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An environmentally friendly ("green") reversed-phase liquid chromatography method for UV filters determination in cosmetics

A. Salvador[*], A. Chisvert

Departamento de Química Analítica, Facultad de Química, Universitat de València, Doctor Moliner St. 50, 46100 Burjassot, Valencia, Spain

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Abstract

A green procedure based on reversed-phase liquid chromatography with gradient elution using environmentally friendly solvents, has been developed to determine 18 UV filters, which are most used in Europe nowadays as sunscreen in cosmetics. Samples were weighed and dissolved in ethanol. Two aliquots were taken from the initial sample solution to prepare two solutions, so analytes could be determined chromatographically in two groups (the most fat-soluble and the easily water-soluble ones) using a different gradient elution program for each group. The mobile phases were based on mixtures of ethanol and 1% acetic acid or 1% sodium acetate buffer pH 4.75. The same C_{18} stationary phase column was employed in both cases. The chromatographic variables such as mobile phase composition, pH, flow rate and temperature were studied and selected in order to achieve total separation of all the peaks involved. The proposed method has been validated by the analysis of 27 commercial sunscreen samples (with different cosmetic forms: cream, lipstick, makeup, sun water, lotion, milk) and two synthetic samples. The method allows any mixture of the 18 UV filters studied to be separated with a good resolution and determined without interference from cosmetic matrices, moreover it does not require the use of highly toxic organic solvents.

Keywords: UV filters; Sunscreens; Cosmetics; Liquid chromatography; Green chemistry

1. Introduction

The use of sunscreens helps to reduce skin damage produced by the UV radiation from sunlight [1], which has increased in over the years and today sunscreens are used not only for the beach, mountain or snow but also as daily products such as face day creams, after shave products, shampoos, lipsticks, makeup formulations, etc.

The concentration of UV filters in cosmetic formulations must be monitored to ensure the labelled sun protection factor in commercial preparations, but without exceeding the maximum authorized legislative levels in order to guarantee the safety of the final product.

However, although EU, US or Japan legislations have restrictions on the total content of UV filters in cosmetics, there are no official methods of controlling them.

Around 80 publications can be found in literature on sunscreen analysis [2]. Most of them are based on extraction pretreatments; derivatization reactions are required in some cases. Liquid chromatography (LC) [3–10] is the most used technique, although gas chromatography [11,12], thin layer chromatography [13], or electrokinetic micellar chromatography [14], have been also used. Few articles are based on other techniques, such as flow injection UV–vis spectrometry [15–17] or chemiluminiscence [18], nuclear magnetic resonance [19], Raman spectrometry [20], or voltametry [21].

However, a detailed study of these publications would indicate that improvement is required in two areas. Firstly, most of the published methods do not reflect the high number of UV filters and mixtures in use today, and moreover only some of the main types of cosmetic formulations such as creams or lotions are considered in most of these studies. On the other hand, the most of the methods are not particularly suitable for periodical production control, because either they require laborious samples pretreatment, with an excessive

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[*] Corresponding author. Tel.: +34 963543175; fax: +34 963544436.
E-mail address: amparo.salvador@uv.es (A. Salvador).

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amount of analysis time or/and use toxic organic solvents. The cosmetic industry requires a general, accurate and green analytical method that can be routinely and safety used in the companies' own quality control laboratories.

Different analytical procedures avoiding the use of toxic organic solvents have been developed by our group before, either based on flow injection spectrometric techniques [22,23], or liquid chromatography [24–26], but they can only be applied to a small number of UV filters. The aim of this work is to propose a general method that makes feasible to separate and determine any mixture of UV filters authorized by EU legislation and in use today, and that can be used to analyze any type of suncreen sample. The proposed LC method is based on the use of non-toxic reagents, which do not generate toxic wastes and are friendly to both the operator and the environment.

2. Experimental

2.1. Apparatus

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 × 4 mm i.d., 5 μm particle size) column from Merck (Darmstead, Germany). A 20 μl internal volume injection loop (Rheodyne®) was employed. A thermostatic water bath was used in order to set the column temperature.

An ultrasonic water bath from Torrecilla (Valencia, Spain) was used to improve sample solving process in the cases of difficulty in solubilization.

