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Short communication

Determination of water-soluble UV-filters in sunscreen sprays by liquid chromatography

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Abstract

Liquid chromatography was used for the determination of the three most used water-soluble UV filters, benzophenone-4 (BZ4), terephthalylidene dicamphor sulfonic acid (TDS), and phenylbenzimidazole sulphonic acid (PBS), in aqueous sunscreen sprays. A C_{18} stationary phase and an isocratic mobile phase of EtOH–20 mM sodium acetate buffer of pH 4.6 (30:70, v/v) were used at a flow-rate of 0.5 ml min^{-1} . Mobile phase was also used as solvent for samples and standards. UV detection was at 313 nm. The analytical run took 5.5 min. The limits of detection were 0.5, 0.9 and $2 \mu\text{g ml}^{-1}$ for BZ4, TDS and PBS, respectively. The proposed method does not involve highly toxic solvents.

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1. Introduction

Exposure to UV radiation from sunlight can cause harmful effects on human health. Sunscreen products may be used to reduce these effects. The concentration of the UV filters in the sunscreen formulations must be monitored to assure the labelled sun protection factor (SPF) in the commercial preparations without exceeding the authorized levels set by different legislations. Therefore, fast, accurate methods are needed to control these products. Benzophenone-4 (BZ4), phenylbenzimidazole

sulphonic acid (PBS) and terephthalylidene dicamphor sulfonic acid (TDS) are water-soluble UV filters used in the called “easy to use” sunscreens. The maximum authorized level for these compounds according to the European legislation [1] is 5% for BZ4, 8% for PBS and 10% for TDS.

Different liquid chromatographic (LC) procedures have been published where the determination of BZ4 and PBS was performed [2–5]. In most of these, BZ4 and PBS were determined in standard solutions or either in spiked sunscreens. Rastogi and Jensen [6] identified 21 organic UV filters (including BZ4, PBS and TDS) in sunscreen products by matching the retention time and spectrum of each peak in the max-plot chromatogram of the sample solutions with the retention time and spectra of standard UV filters

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in a spectral library previously built from standards' data.

This is the first paper reporting the separation and quantification of BZ4, TDS and PBS in sunscreens. The proposed method does not involve highly toxic solvents.

2. Experimental

2.1. Reagents and samples

2-Phenylbenzimidazole-5-sulphonic acid (named phenylbenzimidazole sulphonic acid according to International Nomenclature Cosmetic Ingredients, PBS) 99% from Guinama (Valencia, Spain), 2-hydroxy-4-methoxybenzophenone-5-sulphonic acid (benzophenone-4) (BZ4) 99.9% from Roig Farma (Terrassa, Spain) and 3,3'-(1,4-phenylene-dimethylidene bis(7,7-dimethyl-2-oxo-bicyclo-[2.2.1]heptane-1-methanesulfonic acid) (terephthalylidene dicamphor sulfonic acid, TDS) triethanolamine salt 99% that was kindly supplied by L'Oreal (Madrid, Spain), were used to prepare the standards.

Analytical reagent-grade acetic acid (HAc) and HPLC-grade ethanol (EtOH) from Scharlab (Barcelona, Spain), and de-ionized water using a NANO-pure II ultrapure water system from Barnstead (Boston, USA) were used as solvents. Analytical reagent-grade sodium hydroxide from Probus (Badalona, Spain) was also used.

Ten sunscreen samples containing PBS, BZ4 and/or TDS obtained from commercial manufacturers (RNB-Cosméticos, Berioska, Laboratorios-Vigmar, Laboratoires-Garnier) were analyzed by following the proposed method. A sunscreen sample containing the three UV filters was prepared in our laboratory using reagents of cosmetic-reagent grade kindly provided by Berioska and following the common procedure used by this company.

2.2. Proposed method

A solution composed of EtOH–20 mM sodium acetate buffer of pH 4.6 (30:70, v/v), was prepared and used as mobile phase in the chromatographic determination and also as solvent for samples and

standards. A total of 0.01–0.1 g of sunscreen water was dissolved and diluted to 10 ml with mobile phase. Multicomponent solutions of the three UV filters (15–75 $\mu\text{g ml}^{-1}$ for PBS; 10–50 $\mu\text{g ml}^{-1}$ for BZ4 and TDS) in mobile phase were used as standards. Twenty μl of standard and sample solutions were injected into the LC system at a flow-rate of 0.5 ml min^{-1} . The UV detection was carried out at 313 nm.

A Hitachi LC system equipped with a Hitachi L-7100 high-pressure pump and a Hitachi L-7420 UV-Vis detector was employed, using a LiChrospher RP-18 (12.5-cm \times 4-mm I.D., 5- μm particle size) (Merck) column.

