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Development and validation of ultra-high performance supercritical fluid chromatography method for quantitative determination of nine sunscreens in cosmetic samples

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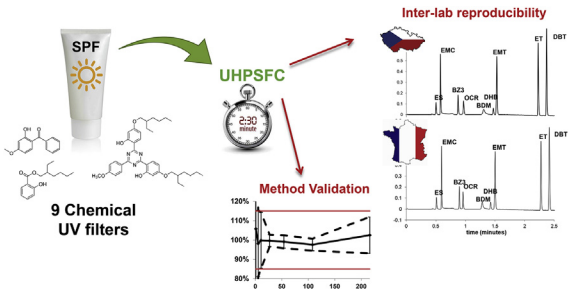
HIGHLIGHTS

- Nine UV filters are resolved within 2.5 min.
- Quantification is demonstrated over a large concentration range.
- Validation with accuracy profiles.
- Inter-laboratory reproducibility is demonstrated.

GRAPHICAL ABSTRACT



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ABSTRACT

A fast and simple utra-high performance supercritical fluid chromatography (UHPSFC) method has been developed for the determination of nine sunscreens (UV filters), namely 2-ethylhexyl-2-hydroxybenzoate (ES), ethylhexyl-methoxycinnamate (EMC), benzophenone-3 (BZ3), octocrylene (OCR), bis-ethylhexyloxyphenol-methoxyphenyl triazine (EMT), butyl-methoxydibenzoyl-methane (BDM), diethylamino-hydroxybenzoyl-hexyl-benzoate (DHB), ethylhexyl-triazone (ET), and diethylhexyl-butamido-triazone (DBT) in cosmetic samples. The separation was achieved with Acquity UPC^2 Torus 2-PIC (100 × 3.0 mm, 1.7 μm) column. The influence of key chromatographic parameters on resolution was evaluated. The optimal mobile phase was a gradient mixture of carbon dioxide and methanol containing ammonium acetate, at flow rate 1.2 mL min^{-1}. The back-pressure of the system was set to 150 bar and the temperature to 40 °C. The compounds were determined with diode-array detection at 280 nm, 305 nm and 340 nm depending on absorbance maxima. The proposed UHPSFC method provided separation of the nine target sunscreens within 2.5 min without labor-consuming sample pretreatment procedure. The method was validated according to the concept of the total error and the accuracy profile. The inter-laboratory reproducibility was evaluated between two independent laboratories (in France and Czech Republic). The reliability of the developed method was shown by application to commercial sunscreen-containing cosmetic sample obtained from French market. The measured limits

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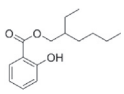
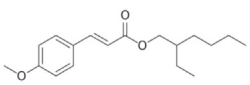
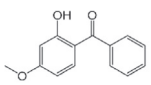
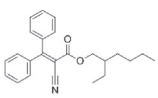
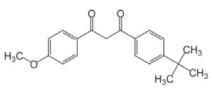
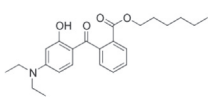
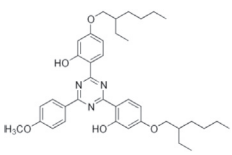
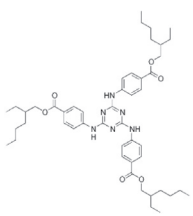
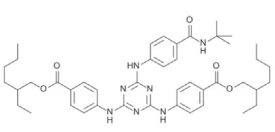
of quantification showed the suitability of the proposed method for determination of UV filters considering the European Union requirements.

1. Introduction

A sunscreen cosmetic could be defined as "*any cosmetic product containing UV filters in its formulation in order to protect the skin from the solar deleterious UV-light, avoiding or minimizing the damage that this radiation might cause on human health*" [1]. While sunscreens are crucial for UV protection, their usage carries some risks. Table 1 shows some of the most frequent compounds that are nowadays permissible as UV filters according to European legislation [1] and their maximum allowed concentration. Countries like United States and Japan have different legislation from European legislation, permitting different compounds and also different concentration levels for authorized substances.

The reason why these compounds are under scope is related to their toxicity and adverse effects like the known estrogenic disruption and interfering with thyroid hormone function. These effects have already been systematically described by Díaz-Cruz and Barceló [2] and they include *in vitro* estrogenic activities, maximum effects on cell proliferation by ethylhexyl-methoxy-cinnamate (EMC), octyl dimethyl PABA (ODP), 4-

Table 1
Physical-chemical properties of the nine UV filters studied here.

Name	Abb.	Structure	MW (g/mol)	Log P	pK[a]	H-bond	Maximum legal concentration[a]
2-Ethylhexyl-2-hydroxybenzoate	**ES**		250.33	5.43	9.8	3A/1D	5% (EU, USA, AUS) 10% (JP)
Ethylhexyl-methoxy-cinnamate	**EMC**		290.40	5.38	–	3A/0D	7.5% (US) 10% (EU, AUS) 20% (JP)
Benzophenone-3	**BZ3**		228.24	3.64	7.0	3A/1D	6% (US) 10% (AUS, EU) 5% (JP)
Octocrylene	**OCR**		361.48	6.78	–	3A/0D	10%
Avobenzone (butylmethoxy dibenzoylmethane)	**BDM**		310.39	4.56	9.8	3A/0D	3% (US) 5% (EU, AUS)10% (JP)
Diethylamino-hydroxybenzoyl-hexylbenzoate	**DHB**		397.51	6.82	3.4	5A/1D	10% (EU, JP)
Ethylhexyl-triazone	**ET**		823.07	15.29	4.8	12A/3D	5% (EU, AUS) 3% (JP)
bis-Ethylhexyloxy-phenol-methoxy-phenyltriazine	**EMT**		627.81	11.62	6.8	8A/2D	10% (EU, AUS) 3% (JP)
Diethylhexyl-butamido-triazone	**DBT**		765.98	12.39	4.8	12A/4D	10% (EU) 5% (JP)

[a] Permitted concentration for suncare products in different areas.

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