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# Spectroelectrochemistry as a new tool for the quantification of UV filters in sun creams

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## Abstract

This study focuses on the spectroelectrochemical quantification of four UV filters, butylmethoxy dibenzoylmethane (BM), benzophenone-3 (BP3), ethylhexyl methoxycinnamate (EM) and octocrylene (OC) used as sunscreens in cosmetics. Three of them exhibited electrochemical activity resulting in the modification of their absorption spectrum under the application of an oxidizing potential of +1.8 V vs. Ag. When working with a mixture containing both electroactive and nonelectroactive UV filters, UV–vis absorption spectra recorded before and after the application of the potential differed. The combination of spectral deconvolution of the spectra pair allowed a more accurate identification and quantification of UV filters than spectral deconvolution of the initial absorbance spectrum alone. This method was effective for the assessment of UV filters in model mixtures and commercial sun creams.

## Keywords

spectroelectrochemistry, UV filter, absorption spectra, spectral deconvolution, sunscreens

## 1. Introduction

UV filters are ubiquitous in our modern world. They are used in plastics [1] and other materials as well as in many personal care products for sun protection. They are released in

the environment where they become xenobiotics and have possible effects on the environment, notably on marine life [2]. Due to their lipophilic properties, UV filters are susceptible to bioaccumulation. A recent study showed that benzophenone-3 (BP3), ethylhexyl methoxycinnamate (EM) and octocrylene (OC) tend to accumulate in fishes, possibly leading to biomagnification [3]. Those UV filters, among others, were also shown to exhibit endocrine disruptive effects [4]. The ecotoxicity of 4 UV filters (including BP3 and EM) toward mussels and other crustaceans was also demonstrated. The predicted no-effect concentration of BP3 was below the measured water concentration, highlighting a potential environmental risk [5]. The impact of UV filters is particularly strong in anthropized areas, but UV filters can now be found all over the world, even in the most remote places [6]. Coastal areas are particularly exposed, as sunscreens are washed off swimmers' skin during leisure activities [7].

In most countries, regulations on the use of UV filters impose concentration limits in cosmetic preparations (regulation No 1223/2009 in EU, monograph M020, OTC000006 in the USA). Most UV filter quantification methods are based on chromatographic approaches (HPLC or GC) requiring separation of individual compounds coupled with detection, usually by UV (for HPLC) [8], flame ionization detection (GC) [9], or mass spectrometry (both) [10]. Nevertheless, alternative tools for the detection and quantification of UV filters have also been published in the literature. For example, the method of Tovar-Sanchez et al. [11] proposed measuring the absorbance of seawater at 303 nm, and the authors demonstrated that the value obtained is a good proxy for the overall concentration of UV filters in water. Differential pulse voltammetry [12] and square wave voltammetry [13,14] have also been used to identify and quantify some UV filters. As an example, differential pulse adsorptive stripping voltammetry was used to quantify BP3 and OC in commercial sun creams with good correlation with HPLC [15].

Different configurations of spectroelectrochemistry, involving Raman, photoluminescence or UV-vis spectrophotometric techniques can be implemented [16]. Because all UV filters are characterized by a broad absorption band in the ultraviolet range, we embarked upon evaluating the interest of spectroelectrochemistry for the quantification of UV filters in mixtures, assuming that UV filters would exhibit different electrochemical activity. Spectroelectrochemistry is mostly used to characterize compounds [17,18] or measure reaction kinetics [19]. In this article, we investigate for the first time the potential of spectroelectrochemistry for the quantification of UV filters in sun creams. More particularly, UV-vis spectroelectrochemistry was already applied to the quantification of dopamine [20] and the resolution of catechol/dopamine and dopamine/epinephrine mixtures [21]. In this work, we apply this technique to the analysis of UV filters complex mixtures using deconvolution of total spectra before and after application of an oxidizing potential.

