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Short Communication

Determination of sun-screen agents in cosmetic products by micellar liquid chromatography

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ABSTRACT

A micellar liquid chromatographic method was developed for the quantitative determination of sun-screen agents in cosmetic products. The qualitative analysis of parabens is also feasible. Excellent linearity was obtained ($r = 0.999$) and recoveries were generally greater than 98%. A variety of commercial formulations were analyzed.

INTRODUCTION

Micellar chromatography continues to find unique applications. Recent applications include the use of micellar chromatography in the quantitation of hydrophobicity [1], determination of heavy-metal cations [2] and the determination of drug substances in biological fluids [3–6]. The solubilizing ability is one of the micelles most important property which allows for the direct quantitation of an analyte contained within a complex matrix.

With greater regulation of over-the-counter (OTC) products by the Food and Drug Administration (FDA), a facile analytical method for the determination of sun-screen agents in cosmetic products is desirable. Determinations based on reversed-phase high-performance liquid chromatography (HPLC) have been reported [7–9]. Due to the complex nature of the cosmetic preparation, the sample preparation may require an extraction step. A micellar solution would solubilize the cosmetic formulation allowing for the direct analysis of the active sun-screen agents.

A simple analytical method based on micellar HPLC which allows for qualitative and quantitative determination of 2-ethylhexyl-*p*-dimethylaminobenzoate (PABA), 2-ethylhexyl-*p*-methoxycinnamate (EMC) and 2-hydroxy-4-methoxybenzophenone (oxybenzone) in OTC sun-screen preparations will be described. PABA, EMC and oxybenzone are the leading UV absorbers in cosmetic products. The method makes use of external standards thus minimizing sample preparation even further.

EXPERIMENTAL

Instrumentation

A modular component HPLC system was used consisting of a Spectra-Physics SP8700 pump (San Jose, CA, USA), a Schoeffel Spectroflow Monitor SF 770 variable-wavelength detector and a Rhe-

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odyne sample injector (Cotati, CA, USA) equipped with a 20-μl injection loop. The column was a Shandon (Sewickley, PA, USA) C_8 Hypersil WP300, 10 μm (250 × 4.6 mm I.D.). A Model 5000 Fisher Recordall strip chart recorder (Springfield, NJ, USA) was used to record the chromatograms.

Reagents

The sodium dodecyl sulfate (SDS), was electrophoresis grade obtained from Bio-Rad Labs. (Richmond, CA, USA) and used as received. The isopropanol, triethylamine and phosphoric acid, 85% (Fisher Scientific) were used as received. The methyl 4-hydroxybenzoate and propyl 4-hydroxy-benzoate (Aldrich, Milwaukee, WI, USA) were used as received. The PABA, EMC and oxybenzone were courtesy of Van Dyk & Co. (Belleville, NJ, USA).

Chromatographic conditions

A 0.10 *M* SDS solution, containing 0.3% (v/v) triethylamine, pH adjusted to 3.0 with phosphoric acid, was used as the micellar solution. The mobile phase was SDS–isopropanol (90:10, v/v). A flow of 1.5 ml/min was used. The column temperature was ambient. Detection wavelength was either 254 or 300 nm. Strip chart recorder speed was 0.25 cm/min.

Standard solution

About 30 mg oxybenzone and either 300 mg PABA or 300 mg EMC were transferred into a 50-ml volumetric flask, dissolved and diluted to volume with methanol. A volume of 5.0 ml of the solution was transferred to a 50-ml volumetric flask and diluted to volume with the mobile phase.

Simulated sun-screen preparation

Accurately weigh 9.0 g of commercial skin lotion which does not contain sun-screen agents into a 50-ml beaker. To the lotion is added 0.30 g oxybenzone and either 0.70 g EMC or 0.70 g PABA. The mixture is allowed to stir at 40–50°C for 1 h.

