Portable Voltammetry: A Rapid and Efficient Technique for Determining UV Filters in Cosmetics: A Comparative Study with HPLC-PDA and HPLC-MS/MS

Portable voltammetry: a rapid and efficient technique for determining UV filters in cosmetics: a comparative study with HPLC-PDA and HPLC-MS/MS

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Author Contributions

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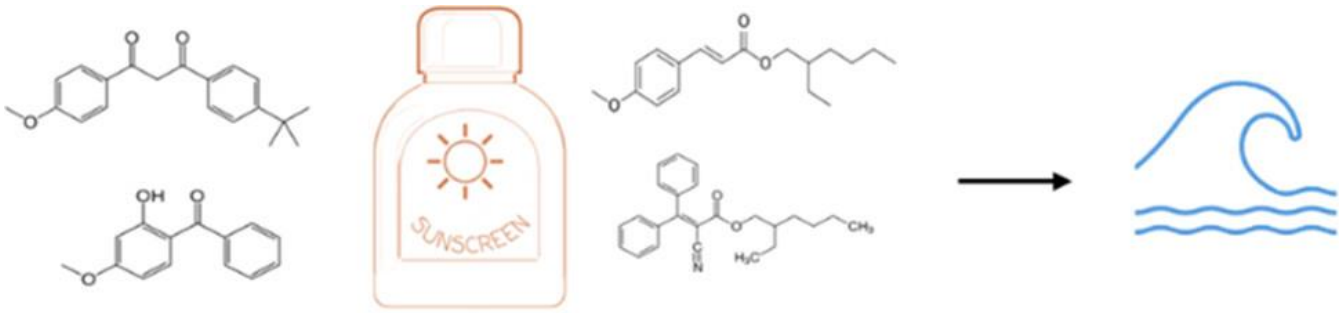
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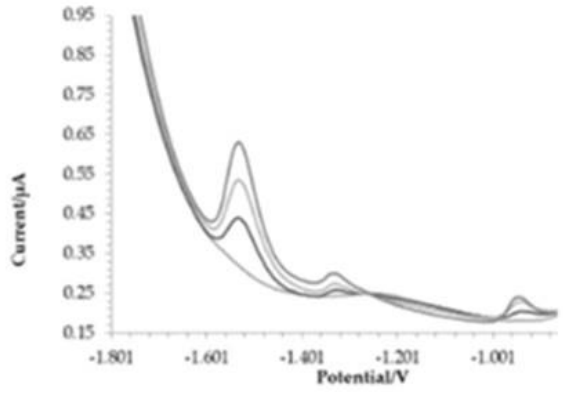
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0.55
0.45
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0.15
Current/μA
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-1.401
-1.201
-1.001
Potential/V

30

31

ABSTRACT

This study addresses the widespread use of UV filters (UVFs) in cosmetic and solar products due to the negative effects of UV radiation, particularly in relation to melanoma risk. While these filters offer protection, their extensive application raises concerns about their environmental and health impacts. Organic UVFs, in particular, have been associated with endocrine disruption in aquatic species and coral reef damage. To mitigate these concerns, regulatory limits have been imposed on certain UVFs. Current analytical techniques for UVF determination, such as HPLC-PDA and HPLC-MS/MS, offer high accuracy but are expensive and lack on-site monitoring capabilities. In response, this research aims to develop a rapid and cost-effective method, utilizing voltammetry for organic UVF quantification in complex matrices like sunscreens. Additionally, HPLC-PDA and HPLC-MS/MS are employed for electrochemical methods and device validation. This approach not only addresses the need for efficient UVF analysis but also provides a basis for regulatory compliance and environmental stewardship in the cosmetics industry.