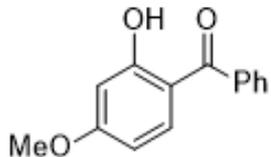
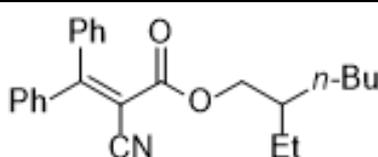
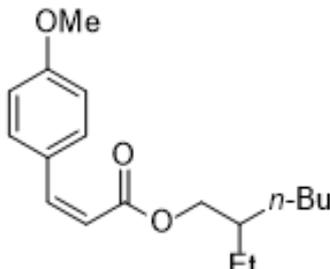
In this approach, four UV filters authorized for cosmetic preparations and frequently found as cosmetic ingredients in commercial products are studied: BP3, EM, OC and butylmethoxy dibenzoylmethane (BM). An application of the method to commercial sun creams is also described.

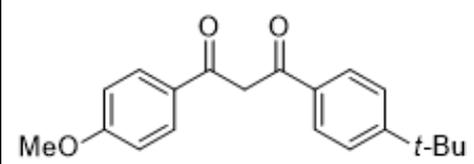
## 2. Experimental

## 2.1 Material

HPLC-grade methanol (MeOH) and ethanol (EtOH) were purchased from VWR. Tetrabutylammonium hexafluorophosphate (3109-63-5, TBAFP) was acquired from Alfa Aesar. It was recrystallized twice from 96% EtOH and absolute EtOH before use. Benzophenone-3 (oxybenzone, 131-57-7, BP3), octocrylene (6197-30-4, OC), ethylhexyl methoxycinnamate (octinoxate, 5466-77-3, EM) and butyl methoxydibenzoylmethane (avobenzene, 70356-09-1, BM) were purchased from Merck. Stock solutions were prepared in MeOH and stored at 4 °C, protected from light.

Table 1: Target UV filters

Chemical structure	Compound name(s)	Abbreviation	CAS	Mass percentage allowed in cosmetics in Europe (%)*
	Benzophenone-3 Oxybenzone	BP3	131-57-7	6
	Octocrylene	OC	6197-30-4	10
	Ethylhexyl methoxycinnamate Octinoxate	EM	5466-77-3	10

	Butyl methoxydibenzoylmethane  Avobenzene	BM	70356-09-1	5
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\*: regulation (EC) n°1223/2009 annexe VI

Two commercial sun creams from the same brand were purchased in local stores: a dry oil spray with a Sun Protection Factor (SPF) of 30 (sun cream 1) and a lotion with an SPF of 50 (sun cream 2). The composition of sun cream 1 was as follows: Alcohol Denat., Octocrylene, Benzophenone-3, Acrylates/Octylacrylamide Copolymer, Butyl Methoxydibenzoylmethane, Paraffinum Liquidum, Phenethyl Benzoate, Parfum, *Cocos nucifera* Oil, Amyl Acetate, *Glycine soja* Oil, PEG-8 Dimethicone, *Zea mays* Oil, *Aloe barbadensis* Leaf Extract, *Carica papaya* Fruit Extract, *Colocasia antiquorum* Root Extract, *Mangifera indica* Fruit Extract, *Passiflora incarnata* Fruit Extract, *Plumeria acutifolia* Flower Extract, *Psidium guajava* Fruit Extract, Beta Carotene, Octyldodecanol, Retinyl Palmitate, Silica, Tocopheryl Acetate, *Daucus carota sativa* Root Extract, Ascorbic Acid, Sodium Propoxyhydroxypropyl Thiosulfate Silica, and Benzyl Alcohol.

Sun cream 2 composition was as follows: Aqua, Octocrylene, Benzophenone-3, Butyl Methoxydibenzoylmethane, Cetearyl Alcohol, Glycerin, VP/Eicosene Copolymer, Diisopropyl Adipate, C12-15 Alkyl Benzoate, Phenethyl Benzoate, Polymethylsilsesquioxane, Phenoxyethanol, Polyethylene, Caprylyl Glycol, Dimethicone, Parfum, Coco-Glucoside, Sodium Polyacrylate, Ceteth-10 Phosphate, Dicaprylyl Phosphate, Methylparaben, Xanthan Gum, Propylparaben, Carbomer, Disodium EDTA, Paraffin, Sodium Hydroxide, Mica, *Butyrospermum parkii* Butter, *Mangifera indica* Seed Butter, Silk Amino Acid, Sodium Ascorbyl Phosphate, Tocopheryl Acetate, Panthenol, *Aloe barbadensis* Leaf Juice, *Carica papaya* Fruit Extract, *Colocasia antiquorum* Root Extract, *Mangifera indica* Fruit Extract, *Passiflora incarnata* Fruit Extract, *Plumeria acutifolia* Flower Extract, *Psidium guajava* Fruit Extract, Hexyl Cinnamal, Linalool, CI 77163, CI 77492, and CI 77491.

