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Technical note

Determination of sunscreen agents in cosmetic products using microwave-assisted extraction and liquid chromatography

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Abstract

Microwave-assisted extraction (MAE), was used to extract sunscreen agents from cosmetic products. The extracts were analyzed by liquid chromatography (LC). The present method allows the determination of three sunscreen agents, Eusolex 2292, 4360 and 6300. The precision of the assay at 40 $\mu\text{g/ml}$ of sunscreen agents ranged from 1.5 to 2.2%, and the detection limits were 2.0–4.0 ng/ml. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Microwave-assisted extraction; Cosmetics; Sunscreen agents

1. Introduction

Sunscreen agents such as Eusolex 2292 (octyl methoxy cinnamate; 2-ethylhexyl *p*-methoxycinnamate), Eusolex 4360 (benzophenone-3; 2-hydroxy-4-methoxybenzophenone), and Eusolex 6300 (3-(4-methylbenzylidene)-camphor) which mitigate the deleterious effects of sunlight [1–3] are used in a variety of cosmetics. The determination of sunscreen agents in cosmetics is usually carried out by liquid chromatography after liquid–liquid extraction [4,5], solid-phase extraction [4–6] or supercritical fluid extraction (SFE) [7–10].

An interesting alternative sample pretreatment procedure is microwave-assisted extraction (MAE) which is often used for the digestion of environmental and biological samples [11–14]. With modern

equipment, uniform heating in MAE provides high extraction recoveries and short extraction times. In the present study, MAE/LC with UV detection was developed to determine sunscreen agents in cosmetics.

2. Experimental

2.1. Apparatus and LC conditions

The LC system consisted of a Beckman 126 pump and a Beckman 168 UV detector set at 300 nm (Beckman Instruments, Taiwan Branch, Taiwan). A microbore column was packed with C₁₈ (150×1.0 mm I.D., G.L. Sciences, Inertsil ODS-2, 5 μm , Tokyo, Japan). The eluent was acetonitrile–water (90:10, v/v) at a flow-rate of 90 $\mu\text{l/min}$. A CMA 200 autosampler with an injection loop of 5 μl (Carnegie Medicin, Stockholm, Sweden) was used.

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A hole was drilled on the top of a Panasonic NN 5556B microwave oven (600 W, 2.45 MHz magnetron, Manaus, Brazil). A condenser was placed in the center of the microwave oven and covered with isolating materials to prevent leakage of microwaves. Cooling water (4°C) was flushed throughout the experiment.

2.2. Reagents

Eusolex 2292, 4360, 6300, LC-grade methanol, and acetonitrile were purchased from Merck (Darmstadt, Germany). Unless otherwise stated, all chemicals were of analytical grade. Water was deionized and doubly distilled. All reagents for LC analysis were filtered through a Millipore filter (pore size, 0.45 μm) and degassed with helium before use.

2.3. Extraction of sunscreen agents from cosmetic creams

Creams (ca. 0.5 g) spiked with sunscreen agents or commercial cosmetics (ca. 0.15 g) were weighed into a 50-ml conical flask, to which 5–30 ml (according to experimental protocol) of methanol were added. The flask was connected to the microwave extraction system, and extraction was performed for 5–25 s. After 10 min cooling, the solution was filtered through a Lida filter (Lida, Nylon-66, and 0.22 μm). Aliquots of 5 μl filtrates were injected onto LC.

2.4. Calibration curves

Calibration curves of peak areas versus concentrations were generated with known amounts of sunscreen agents (range, 0.2–80 $\mu\text{g}/\text{ml}$). The percentage recovery was calculated by comparing the peak areas of sunscreen agents extracted from the test samples with peak areas obtained from standard mixtures.