INTRODUCTION

Melanoma is definitely the most common cancer of the skin, and among the causes is reported exposure to UV rays. Protection from these rays could be reached using filters that reduce the exposure or absorption, and this option is common in the cosmetic industry. In fact, many cosmetics report sunscreen inside.[1] UV filters (UVFs) are substances added to different cosmetic products such as sunscreen, lip balm, hair spray, and shampoo both to protect the skin from the possible harmful effects of UV radiation and to improve the stability and durability of the product.[2,3] In addition, UVFs are also added in plastics, paints, polymeric materials, and textiles to prevent sunlight-induced photodegradation and to prevent color changes in materials.[3,4] In sunscreen products, a mixture of UVFs is used both to protect the skin from the entire range of harmful UV rays and to avoid the photodegradation of organic filters and preserve their potential for protection.[5] As European Union (EU) Regulation 1223/2009-Cosmetic Regulation reported, UVFs are "substances which are exclusively or mainly intended to protect the skin against certain UV radiation by absorbing, reflecting or scattering UV radiation".[6] Sunscreen products are characterized by SPF (sun protection factor), a numerical index indicating the effective- ness of sunscreen that also depends on the amount of UVFs present in the formulation and is determined by in vitro or in vivo testing. UVFs are distinguished in chemical (organic) or physical (inorganic), and these differ in the mechanism of protection. The former absorb UV-A (315−400 nm) and UV- B (280−315 nm) radiations and convert them into heat,[7] while the latter block UV radiation by diffusion and reflection processes.[5,8,9] In addition to the wide pollution produced, chemical UVFs are considered possible endocrine disrupters for various animal species.[10] For example, prolonged exposure of fish to benzophenone-3 (BP3) has been shown to cause endocrine disruption, inducing reproductive disease, reducing egg production and hatching, and stimulating the production of vitellogenin protein in male fish.[11] UVFs also have negative impacts on coral reefs,[12] and BP3 has been called a threat to coral reefs around the world. It is estimated that up to 14000 tons of sunscreen, some containing up to 10% BP3, are released every year in areas of the coral reef, and this puts about 10% of global coral reefs and up to 40% of coastal reefs at the risk of coral bleaching.[13] Thus, for these side effects of UVFs on human health and their possible bioaccumulation in animals and waters, the European Commission established limits of concentration for UVFs, such as benzophenone-3 and octocrylene (that were indicated as endocrine disruptors), in order to reach a compromise between accurate protection and minimal negative impact.[6,14] Conventional analytical techniques such as high-performance liquid chromatography coupled to photodiode array (HPLC-PDA) and high-performance liquid chromatography coupled to tandem mass spectrometry (HPLC-MS/MS) are mainly used for the determination of chemical UVFs.[15−17] These two analytical approaches make it possible to perform very

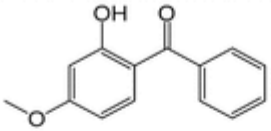
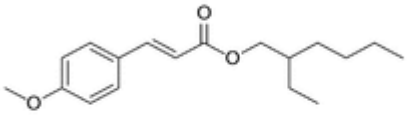
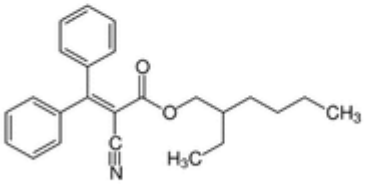
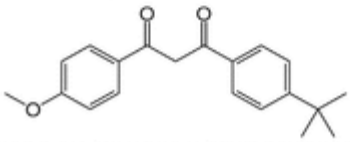
accurate analyses but are found to be expensive. Moreover, they are techniques that do not allow "on-site" monitoring. The aim of this work is to develop a method and a portable device for the rapid determination of organic UVFs in complex matrices such as sunscreen products, using square wave voltammetry (SWV) as an analytical technique, allowing rapid, simple, and inexpensive quantification of UVFs. In addition, HPLC-PDA and HPLC-MS/MS were used as comparison techniques to validate the developed method and the portable device.

EXPERIMENTAL SECTION

Chemicals and Reagents

All chemicals were analytical reagent grade and used without further purification. High-purity water (HPW) was used in all of the experiments and was obtained using an Elix Advantage reverse osmosis system and a Millipore-Milli-Q Plus from Merck (Darmstadt, Germany). Certified UVF standards (Table 1) of octocrylene (OC-CAS-No: 6197-30-4), benzophenone-3 (BP3-CAS-No: 131-57-7), ethylhexyl methoxycinnamate (EHMC-CAS-No 5466-77-3), and butyl methoxydibenzoylmethane (BMDM-CAS-No: 70356-09-1) were purchased from Sigma-Aldrich (Darmstadt, Germany) and were prepared by dissolving a known amount of standard in ethanol. Methanol (CAS-No: 67-56-1) and ethanol (CAS-No: 64-17-5) were purchased from VWR Chemicals (Milan, Italy). Sodium chloride (NaCl, CAS-No: 7647-14-5) was purchased from Sigma-Aldrich (Darmstadt, Germany), while acetonitrile (CAS-No: 75-05-8) and formic acid (CAS-No: 64-18-6) were purchased from Carlo Erba Reagent (Milan, Italy). Cetyltrimethylammonium bromide (CTAB, CAS-No: 57-09-0) was purchased from Sigma-Aldrich (Darmstadt, Germany).