Spectroelectrochemical experiments were performed in a spectrochemical cell from Metrohm. The working electrode was a platinum grid, the counter electrode was in glassy carbon, and a silver wire was used as a pseudo reference electrode. An Autolab potentiostat (type PGSTAT204) and spectrophotometric equipment (TSC Spectro cell 840216) from Metrohm controlled with Nova 2.4.1 software were used. A scheme and a picture of the experimental setup can be found in the supporting information (Figure S2).

HPLC experiments were performed using a VWR-Hitachi LaChrom Elite (L-2130) equipped with an autosampler (L-2200) and a diode array detector (L-2455). Separation was performed with a Supelco Discovery C18 (25 cm x 4.6 mm, 5- $\mu$ m column) at room temperature.

## 2.2 Extraction method

UV filters were extracted from commercial sun creams with the following protocol: 1 g of sun cream was weighed and transferred into a 100-mL volumetric flask. The flask was gradually filled to volume with MeOH under agitation using an orbital shaker at 200 rpm for 6 h at room temperature. The solution obtained with sun cream 1 was homogeneous and used without further handling. The solution obtained with sun cream 2 was centrifuged for 10 min at 700 g to separate the undissolved material. A 1-mL aliquot of the solution was diluted in a 5-mL volumetric flask with MeOH. Then, a 1-mL aliquot was transferred to a 10-mL volumetric flask and completed with MeOH containing 0.05 M TBAFP. The resulting solutions were analysed by HPLC and spectroelectrochemistry.

## 2.3 HPLC method

The mobile phase consisted of a mix of water (A) and MeOH (B), both modified with 0.1% acetic acid. The linear gradient, with a flow rate of 0.8 mL/min, was as follows: 0 to 1 min 70% B, increasing to 95% B in 9 min followed by 8 min at 95% B. Mobile phase conditions were reverted back to 70% B in 1 min and kept constant for 4 min at the end of the method to equilibrate the system for the next injection. The wavelengths used for the quantification of BP3, both EM and OC, and BM were 285 nm, 300 nm and 357 nm, respectively.

## 2.4 Spectroelectrochemical methods

### 2.4.1 Voltabsorptometry

Voltabsorptometry experiments were performed on UV filter solutions prepared at 60  $\mu\text{M}$  in MeOH containing 0.1 M TBAFP. Voltabsorptometry experiments consist of linear sweep voltammetry experiments during which the absorbance of the solution is recorded. Voltabsorptometries were recorded towards either positive potentials (from 0 to +2 V vs. Ag) or negative potentials (from 0 to -2 V vs. Ag) with a scan rate of 1 mV/s. Absorbance spectra were recorded between 240 nm and 500 nm for each 0.1-V step.

### 2.4.2 Chronoabsorptometry

Chronoabsorptometry experiments were performed by applying a fixed potential for 30 min. For each experiment, the absorbance spectrum was recorded before the potential was applied ( $t_0$ ). This spectrum at  $t_0$  will allow for the further quantification of OC. The absorbance spectrum of the solution was then set to 0. Differential absorption spectra from the solution at  $t_0$  were then recorded upon application of a potential every 100 s until 30 min ( $t_{\text{final}}$ ).

Initial experiments on pure UV filters were performed using solutions at 60  $\mu\text{M}$  prepared in MeOH containing 0.05 M TBAFP.