Sample and standard solutions must be kept in the dark because experiments carried out showed that TDS solutions are sensible to light exposure.

3. Results and discussion

3.1. Study of the chromatographic variables

The effect of pH, composition of the mobile phase and flow-rate was investigated in order to select the values that provided good resolution of the peaks with the shortest analysis time. Fig. 1 shows the effect of the mobile phase pH (a) and the percentage of EtOH in the mobile phase (b) on the retention time of a 25- $\mu\text{g ml}^{-1}$ solution of the three analytes in water. As can be seen, the retention time increased with pH (Fig. 1a) and/or with EtOH diminution (Fig. 1b). A methodology based on a simplex algorithm [7] was used to optimize both variables jointly. The initial conditions were pH 3.0 and 30% EtOH and the studied range 3.0–6.0 and 15–35% for pH and percentage of EtOH, respectively. The flow-rate was kept constant at 1 ml min^{-1} and the buffer concentration was 20 mM. The best results was obtained by employing a mobile phase with 30% EtOH and pH in the 4.5–4.7 range. Thus, the chosen composition of the mobile phase was EtOH–20 mM sodium acetate buffer of pH 4.6 (30:70, v/v).

The mobile phase flow-rate was also studied over the range 0.25–1.25 ml min^{-1} and 0.5 ml min^{-1} provided the best results.

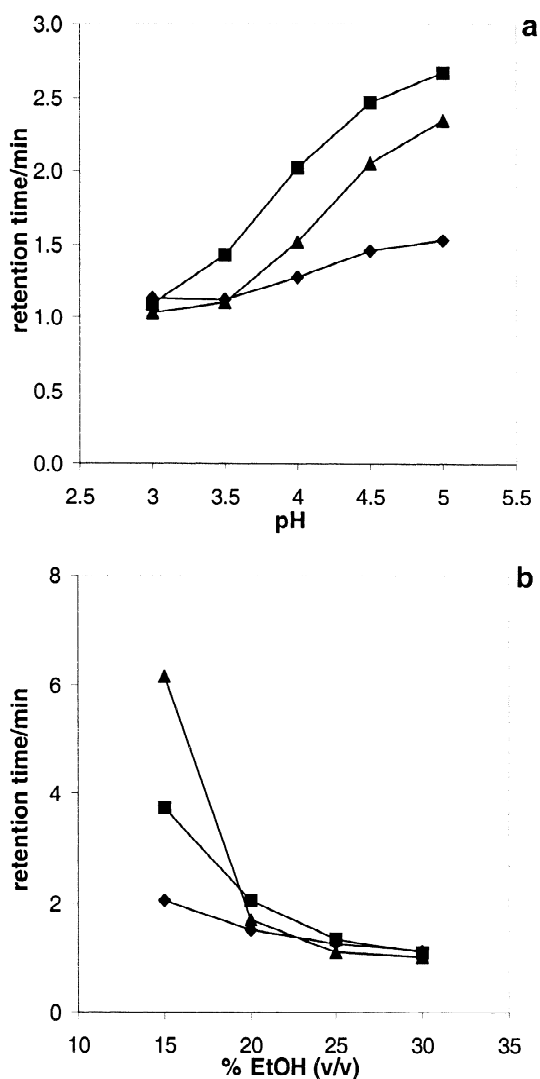


Fig. 1. Effect of chromatographic variables on the retention times of the studied UV filters. (♦) PBS, (▲) TDS and (■) BZ4. (a) Effect of mobile phase pH. Mobile phase EtOH–20 mM sodium acetate buffer of variable pH (30:70, v/v) at 1 ml min⁻¹ flow-rate. (b) Effect of percentage (v/v) of EtOH in the mobile phase. Mobile phase: EtOH–20 mM sodium acetate buffer of pH 3, at 1 ml min⁻¹ flow-rate.

Since PBS elutes at a retention time very close to the dead time, mobile phase was used as solvent of samples and standards in order to avoid the fluctuation caused by the elution front, which might cause serious problems at low concentrations.

Table 1
Results obtained in the analysis of sunscreen samples

Sample	Found concentration ± s ^a (% , m/m)		
	PBS	TDS	BZ4
A	1.59 ± 0.01	N.D. ^b	0.541 ± 0.003
B	3.17 ± 0.04	N.D.	1.097 ± 0.009
C	4.24 ± 0.09	N.D.	1.59 ± 0.05
D	3.28 ± 0.01	N.D.	1.088 ± 0.004
E	5.01 ± 0.09	N.D.	1.63 ± 0.03
F	N.D.	N.D.	0.50 ± 0.02
G	0.44 ± 0.03	N.D.	N.D.
H	0.931 ± 0.003	N.D.	N.D.
I	1.48 ± 0.04	0.210 ± 0.007	N.D.
J	1.48 ± 0.03	1.88 ± 0.05	N.D.
K ^c	1.818 ± 0.009	1.90 ± 0.01	1.15 ± 0.01

Retention times: PBS, 2.69 ± 0.01 min; TDS, 3.65 ± 0.02 min; BZ4, 4.74 ± 0.02.