Table 1. Certified UVFs

CHEMICAL NAME (OTHERS)	INCI (UV Protection)	STRUCTURE	ACRONYM
2-HYDROXY-4-METHOXYBENZOPHENONE (OXYBENZONE)	BENZOPHENONE-3 (UVA2 – UVB)		BP-3
2-ETHYLHEXYL 3-(4-METHOXYPHENYL)PROP-2-ENOATE (OCTINOXATE)	ETHYLHEXYL METHOXYCINNAMATE (UVA2 – UVB)		EHMC
ETHYLHEXYL 2-CYANO-3,3-DIPHENYL-2-PROPENOATE	OCTOCRYLENE (UVA1 – UVB)		OC
1,3-PROPANEDIONE, 1-[4-(1,1-DIMETHYLETHYL)PHENYL]-3-(4-METHOXYPHENYL) (AVOBENZONE)	BUTYL METHOXYDIBENZOYLMETHANE (UVA1)		BMDB

Electrochemical Instrumentation

The analyses were performed using an electrochemical cell consisting of a glass carbon electrode (GCE) as a working electrode (WE), a reference electrode (RE) Ag/AgCl filled with a solution of 3 M KCl, and a counter electrode (CE) in Pt from Metrohm s.r.l. (Origgio, Italy). The electrochemical cell is connected to a PalmSens3 portable potentiostat from Palmsens (Houten, Netherlands). PSTrace5.9 software allows us to set working conditions and view and process voltammograms. A solution consisting of 0.1 M NaCl, methanol, ethanol, and 0.30 mM CTAB was used as a supporting electrolyte. The voltammetric method used for the analysis is cathodic stripping voltammetry with square wave potential scanning (SWV). The procedure for the preparation of standards for electrochemical analysis is given in the Supporting Information (SI).

Chromatographic Instrumentation

Analyses were performed using an HPLC Thermo Fisher Scientific liquid chromatography system (Spectra System P2000) coupled to a photodiode array detector (PDA) (Spectra System UV6000LP). The mobile phase was degassed directly online by using a Biotech Degasi Classic (LabService, Italy). Excalibur v.2.0 Software (Thermo Fisher Scientific, Waltham, MA) was used to collect and analyze data. The Hypersil GOLD PFP (5 × 2.1 mm, 1.9 µm particle size; Thermo Fisher Scientific) column was

used to separate UVFs. The column was thermostated at 30 °C (±1 °C) by using a Jetstream2 Plus column oven during the analysis. The mobile phase was a mixture of HPW (A) and acetonitrile (B) both with 0.1% formic acid. The mobile phase composition was A/B = 52%:48% (v), and the analysis was performed in isocratic mode at a flow rate of 0.4 mL/min. The entire chromatographic run was performed in 25 min. The injection volume was set at 5 µL. UVFs were detected at their maximum wavelengths and at their respective retention times, as reported in the SI (Table S1) with the chromatogram of the mixture of UVFs considered (Figure S1). In the SI, there are also the total method validation figure of merits (see Tables S3 and S4 for intra- and interday analytical parameters, and Table S5 for ruggedness). The possible adsorption of analytes on the surface of the vials used has also been evaluated, as reported in SI Figure S2 and Table S6, with the aim of choosing the best material to conduct the extraction procedure.

Regarding the HPLC-MS/MS method

Analyses were carried out on a Waters (Milford, MA) Alliance 2695 chromatographic system with an autosampler coupled to a Waters Micromass Quattro Micro triple-quadrupole tandem mass spectrometer, interfaced with an electrospray ion source working in positive and negative ionization modes (ESI+/ESI−) with polarity switching. Data processing was performed using Waters MassLynx 4.1 software. Chromatography was obtained by exploiting the same combination of stationary and mobile phases as the HPLC-PDA system.