A micropH Crison 2001 pHmeter was used to adjust the pH of the buffer solution.

2.2. Reagents

Analytical reagent-grade acetic acid (AcOH) and LC-grade ethanol (EtOH) from Scharlab (Barcelona, Spain), and de-ionized water obtained by using a NANOpure II ultrapure water system from Barnstead (Boston, USA) were used as solvents. Reagent-grade NaOH from Probus (Badalona, Spain) was used to adjust the $AcOH/AcO^-$ buffer pH.

The standards used for the determination of the most fat-soluble UV filters were: benzophenone-3 (BZ3) 98% and octyl salicylate (OS) 99% from Aldrich (Barcelona, Spain), isoamyl methoxycinnamate (IMC) 99.3% from Haarmann and Reimer (Parets del Vallés, Spain), 4-methylbenzylidene camphor (MBC) 99.7% from Guinama S.L. (Valencia, Spain), octocrylene (OCR) >98% from F. Hoffmann-La Roche Ltd. (Basel, Switterland), octyl dimethyl PABA (ODP) 100 ± 2%, octyl methoxycinnamate (OMC) 99.8% and butyl methoxydibenzoylmethane (BDM) 98% from Roig Farma S.A. (Terrassa, Spain), homosalate (HS) >98% from Chemir S.A. (Barcelona, Spain), diethylhexyl butamido triazone (DBT) 99% from 3V Iberia S.A. (Barcelona, Spain), octyl triazone (OT) 100 ± 1% from BASF (Barcelona, Spain) and drometizole trisiloxane (DRT) 99.9% from L'Oréal (Paris, France).

The following standards were employed to determine the easily water-soluble UV filters: phenyldibenzimidazole tetrasulphonic acid (PDT) (disodium salt) >99% from Haarmann and Reimer (Parets del Vallés, Spain), *p*-aminobenzoic acid (PAB) 99.7% and phenylbenzimidazole sulphonic acid (PBS) 99% from Guinama S.L. (Valencia, Spain), terephthalydene dicamphor sulphonic acid (TDS) (triethanolamine salt) 99% from L'Oreal (Paris, France), benzophenone-4 (BZ4) 99.9% from Roig Farma S.A. (Terrassa, Spain) and PEG-25 PABA (P25) 98% from BASF (Barcelona, Spain).

2.3. Samples

Twenty-seven commercial samples containing different mixtures of the target compounds were analysed. They were from different laboratories: Berioska S.L. (Valencia, Spain), Dr. Babor GmbH and Co. (Aachen, Germany), Clinique Laboratories (Paris, France), Elizabeth Arden (London, United Kingdom), Fortbenton Co. Laboratories (Buenos Aires, Argentina), Helena Rubinstein (Paris, France), Laboratories Garnier (Paris, France), Lancôme (Paris, France), L'Oreal (Paris, France), Margaret Astor (Paris, France), Parfums Christian Dior (Paris, France), Revlon (London, United Kingdom), RNB S.L. (Valencia, Spain).

A laboratory-made cream sunscreen sample containing the 12 fat-soluble UV filters and a laboratory-made water sunscreen sample containing the six water-soluble UV filters were prepared in our laboratory according to two procedures used in cosmetic industries (Guinama S.L. (Valencia) and RNB S.L. (Valencia), respectively). These formulations contained other usual ingredients (emollients, surfactants, smoothing agents, bronzing agents, hydrating agents, preservatives, perfumes) employed in sunscreen cosmetics formulations, which were of cosmetic-grade and were from Guinama S.L. and RNB S.L.

2.4. Procedures

To perform the chromatographic separation, analytes were classified in two groups according to their different solubility properties.

2.4.1. Preparation of standard solutions

Two 500 $\mu g\,ml^{-1}$ multicomponent stock solution of the 12 most fat-soluble UV filters and the 6 easily water-soluble UV filters were, respectively prepared. The stock solution for the fat-soluble group was prepared in EtOH and that for the water-soluble group was prepared in water (containing 2–3 drops of 10% NaOH).

A set of working standard solutions (from 10 to 50 $\mu g\,ml^{-1}$) was prepared from these stock solutions. Fat-soluble group working standards solutions were prepared by the appropriate dilution in order to reach solutions contain-