standard solutions with THF to 50 ml in volumetric flasks. The concentration of each compound for the calibration graphs ranged from 20 to 100 $\mu\text{g/ml}$.

Sample solution

An amount of a cosmetic product equivalent to about 1–5 mg of a sunscreen agent was weighed accurately in a 50-ml beaker, dissolved in about 20 ml of THF by sonication and transferred into a 50-ml volumetric flask. The beaker was rinsed twice with 5-ml portions of THF and the rinsings were combined in a volumetric flask. The solution was diluted to volume with THF.

Gas chromatography

Determination of sunscreen agents was performed on a Model GC-15A gas chromatograph (Shimadzu, Kyoto, Japan) equipped with a flame ionization detector. All samples were automatically injected into the gas chromatograph by a Model AOC-9 automatic sampler (Shimadzu). Chromatograms and peak areas were obtained with a Model C-R5A reporting integrator (Shimadzu). The megabore column used (15 m \times 0.53 mm I.D.) contained DB-17 (50% phenylmethylpolysiloxane, 1.0- μm film thickness; J & W Scientific, Folsom, CA, U.S.A.). The injection temperature was 280°C. The oven temperature was set at 160°C for 10 min, then programmed from 160 to 250°C at 5°C/min followed by a 10-min hold at 250°C. Helium was used as the carrier gas at a flow-rate of 20 ml/min.

By means of the automatic sampler, 5 μl of the prepared sample solution and standard solution were chromatographed under the operating conditions described above. Quantification was based on peak areas.

Gas chromatography-mass spectrometry

Confirmation of sunscreen agents was performed on a Model HP 5890A gas chromatograph (Hewlett-Packard, Avondale, PA, U.S.A.) interfaced to a VG Analytical (Manchester, U.K.) Model 70S high-resolution mass spectrometer. Electron impact (EI) mass spectra were recorded at an ionization potential of 70 eV. The megabore column used and the operating conditions for GC-MS analysis were the same as described under *Gas chromatography*. The mass spectrometer was scanned repetitively from m/z 50 to 400 at a rate of one scan per second.

RESULTS AND DISCUSSION

A representative chromatogram obtained with the proposed GC method is shown in Fig. 1. Under the experimental conditions, the six sunscreen agents were well resolved. Calibration graphs were constructed by plotting the peak area against the concentration of standard injected. Good linearity over the range 20–100 $\mu\text{g/ml}$ for each sunscreen agent was obtained. The detection limits were 1 $\mu\text{g/ml}$ for Oxybenzone, Cinoxate, Escalol 507 and Parsol MCX, 3 $\mu\text{g/ml}$ for Eusolex 8020 and 5 $\mu\text{g/ml}$ for Parsol 1789.

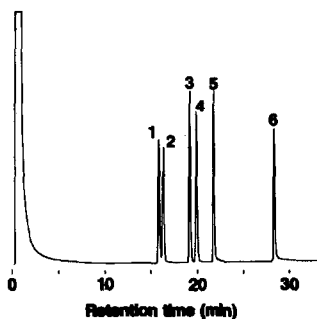


Fig. 1. GC of sunscreen agents. Amount injected: 500 ng of each sunscreen agent. Peaks: 1 = Oxybenzone; 2 = Cinoxate; 3 = Escalol 507; 4 = Parsol MCX; 5 = Eusolex 8020; 6 = Parsol 1789.

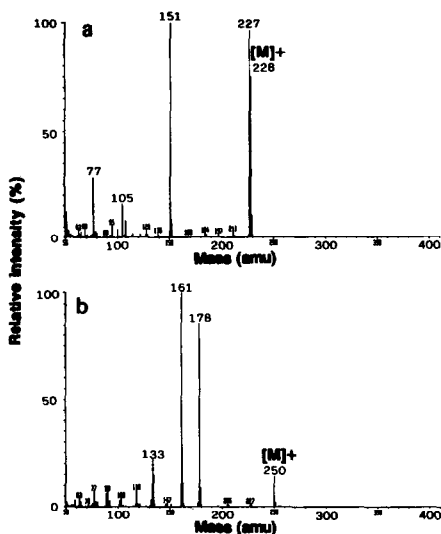


Fig. 2. EI mass spectra for (a) Oxybenzone and (b) Cinoxate.