In order to develop an original HPLC-MS/MS method for the purpose, a multiple reaction monitoring (MRM) method was set up exploiting exclusive m/z transitions for each analyte. Parameter settings were optimized via direct infusion of individual analytes (1 µg/mL methanolic solutions) at 20 µL/min. Optimized m/z transitions for each considered analyte, HPLC-MS/MS MRM parameters, and method validation results are reported in Supplementary Table S7.

Cosmetic Samples

The cosmetic products considered in this study were purchased at local markets, trying to evaluate all of the types of products and the main sun protection factors (SPFs) generally used. The table containing all of the samples, the UVFs of interest, and the SPF are reported in the SI Table S8.

RESULTS AND DISCUSSION

Optimizing Conditions for Voltammetric Analysis

The objective of this work is to develop a voltammetric procedure for the determination of UVFs in cosmetic products18. However, before analyzing real samples, it is necessary to assess the instrumental response of UVFs using certified standards at known concentrations. In particular, octocrylene (OC), benzophenone-3 (BP3), ethylhexyl methoxycinnamate (EHMC), and butyl methoxydibenzoylmethane (BMDM) have been studied. Initially, UVFs were considered individually, and after optimizing the operational parameters, the application of the technique for the simultaneous determination of the analytes was also evaluated. Voltammograms were recorded by using a square wave potential scan in the cathodic direction, capturing the signal corresponding to their reduction at the electrode.

Different compositions of the supporting electrolyte were varied to obtain a linear background signal with low currents. The solution for obtaining linear signals and low currents is 8 mL of 0.1 M NaCl, 1.0 mL of ethanol, 1.0 mL of methanol, and 0.30 mM of CTAB. Subsequently, the instrumental parameters of the SWV were optimized in order to improve instrumental sensitivity. Among the different parameters, the parameter that most affects sensitivity is frequency. Table 2shows the optimized SWV parameters.

Table 2. SWV parameters (E_{dep}= Deposition potential, t_{dep}= Deposition time, t_{eq}= Equilibration time, E_{start}= Start potential, E_{end}= End potential, E_{step}= Step of potential, A = Amplitude, and F = Frequency)

parameter	value
E_{dep}	−0.4 V
t_{dep}	60 s
t_{eq}	20 s
E_{start}	−0.8 V
E_{end}	−1.7 V
E_{step}	0.009 V
A	0.021 V
F	50 Hz

Using these parameters set and as a solution consisting of 8.0 mL of 0.1 M NaCl, 1.0 mL of methanol, 1.0 mL of ethanol, and 0.30 mM CTAB as support electrolytes, the quantifications on the single analytes were evaluated. SI Figure S3 reports the calibration curves for the single titled analytes obtained after five additions in a solution of 0.1 M NaCl, EtOH, MeOH, and 0.30 mM CTAB. In Figure 1, OC: octocrylene, BP3: benzophenone-3, EHMC: ethylhexyl methoxycinnamate, and BMDM: butyl methoxydibenzoylmethane were reported for the voltammograms obtained during the analyses of the single UVFs subjected to the standard addition method, while Table 3 shows the performance of the method for their determination in the solution, highlighting the excellent results in terms of linearity, accuracy, repeatability, and sensitivity achieved.