Calibration data. Calibration lines, PBS area = (30 ± 10) 10⁺⁴ + (1850 ± 30) 10⁺² C; TDS area = (-10 ± 3) 10⁺⁴ + (948 ± 9) 10⁺² C; BZ4 area = (-2 ± 1) 10⁺⁴ + (722 ± 4) 10⁺² C; C expressed in μg ml⁻¹. Limit of detection: PBS, 2 μg ml⁻¹; TDS, 0.9 μg ml⁻¹; BZ4, 0.5 μg ml⁻¹.

^a Average values of three determinations.

^b N.D., not detectable.

^c Laboratory-made sample containing 1.85% of PBS, 1.93% of TDS and 1.16% of BZ4.

3.2. Analytical performance and application

The method was applied to the analysis of 10 commercial sunscreens. Table 1 shows the found concentration ± standard deviation for each analyte.

In order to evaluate the accuracy of the method the recoveries were studied. They were 100 ± 1% for PBS, 100 ± 2% for TDS and 102 ± 2% for BZ4, which means that no proportional errors existed. A laboratory-made sunscreen containing known concentrations of the three UV filters was also analyzed following the proposed method. Results are also given in Table 1; they agree with the real contents ($P=95\%$), which shows the accuracy of the method.

Data on retention times and calibration are shown in Table 1 as a footnote. Linear ranges up to 100 μg ml⁻¹ of PBS and 200 μg ml⁻¹ of TDS and BZ4 were obtained ($R^2 > 0.999$ in all cases).

Fig. 2 shows the chromatograms obtained from two commercial samples (A and J), where it can be observed the good resolution of the peaks in a total run time lower than 5.5 min.

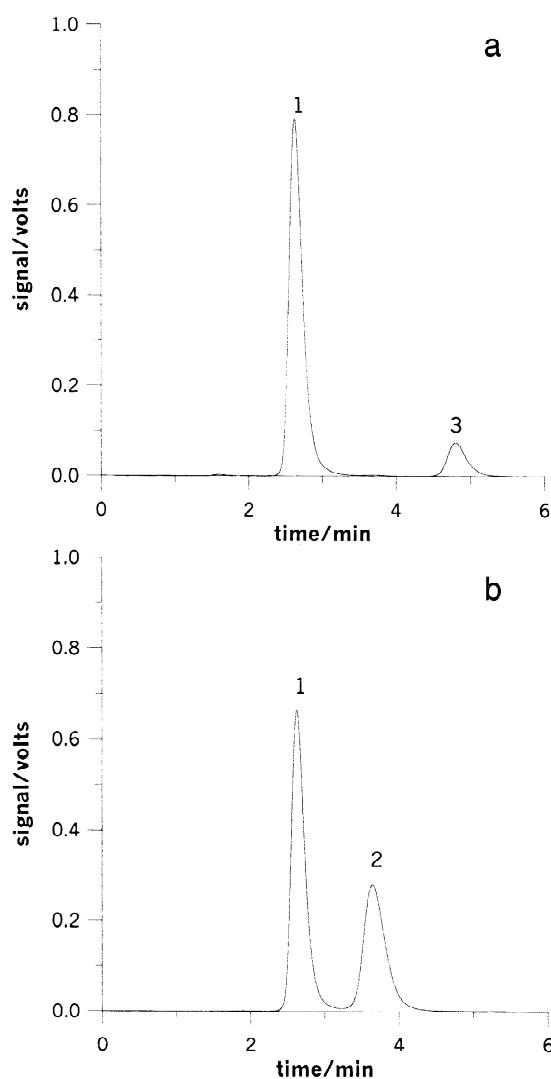


Fig. 2. Chromatograms obtained from two commercial sunscreens. Peaks: (1) PBS, (2) TDS and (3) BZ4.

4. Conclusions

A LC method for quantitative determination of three UV filters (BZ4, PBS and TDS) in aqueous sunscreen sprays has been developed. To our knowledge, no articles were published before on the TDS

determination and therefore this is the first study involving the simultaneous determination of these three UV filters. The method was employed to determine these UV filters in 10 commercial sunscreen samples. Good recoveries were obtained for all the studied samples. A home-made sample was analyzed by the proposed method and results agreed with real contents. The sample throughput was 10 samples per hour. Ethanol was used in mobile phase and as solvent for samples and standards, thus avoiding the use of other organic solvent of higher toxicity. The analytical features of the method make it suitable for quality control application.

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