When working with either model mixtures or real sample extracts, chronoabsorptometry experiments were performed in triplicate in the same solvent. On the same day, chronoabsorptometry responses of each UV filter were independently recorded to be used as a reference. The optimal oxidation potential for quantification of the four studied UV filters was +1.8 V vs. Ag.

### 2.4.3 UV–vis spectra deconvolution

The UV–vis absorbance spectrum at  $t_0$  and the relative UV–vis absorbance spectrum at  $t_{\text{final}}$  were used to identify and quantify UV filters. The relative absorbance spectra represent absorbance variations from the initial spectrum, reset at 0. Deconvolutions were performed using the Excel solver tool. The experimental spectrum (either at  $t_0$  or at  $t_{\text{final}}$ ) of a complex solution was compared to a theoretical spectrum calculated by Excel from the sum of the spectra of pure molecules. The difference between the experimental and theoretical spectra was minimized using the least square method.

For each model mixture, deconvolution was conducted on the spectrum obtained at the end of the chronoabsorptometry experiment ( $t_{\text{final}}$ ). The concentration for the four UV filters was computed. As the absorbance of OC showed very little variation, the OC computed concentration was either greatly underestimated or calculated as null and was therefore discarded. A second deconvolution using the  $t_0$  spectrum was then conducted. BM, BP3 and EM concentrations were restricted into a  $\pm 10\%$  window from their concentrations calculated at  $t_{\text{final}}$ . Concentrations of the four UV filters were again computed; BM, BP3 and EM concentrations were refined, and the OC concentration was determined. This double deconvolution approach was found to provide the best results for mixtures with different proportions of these four compounds. The concentrations taken as the final quantification are the adjusted concentrations in BM, BP3 and EM as well as the OC concentration. When working with real sample extracts, only three UV filters were investigated. EM was not present in the tested sun creams; hence, the same calculation was made without taking EM into account.

## 3. Results and discussion

### 3.1 Spectroelectrochemical detection of UV filters

The electrochemical activity of each UV filter was studied by performing linear sweep voltammetry experiments at 10 mM (supplementary information). No specific signal was obtained in reduction, while BM, BP3 and EM showed an oxidation wave at such concentrations. In these cases, UV–vis absorption spectra were saturated in our system and were therefore not recorded. At lower concentrations, electrochemistry alone was not sufficiently sensitive; therefore, spectroelectrochemistry was used to improve UV filter detection in real samples.

Absorbance evolution at the optimal absorption wavelength was plotted as a function of the applied potential. As oxidation or reduction of the molecule would lead to a modification of the absorbance spectrum, the variation in the absorbance was matched to electrochemical activity. When sweeping towards negative potentials, the absorbance of BP3, BM and EM solutions decreased for potentials lower than -1 V vs. Ag (Figure 1a). The OC solution absorbance did not change until up to -2 V. When sweeping towards positive potentials, the absorbance of EM, BM, and BP3 solutions decreased for potentials above +0.7, +1.0, and +1.2 V vs. Ag, respectively (Figure 1b). Again, the OC solution did not show any absorbance variation.