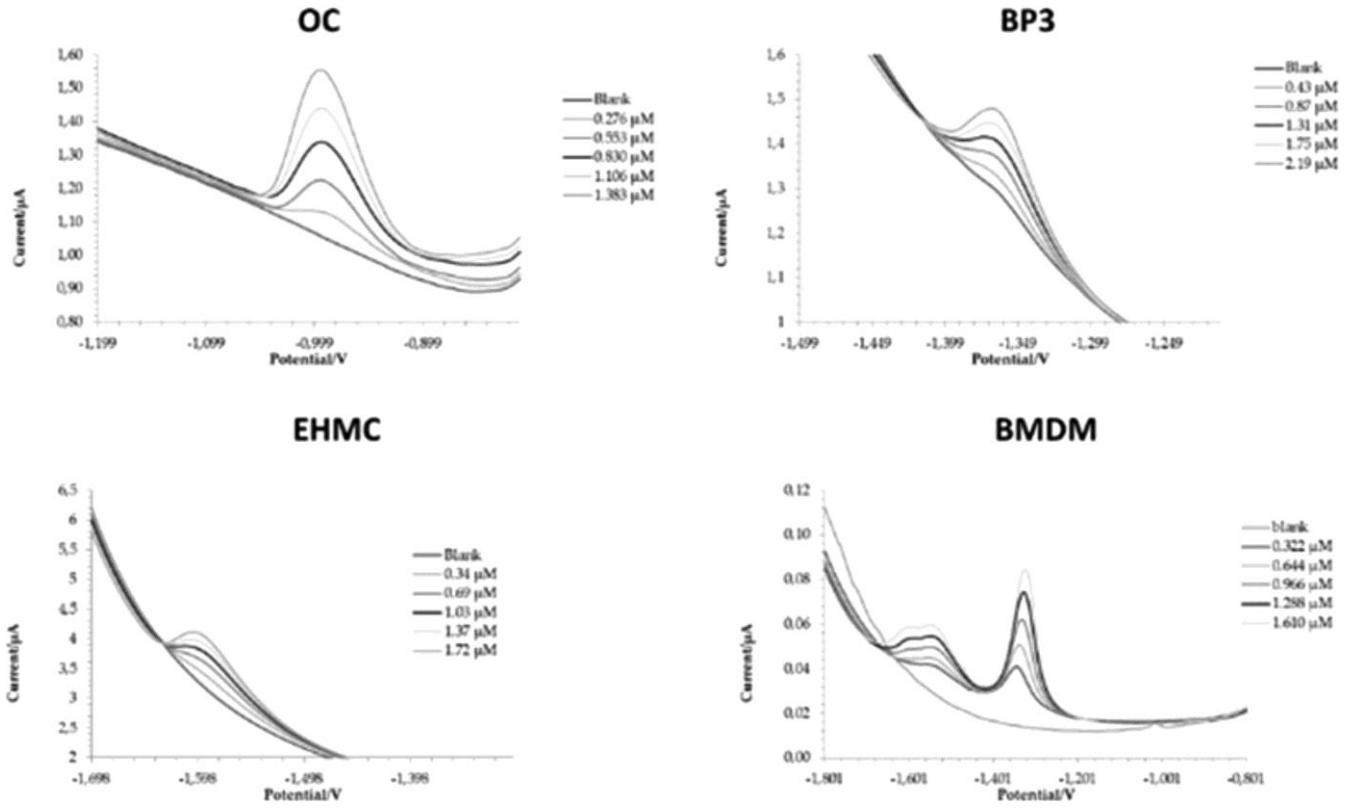


Figure 1. Voltammograms for the titled analytes obtained after five additions in a solution of 0.1 M NaCl, EtOH, MeOH, and 0.30 mM CTAB.

Table 3. Performance obtained by the method in a single UVF chemical standard solution consisting of 0.1 M NaCl, MeOH, EtOH, and 0.30 mM CTAB

parameters	OC[a]	BP3[a]	EHMC[a]	BMDM[a]
concentration range (μM)	0.276–1.38	0.483–2.19	0.34–1.72	0.322–1.61
correlation coefficient (R^2)	0.998	0.997	0.994	0.997
sensitivity (μA/μM)	0.35	0.058	0.55	0.28
recovery (%)	93.2	96.7	93.2	97.0
RSD (%)	3.62	3.22	0.67	3.19
LOD (μM)	0.07	0.11	0.065	0.05
LOQ (μM)	0.25	0.39	0.223	0.17

[a]Five additions of additions of: OC (0.276 μM); BP3 (0.483 μM); EHMC (0.34 μM); BMDM (0.322 μM).

Simultaneous Determination of OC, BP3, and EHMC in Solution

Given the satisfactory results obtained for individual analytes using the supporting electrolyte consisting of NaCl, ethanol, methanol, and 0.30 mM CTAB, it was decided to use the same solution and simultaneously add the three analytes. Three additions were made for OC, each at 0.69 µM, three additions for BP3, each at 1.09 µM, and three additions for EHMC, each at 0.86 µM. The optimized parameters shown in Table 2 were adopted for the voltammetric measurement. The corresponding voltammograms are displayed in Figure 2.

Using all of the previously optimized conditions, good results were obtained in terms of linearity, repeatability, and accuracy for all analytes simultaneously present in the solution. The performances obtained for the simultaneous determination of OC, BP3, and EHMC are reported in Table 4.