The total ion current chromatogram of a full-scan GC-EI-MS analysis of 500 ng of each sunscreen agents is essentially identical with the gas chromatogram in Fig. 1. Figs. 2, 3 and 4 show the EI mass spectra of the sunscreen agents. Each spectrum showed an $[M]^+$ ion and Oxybenzone and Eusolex 8020 also showed a strong $[M - H]^+$ ion. The base peaks of the sunscreen agents were as follows: Oxybenzone,

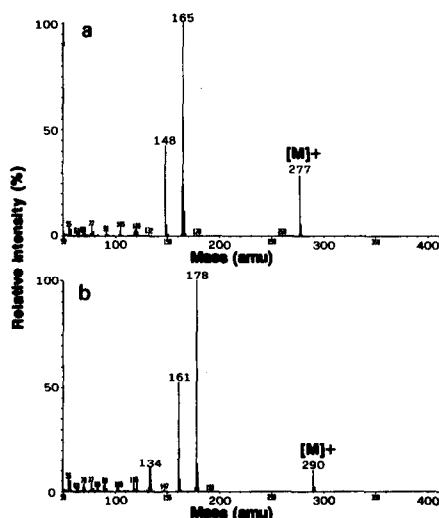


Fig. 3. EI mass spectra for (a) Escalol 507 and (b) Parsol MCX.

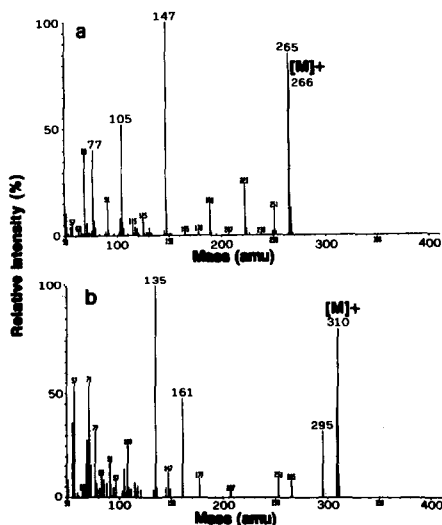


Fig. 4. EI mass spectra for (a) Eusolex 8020 and (b) Parsol 1789.

m/z 151 ($[M - C_6H_5]^+$); Cinoxate, m/z 161 ($[M - C_4H_9O_2]^+$); Escalol 507, m/z 165 ($[M - C_8H_{16}]^+$); Parsol MCX, m/z 178 ($[M - C_8H_{16}]^+$); Eusolex 8020, m/z 147 ($[M - C_8H_7O]^+$); and Parsol 1789, m/z 135 ($[M - C_{12}H_{15}O]^+$). Cinoxate and Parsol MCX showed intense peaks at m/z 178 and 161 due to the 3-(4-methoxyphenyl)-2-propenoic acid moiety.

The peaks of the sunscreen agents in practical GC analysis sometimes overlap those of other ingredients containing in cosmetic products. In such a case, the information obtained from monitoring the characteristic ions (molecular ion and major ion) by GC-MS is useful to confirm whether particular sunscreen agents are present or not. The characteristic ions are as followed: Oxybenzone, m/z 228 ($[M]^+$), 227 ($[M - H]^+$) and 151; Cinoxate, m/z 250 ($[M]^+$), 178 ($[M - C_4H_8O]^+$) and 161; Escalol 507, m/z 277 ($[M]^+$), 165 and 148 ($[M - C_8H_{17}O]^+$); Parsol MCX, m/z 290 ($[M]^+$), 178 and 161 ($[M - C_8H_{17}O]^+$); Eusolex 8020, m/z 266 ($[M]^+$), 265 ($[M - H]^+$) and 147; and Parsol 1789, m/z 310 ($[M]^+$), 295 ($[M - CH_3]^+$), 161 ($[M - C_9H_9O_2]^+$) and 135.

Recovery tests were carried out on cosmetic products to evaluate the reproducibility and accuracy of the proposed GC method. Three cosmetic products were spiked with the amounts of the agents reported in Table I and subjected to the whole procedure. As shown in Table I, excellent recoveries and precision were observed.