3. Results and discussion

Fig. 1 shows the effect of variation of the percentage of acetonitrile in the eluent on the retention of Eusolex 2292, 4360 and 6300. Under optimal conditions (acetonitrile–water, 90:10, v/v) all ana-

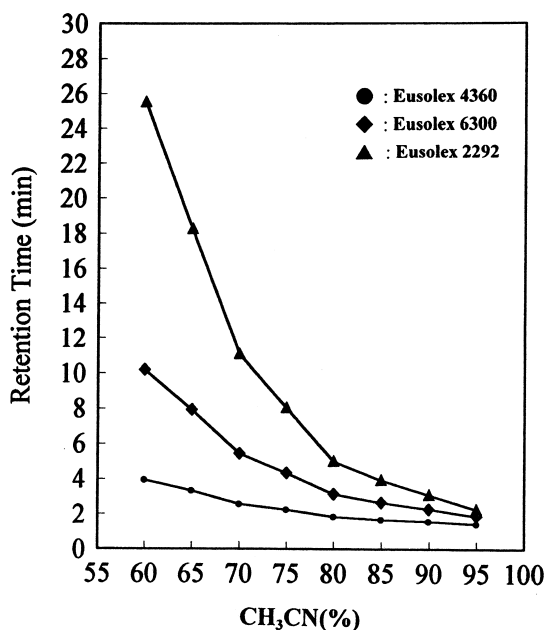


Fig. 1. Effect of percentage of acetonitrile in eluent on the retention of Eusolex 2292, 4360 and 6300.

lytes were well resolved within 4 min. Fig. 2A shows a chromatogram of a standard mixture of Eusolex 2292, 4360 and 6300.

The response linearity of the tested sunscreen compounds was examined, and the data are shown in Table 1. An excellent linearity of each sunscreen agent was obtained with the concentration range of 0.2–80 $\mu\text{g}/\text{ml}$ (triplicates). The detection limits (signal-to-noise ratio=3) were 3, 4 and 2 ng/ml for Eusolex 2292, 4360 and 6300, respectively.

A typical liquid–liquid extraction of cosmetic products consumed approximately 100 ml of organic solvents in 1–2 h [4,13]. For MAE, the effects of solvent volume (5–30 ml) and reaction time (5–25 s) were studied. One-step MAE requires only 5–15 ml of organic solvent, and can be completed in 5–15 s. A typical chromatogram of an extract containing Eusolex 2292, 4360, and 6300 obtained from a sunscreen cream is shown in Fig. 2B. Indeed, MAE technique is superior to liquid–liquid extraction because it is rapid and consumes a relatively smaller amount of organic solvents.

In order to evaluate the precision of the method, a sunscreen cream containing 40 $\mu\text{g}/\text{ml}$ of each