For BMDM, it was not possible to perform a simultaneous analysis with the other analytes, as it has a reduction potential of −1.4 V, equal to that of BP3. In addition, the BMDM has a second peak that falls to −1.6 V, the region of potential where the EHMC reduction signal is present. It can be observed that the simultaneous presence of the three analytes (OC, BP3, and EHMC) does not seem to affect quantification, as the results obtained exhibit high accuracy and precision. When compared with the method developed by Sunyer et al.,[19] the proposed methodology appears to be more sensitive and has lower LOD and LOQ values. Compared to the method developed by Ferreira et al.,[20] the proposed methodology has higher LOD and LOQ values for OC. The developed method is not only more sensitive for EHMC detection but even more environmentally friendly, in comparison with Ferreira and Cardoso et al., since they use a hanging mercury drop electrode[2,19].

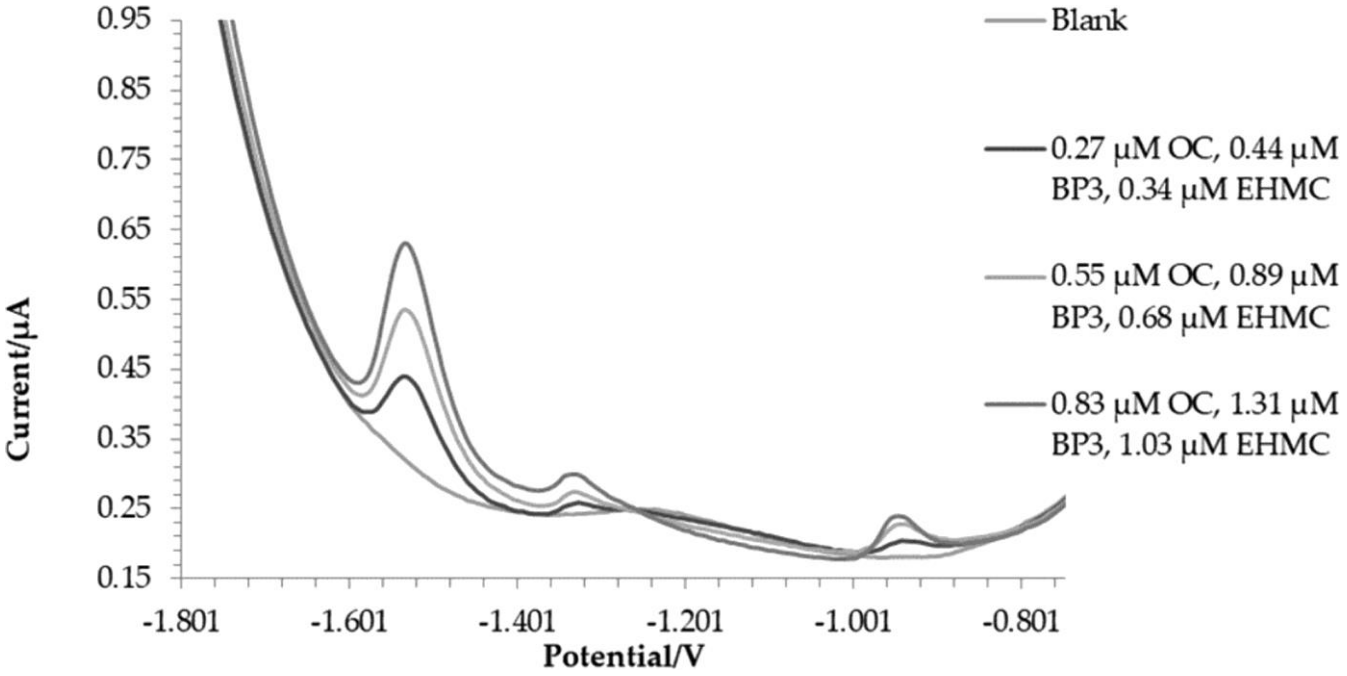


Figure 2. Voltammograms obtained following three additions of OC (0.27 µM), BP3 (0.44 µM), and EHMC (0.34 µM) in a solution of 0.1 M NaCl, EtOH, MeOH, and 0.30 mM CTAB.