Sample preparation

Accurately weigh 1.0–1.5-g sample of sun-screen lotion into a 50-ml volumetric flask. The sample is dissolved with isopropanol and diluted to volume. A volume of 5.0 ml of the solution is diluted to a 50-ml volumetric flask with mobile phase. An aliquot of the solution is filtered through a 0.45-μm membrane filter prior to HPLC analysis.

RESULTS AND DISCUSSION

PABA, EMC and oxybenzone are active ingredients in sunscreen products because of their relatively high molar absorptivities in the ultraviolet range. In ethanol or methanol, PABA and oxybenzone have wavelength maximum values of 310 and 290 nm, respectively [10]. The analytical wavelength of 254 nm was initially selected as cited by Tan *et al.* [11]. Fig. 1 depicts a chromatogram of a commercial preparation containing methyl- and propylparaben, PABA and oxybenzone. As evident, good resolution of the compounds is obtained. The qualitative analysis of parabens which are utilized as antimicrobial agents [12] in cosmetic preparations is feasible. *p*-Hydroxybenzoic acid possesses a maximum absorbance at 246 nm [13]. At 254 nm a qualitative method of determining parabens with a quantitative determination of sun-screen agents is feasible. The drawback of the analysis is the poor response factor of PABA and EMC at this wavelength as compared to the response factor of oxybenzone.

To insure accurate quantitation, the analytical wavelength of 300 nm resulted in a greater response

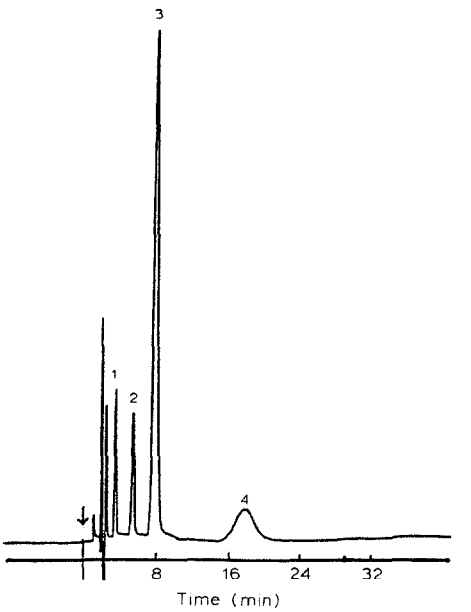

Fig. 1. Typical chromatogram of a commercial sun-screen preparation obtained by setting the detector at 254 nm. Peaks: 1 = methylparaben; 2 = propylparaben; 3 = oxybenzone; 4 = PABA. Chromatographic conditions as in text.

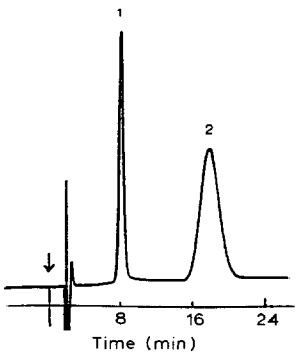

Fig. 2. Typical chromatogram of a commercial sun-screen preparation obtained by setting the detector at 300 nm. Peaks: 1 = oxybenzone; 2 = PABA.

factor of the analytes. The chromatogram of a commercial preparation containing oxybenzone and PABA is depicted in Fig. 2 which shows the enhanced response factor of PABA at 300 nm. Good resolution of the sun-screens is evident but the qualitative analysis of the parabens is diminished at the higher wavelength. The retention times under the experimental conditions described, were 3.92, 17.36 and 19.40 min for oxybenzone, PABA and EMC, respectively.

Quantitative analysis is obtained by the use of an external standard method which further simplified the sample preparation. Calibration curves were constructed for each of the three sun-screens. Excellent linearity was obtained throughout the investigated range of commercial preparations for PABA, oxybenzone and EMC. Typical sun-screen concentrations in a commercial preparation are as follows: 1.4–8.0% PABA, 2.0–7.5% EMC and 2.0–6.0% oxybenzone. Correlation coefficients $r = 0.9999$ were achieved for PABA, oxybenzone and EMC.