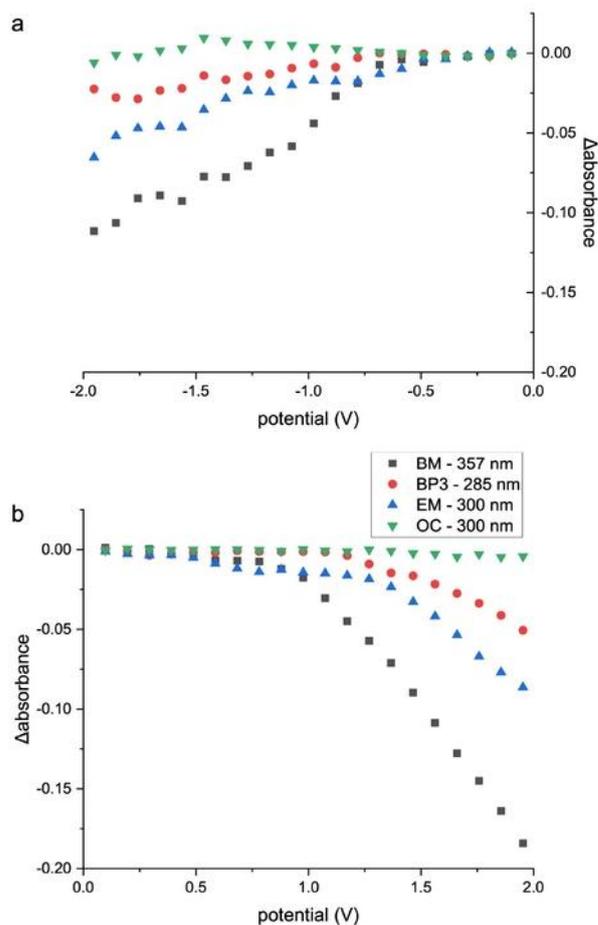


Figure 1: Absorbance variations of BM, BP3, EM and OC during a voltabsorptometry in either (a) reduction (from 0 to -2 V vs. Ag.) or (b) oxidation (from 0 to +2 V vs. Ag.) mode. Absorbance was recorded at the optimal absorption wavelength for each compound.

The absorbance evolution amplitude was twice as important when working towards positive potentials than negative ones. Chronoabsorptometry experiments were thus recorded using positive potentials. An oxidation potential of +1.8 V vs. Ag applied for 30 min was eventually found to be optimal for the three compounds EM, BM, and BP3 even if the variation in absorbance started from approximately +1.2 V vs. Ag. When molecules were studied independently, the limits of detection (LODs) were found to be 0.6  $\mu\text{M}$ , 1.6  $\mu\text{M}$ , 1.0  $\mu\text{M}$ , and 1.2  $\mu\text{M}$ , and the limits of quantification (LOQs) were 2.2  $\mu\text{M}$ , 5.5  $\mu\text{M}$ , 3.4  $\mu\text{M}$  and 4.1  $\mu\text{M}$  for

BM, BP3, EM and OC, respectively. LOD and LOQ were calculated using the ratios  $3S/N$  and  $10S/N$ , with  $S$  being the signal amplitude and  $N$  the noise amplitude.

### 3.2 Quantification in model mixtures

We performed calibration measurements by recording the UV-vis spectra of solutions of the four UV filters, OC included, in pure form at varying concentrations (Figure 2). This set of UV-vis spectra was then used to determine UV filter concentrations by deconvolution of total spectra recorded under the same conditions for model UV filter mixture solutions. The concentrations of UV filters in the model mixtures were chosen arbitrarily in the range 10 - 80  $\mu\text{M}$ . The composition of these mixtures is given in Table 2 along with the quantification results.

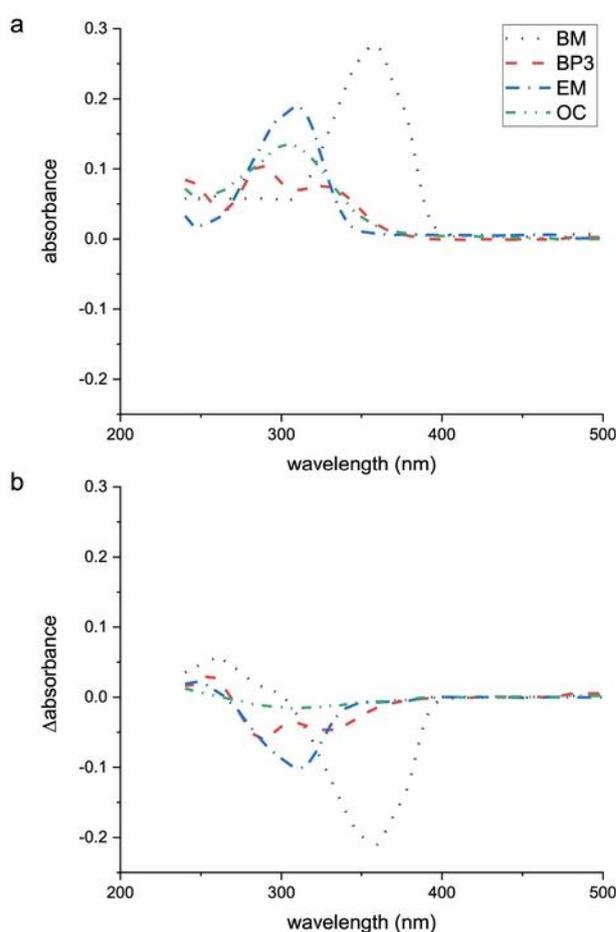


Figure 2: (a) Absorbance spectra at  $t_0$ ; (b) relative absorbance spectra at  $t_{\text{final}}$  for BM, BP3, EM and OC in MeOH containing 0.05 M TBAFP.