Table 4. Performance Obtained by the Method Following Three Additions of OC (0.27µM), BP3 (0.44 µM), and EHMC (0.34 µM) in a Solution Consisting of 0.1 M NaCl, MeOH, EtOH, and 0.30 mM CTAB

parameters	OC	BP3	EHMC
concentration range (µM)	0.27–0.83	0.44–1.31	0.34–1.03
correlation coefficient (R^2)	0.995	0.994	0.995
sensitivity (µA/µM)	0.16	0.08	0.42
recovery (%)	91.7	96.7	100.0
RSD (%)	1.96	0.93	3.48
LOD (µM)	0.06	0.09	0.08
LOQ (µM)	0.21	0.29	0.26

Analysis on Cosmetic Samples

Optimization of the Extraction of Analytes from Cosmetics

Several extraction procedures were tested to extract analytes from the sunscreens. In order to obtain an exhaustive extraction of the different analytes, the type of solvent, the amount of solvent, and the type of mechanical pretreatment (ultrasound and mechanical agitation) have been tested. All extraction procedures were tested on a sunscreen sample (reported in Table S9 in the SI).

The procedure for exhaustively extracting analytes is as follows: (i) the sunscreen is carefully weighed (0.1 g) and placed in 50 mL of plastic test tube; (ii) 50 mL of 0.1 M NaCl is added; (iii) the solution is kept under stirring for 30 min; (iv) 0.1 mL of the solution is placed in an electrochemical cell with 8 mL of 0.1 M NaCl, 1.0 mL of methanol, 1.0 mL of ethanol, and 0.30 mM CTAB; and (v) quantification is performed by the method of standard additions. Finally, the percentage (% w/w) of UV filters present in each sunscreen sample was calculated.

The results obtained by voltammetry were compared with those obtained through HPLC-PDA and HPLC-MS/MS analyses, if the latter provides accurate results.

For both the HPLC-PDA and HPLC-MS/MS analyses, 0.1 g of sunscreen was added to 4 mL of ethanol, and the solution was sonicated for 15 min. To the sample, 6 mL of mobile phase, composed of HPW and acetonitrile acidified with 0.1% of formic acid (52:48 v/v), was added, and the mixture was centrifuged for 10 min (4000g). Subsequently, the sample was diluted 1:200 with the mobile phase, and after filtration through a 0.45 mm PTFE syringe filter, 5 µL of the solution was injected.

In the SI, various previous tests were reported, first to obtain the optimized extraction procedure. It was observed that the extraction procedure yielding the best results in terms of % w/w is extraction procedure A. This procedure provides percentages that closely approximate those obtained with HPLC-PDA and HPLC-MS/MS. After optimizing the sample pretreatment, various cosmetics were analyzed. The results are reported in Table 5 compared to those obtained with other instruments. Some voltammograms of the analysis of the samples are reported in the SI, Figure S4.

For all of the analyzed cosmetic samples, the results obtained by means of the voltammetric technique were in good agreement with those obtained using a conventional method, such as HPLC-PDA and HPLC-MS/MS. Therefore, the optimized analytical procedure proved to be suitable for determining UV filters in complex matrices such as sunscreens or lipsticks.

Table 5. Quantification of UV filters in cosmetics–Results reported as % (w/w) of UVFs, voltammetry vs HPLC-PDA and HPLC-MS/MS