TABLE I

RECOVERIES OF SUNSCREEN AGENT FROM COSMETICS

Amounts of standard samples added were as follows: suntan lotion, 2.5% (w/w); foundation, 1% (w/w); lipstick, 2% (w/w).

Sunscreen agent	Suntan lotion		Foundation		Lipstick	
	Recovery (%)	R.S.D. (%) ^a	Recovery (%)	R.S.D. (%) ^a	Recovery (%)	R.S.D. (%) ^a
Oxybenzone	99.9	1.8	100.9	1.2	101.2	1.4
Cinoxate	99.8	0.4	99.9	1.5	97.0	2.1
Escalol 507	100.0	1.2	103.5	1.5	98.7	1.5
Parsol MCX	100.0	0.5	100.0	2.8	99.9	1.9
Eusolex 8020	100.4	0.3	98.3	1.1	104.2	1.0
Parsol 1789	101.2	0.4	95.8	3.3	103.7	1.7

^a Relative standard deviation ($n = 5$).

The proposed GC method was applied to the determination of sunscreen agents in various cosmetic products (suntan lotion, foundation and lipstick). A representative chromatogram of a commercial suntan lotion is shown in Fig. 5. Analytical results are given in Table II. These results agreed with those obtained by HPLC⁸. The suntan lotion, foundation and lipstick contained about 1–7% of sunscreen agents.

The concentrations of sunscreen agents in the cosmetic products could be determined by monitoring the characteristic ions because the absolute intensity of each ion increases in proportion with the amount of compound injected. Fig. 6 shows total

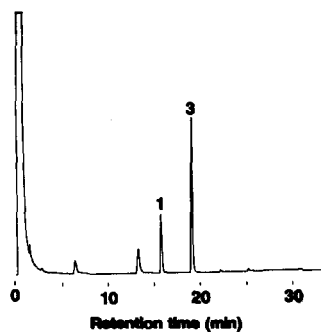


Fig. 5. GC of sunscreen agents in a commercial suntan lotion (No. 2 in Table II). Peaks: 1 = Oxybenzone; 3 = Escalol 507.

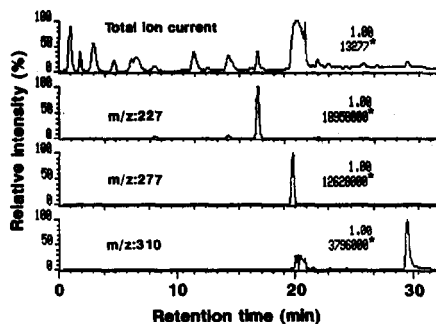


Fig. 6. Total ion current and mass chromatograms from the GC-EI-MS analysis of a commercial milk lotion. The values with asterisks are the absolute intensities on the 100% intensity axis.

ion current and mass chromatograms obtained from the GC-EI-MS analysis of a commercial milk lotion. It was confirmed from these chromatograms that the lotion contained Oxybenzone, Escalol 507 and Parsol 1789. The concentrations of each of these sunscreen agents were also determined from intensities of the characteristic ions; the results of 0.1% for Oxybenzone, 0.1% for Escalol 507 and 0.05% for Parsol 1789 were in agreement with the results obtained by GC analysis. The detection limits were the same as those in GC.

In conclusion, a simple, precise and accurate method has been developed for the determination of sunscreen agents in cosmetic products by GC using a megabore capillary column without any derivatization such as silanization as reported by Cumpelik¹. It is suitable for the routine analysis of cosmetic products. The GC-MS method allows the determination and confirmation of sunscreen agents even if the cosmetic products contain many ingredients.

TABLE II
CONTENTS OF SUNSCREEN AGENTS IN COSMETICS

Values in parentheses obtained by HPLC⁸.

Sample	No.	Concentration (% , w/w)		
		Oxybenzone	Escalol 507	Parsol MCX
Suntan lotion	1	3.2 (3.5)	6.6 (7.0)	2.2 (2.1)
	2	3.1 (2.8)	7.1 (6.9)	
Foundation	1		3.0 (2.8)	
	2			1.3 (1.3)
Lipstick	1			0.96 (0.95)
	2	2.7 (2.8)		

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