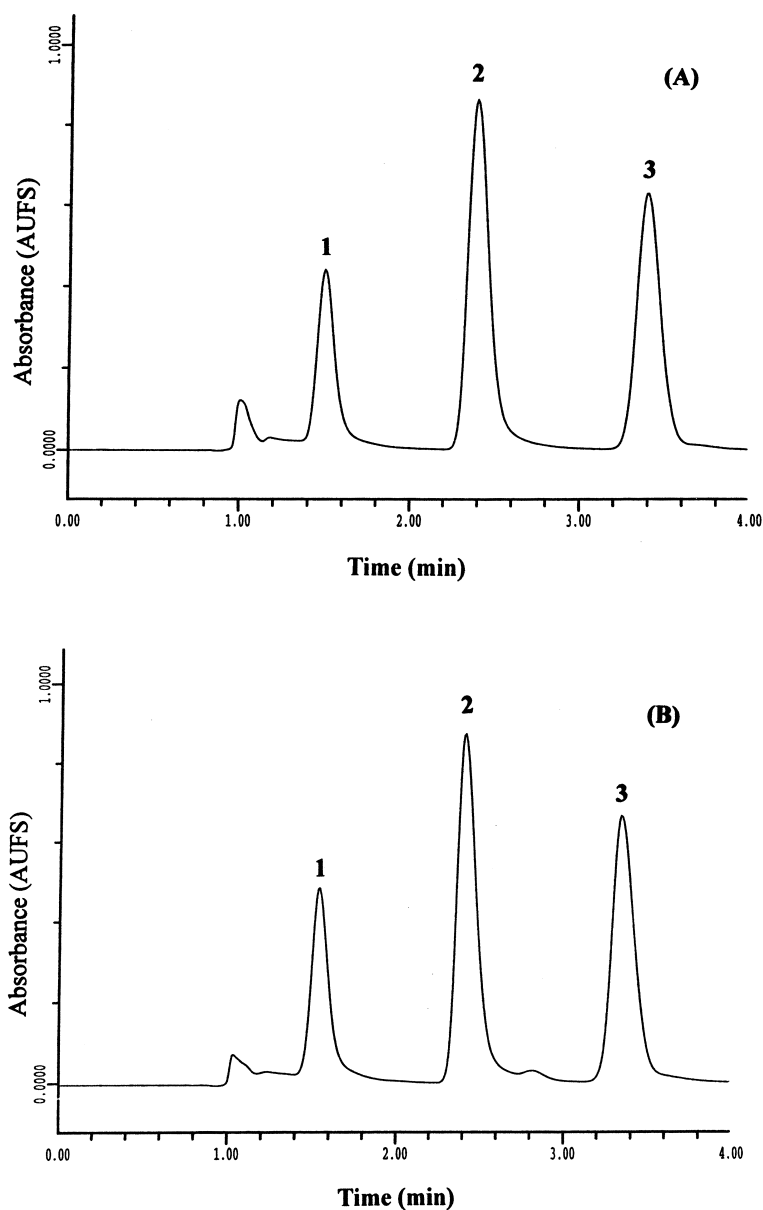


Fig. 2. LC-UV chromatograms obtained for (A) a standard mixture of sunscreen agents and (B) a commercial sunscreen cream product. Peaks: (1) Eusolex 4360; (2) Eusolex 6300; and (3) Eusolex 2292.

analyte was used. For the total analytical procedure of MAE the coefficients of variation of Eusolex 2292, 4360 and 6300 were 2.2, 1.5 and 1.6% ($n=8$), respectively.

The accuracy of the method was determined by spiking experiments. A sunscreen cream was spiked

with the sunscreen agents at final concentrations of 10–40 $\mu\text{g/ml}$. The analyte recoveries from the cream were satisfactory, with values ranging from 99 to 103%, showing that quantitative and reproducible results can be obtained with this MAE/LC method (Table 1).

Table 1
Analytical data of sunscreen agents extracted from cosmetic samples^a

Sunscreen agents	Amount present (µg/ml)	Recovery (%)	<i>r</i>
Eusolex 2292	10	101.1	0.999
	20	101.1	
	30	100.6	
	40	101.4	
Eusolex 4360	10	101.0	0.999
	20	99.7	
	30	101.2	
	40	100.2	
Eusolex 6300	10	98.5	0.999
	20	102.8	
	30	100.0	
	40	99.4	

^a All data measured in triplicate and linearity range of 10–40 (µg/ml).

As an application, three commercial sunscreen cream products were analyzed. The amounts of the sunscreen agents experimentally found were very close to the known amounts (Table 2).

In conclusion, MAE/LC-UV is a rapid and

Table 2
MAE/LC-UV of sunscreen agents in commercial cosmetic samples

Product	Eusolex 2292 (µg/ml)	Eusolex 4360 (µg/ml)	Eusolex 6300 (µg/ml)
A	Present	20.0	No
	Determined	19.5	N.D. ^a
B	Present	10.0	No
	Determined	10.3	21.6
C	Present	10.0	10.0
	Determined	9.3	10.1

^a N.D., not detected.

straightforward procedure for the quantitative analysis of sunscreen agents in cosmetics. In addition, MAE consumes a limited amount of organic solvent and can be used for routine purpose.

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