	HPLC-PDA			HPLC-MS/MS			voltammetry		
sample	EHMC	OC	BMDM	EHMC	OC	BMDM	EHMC	OC	BMDM
1	3.49 ± 0.3			2.17 ± 0.20			3.54 ± 0.4		
2	2.48 ± 0.3	2.30 ± 0.2	0.14 ± 0.02	2.06 ± 0.17	1.80 ± 0.14	0.09 ± 0.01	2.47 ± 0.24	2.31 ± 0.08	
3		3.64 ± 0.4	1.51 ± 0.2		2.01 ± 0.21	1.10 ± 0.12		3.44 ± 0.21	1.51 ± 0.11
4		2.80 ± 0.3	1.85 ± 0.2		2.49 ± 0.29	1.01 ± 0.11			
5			3.81 ± 0.4			1.95 ± 0.23			3.81 ± 0.07
6			2.19 ± 0.2			1.53 ± 0.17			2.04 ± 0.03
7			1.26 ± 0.1			1.09 ± 0.12			1.53 ± 0.04
8	1.38 ± 0.1	2.46 ± 0.2	1.73 ± 0.2	0.80 ± 0.09	1.99 ± 0.22	1.97 ± 0.23	1.25 ± 0.08	2.42 ± 0.21	1.75 ± 0.1
9			0.17 ± 0.02			0.03 ± 0.01			<LOQ
10	2.32 ± 0.2			2.00 ± 0.22			2.09 ± 0.12		
11	0.03 ± 0.01		4.28 ± 0.4	0.18 ± 0.03		3.87 ± 0.39	<LOQ		4.42 ± 0.23
12	1.13 ± 0.1	0.26 ± 0.03	1.03 ± 0.1	1.87 ± 0.21	0.22 ± 0.03	1.32 ± 0.16	1.3 ± 0.2	<LOQ	
13	4.14 ± 0.4		0.74 ± 0.1	4.52 ± 0.38		0.99 ± 0.12	4.22 ± 0.54		<LOQ
14		1.17 ± 0.1	1.30 ± 0.1		1.01 ± 0.11	1.11 ± 0.13		1.3 ± 0.35	1.32 ± 0.05
15			0.26 ± 0.03			0.35 ± 0.03			<LOQ
16		5.37 ± 0.5			6.66 ± 0.54			4.11 ± 0.02	
17	3.70 ± 0.4			2.01 ± 0.18			2.68 ± 0.33		
18		8.85 ± 0.7	4.61 ± 0.4		6.64 ± 0.73	3.92 ± 0.42		8.38 ± 0.67	3.6 ± 0.48
19	1.84 ± 0.2		1.29 ± 0.1	1.88 ± 0.21		1.29 ± 0.13	2.1 ± 0.19		1.17 ± 0.28

In terms of the percentage of filters found in the products, all results comply with the limits set by the European Chemicals Agency (ECHA) (OC < 10%, EHMC < 10%, BMDM < 5%). In fact, all analyzed sunscreen samples exhibit UV filter percentages much lower than the legal limits. Therefore, these sunscreens are considered “safe” from an environmental standpoint, although continued use could potentially have various impacts on the aquatic ecosystem.

Table 6. Pearson correlation matrix

variable	EHMC PDA	EHMC MSMS	EHMC ASV
EHMC PDA	1	0.716	0.902
EHMC MSMS	0.716	1	0.916
EHMC ASV	0.902	0.916	1
	OC PDA	OC MSMS	OC ASV
OC PDA	1	0.928	0.990
OC MSMS	0.928	1	0.876
OC ASV	0.990	0.876	1
	BMDM PDA	BMDM MSMS	BMDM ASV
BMDM PDA	1	0.887	0.966
BMDM MSMS	0.887	1	0.816
BMDM ASV	0.966	0.816	1

CONCLUSIONS

In this work, the possibility of using electrochemical techniques for the determination of UVFs contained in sunscreens was demonstrated and validated. In particular, the whole method has been optimized for the determination of OC, BP3, EHMC, and BMDM; the results, reported as a percentage w/w, have been compared with those obtained by means of originally “ad hoc” developed and validated methods based on HPLC-PDA and HPLC-MS/MS.

An interesting element is represented by the fact that in the present work not only are the SWV method and a portable device developed and validated but also everything is compared with two reference configurations (HPLC-PDA and HPLC-MS/MS). In this case, the chromatographic method has demonstrated the necessary ruggedness to be applied directly to two different instrumentations, obtaining comparable performance and without any method transfer problem.

The electrochemical method developed herein allows for carrying out reliable analyses potentially everywhere, as it uses completely portable instrumentation. This represents a great innovation to increase the number of controls on different matrices by using a low-cost, portable, easy-to-use, and green technology.

One of the main objectives of green analytical chemistry (GAC) and green sample preparation (GSP) lies in the possibility of carrying out in situ measurements using simple instrumentation and with the use of nontoxic reagents and solvents, reducing sample manipulation and the number of steps related to pretreatment. The method and portable device presented here allow us to be compliant with these principles, highlighting how this approach can be considered green and low impact, paving the way for its new applications also in other fields (i.e., environmental and biological ones), in order to monitor the presence of these potential CECs in different settings.

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