Recovery studies were performed by adding known amounts of sun-screen in the concentration range of a typical preparation to a commercial skin lotion preparation which does not contain sun-screens as part of the formula. The results of the analysis which were calculated using the calibration curves described above are summarized in Table I. As is evident, good recoveries and precision were obtained.

The method was applied to a variety of commercial preparations with a sun protection factor (SPF) ranging from 4 to 15. A SPF of 2 to 4 provides minimal sunscreen protection. Where as, a SPF of 8 to 15 provides greater sun-screen protection. Table II provides the results of the analysis of the commer-

TABLE I

RECOVERY DATA FROM SIMULATED FORMULATIONS

Each value is the mean of three determinations.

Compound	Amount added (mg/g sample)	Recovery (%) + S.D.
Lotion A		
Oxybenzone	10.7	97.7 ± 2.4
EMC	18.3	99.3 ± 2.5
Lotion B		
Oxybenzone	6.26	99.5 ± 2.5
PABA	14.4	98.2 ± 2.2

TABLE II

ANALYSIS OF COMMERCIAL SUN-SCREEN PRODUCTS

Representing three vendors (1, 2 and 3).

Compound	SPF	Amount found (%, w/w)
Lotion 1A	4	
Oxybenzone		1.35 ± 0.03
PABA		3.22 ± 0.08
Lotion 1B	8	
Oxybenzone		3.08 ± 0.08
PABA		6.36 ± 0.16
Lotion 1C	15	
Oxybenzone		2.92 ± 0.07
PABA		7.00 ± 0.18
Lotion 2A	4	
Oxybenzone		0.89 ± 0.02
EMC		3.02 ± 0.08
Lotion 2B	15	
Oxybenzone		2.72 ± 0.07
EMC		6.79 ± 0.17
Lotion 3A	8	
Oxybenzone		2.05 ± 0.05
PABA		4.38 ± 0.12
Lotion 3B	15	
Oxybenzone		3.04 ± 0.08
PABA		5.36 ± 0.13

cial preparations along with the SPF claimed by the manufacturer.

The HPLC assay reported here is suitable for routine analysis of sunscreen agents. The method is facile and reproducible. No deterioration of the column was detected due to the direct injection of a cosmetic matrix. The study exceeded 200 injections onto the column.

REFERENCES

1 M. G. Khaledi and E. D. Breyer, *Anal. Chem.*, 61 (1989) 1040.
2 T. Okada, *Anal. Chem.*, 60 (1988) 2116.
3 L. J. Cline Love and J. J. Fett, *J. Pharm. Biomed. Anal.*, 9 (1991) 323.
4 F. Palmisano, A. Guerrieri, P. G. Zambonin and T. R. I Cataldi, *Anal. Chem.*, 61 (1989) 946.
5 J. Haginaka, J. Wakai, H. Yasuda and T. Nakagawa, *Anal Chem.*, 59 (1987) 2732.
6 F. J. DeLuccia, M. Arunyanart and L. J. Cline Love, *Anal Chem.*, 57 (1985) 1564.
7 L. Gagliardi, G. Cavazzutti, L. Montanarella and D. Tonelli *J. Chromatogr.*, 464 (1989) 428.
8 K. Ikeda, S. Suzuki and Y. Watanabe, *J. Chromatogr.*, 48 (1989) 240.
9 Y. Maeda, M. Yamamoto, K. Owada, S. Sato, T. Masui, H Nakazawa and M. Fujita, *J. Chromatogr.*, 410 (1987) 413.
10 Food and Drug Administration, *Fed. Reg.*, 43 (1979) 38264
11 H. S. Tan, R. Sih, S. E. Moseley and J. L. Lichtin, *J Chromatogr.*, 291 (1984) 275.
12 F. F. Cantwell, *Anal. Chem.*, 48 (1976) 1854.
13 A. M. Wahbi and M. A. H. Barary, *Anal. Chem.*, 16 (1983 1617.