Table 2: Quantification of UV filters in model mixtures obtained through the spectroelectrochemistry-assisted deconvolution method

Model mixture	Theoretical concentration ( $\mu\text{M}$ )	Calculated concentration ( $\mu\text{M}$ )				
		BM/BP3/EM/OC	BM	BP3	EM	OC
1	40/40/40/40		41.9 $\pm$ 0.8	46.5 $\pm$ 1.6	50.6 $\pm$ 1.7	54 $\pm$ 4
2	60/20/40/80		57.7 $\pm$ 1.0	31.7 $\pm$ 0.9	54.1 $\pm$ 0.2	80 $\pm$ 2
3	40/20/60/80		37.0 $\pm$ 0.4	25.2 $\pm$ 1.5	69.7 $\pm$ 2.8	96 $\pm$ 7
4	60/20/80/40		56.5 $\pm$ 0.6	29.7 $\pm$ 0.5	90.8 $\pm$ 1.7	51 $\pm$ 6
5	40/60/0/80		38.5 $\pm$ 0.1	61.4 $\pm$ 0.3	4.3 $\pm$ 1.0	98 $\pm$ 4
6	30/10/20/40		29.7 $\pm$ 0.5	12.9 $\pm$ 1.0	21.5 $\pm$ 0.5	46 $\pm$ 2
7	20/10/30/40		21.1 $\pm$ 0.7	13.6 $\pm$ 0.9	34.2 $\pm$ 1.8	41 $\pm$ 1
8	30/10/40/20		27.5 $\pm$ 1.1	5.3 $\pm$ 3.7	53.2 $\pm$ 3.7	12 $\pm$ 10
9	20/30/0/40		17.0 $\pm$ 0.2	33.8 $\pm$ 1.6	5.0 $\pm$ 0.8	18 $\pm$ 1
10	20/20/20/20		16.4 $\pm$ 0.2	24.2 $\pm$ 0.2	26.6 $\pm$ 0.2	11 $\pm$ 1
Average recovery rate (%)			95 $\pm$ 7	120 $\pm$ 27	122 $\pm$ 11	98 $\pm$ 31

Examination of Table 2 shows that the quantification of BM was good at all concentrations of BM in solution and regardless of the concentrations of other filters. This result can be explained quite well by the relative uniqueness of the absorbance spectrum of BM, which is notably the only one of these four compounds detectable above 350 nm. The quantification results for BP3 in the concentration range of 10 to 40  $\mu\text{M}$  were acceptable but tended to be slightly overestimated, with a mean recovery of 120%. This was also the case for EM, the mean recovery of which was 122%. OC average recovery seems satisfactory, 98%; however, it showed the highest standard deviation. For each solution in Table 2, Figure 3 represents the calculated concentration of each of the UV filters as a function of its nominal concentration. BM showed good correlation between both values, with a slope of 0.97 showing trueness and a  $r^2$  of 0.98 showing precision, demonstrating the accuracy of BM quantification. Despite the overestimation of BP3 and EM, the correlation between the calculated and nominal concentrations was still good, with  $r^2$  values of 0.92 and 0.99, respectively. In a four-molecule mixture, OC quantification was the least reliable ( $r^2$  0.88 and 1.29 slope) but could still be considered relevant as an indication of the order magnitude of OC concentration (absolute relative error mean: 25.79%). The imprecision in the quantifications can be explained by the low optical path and the static conditions in the cell. Experimental conditions only allow the optical path to be set to approximately 1 mm.

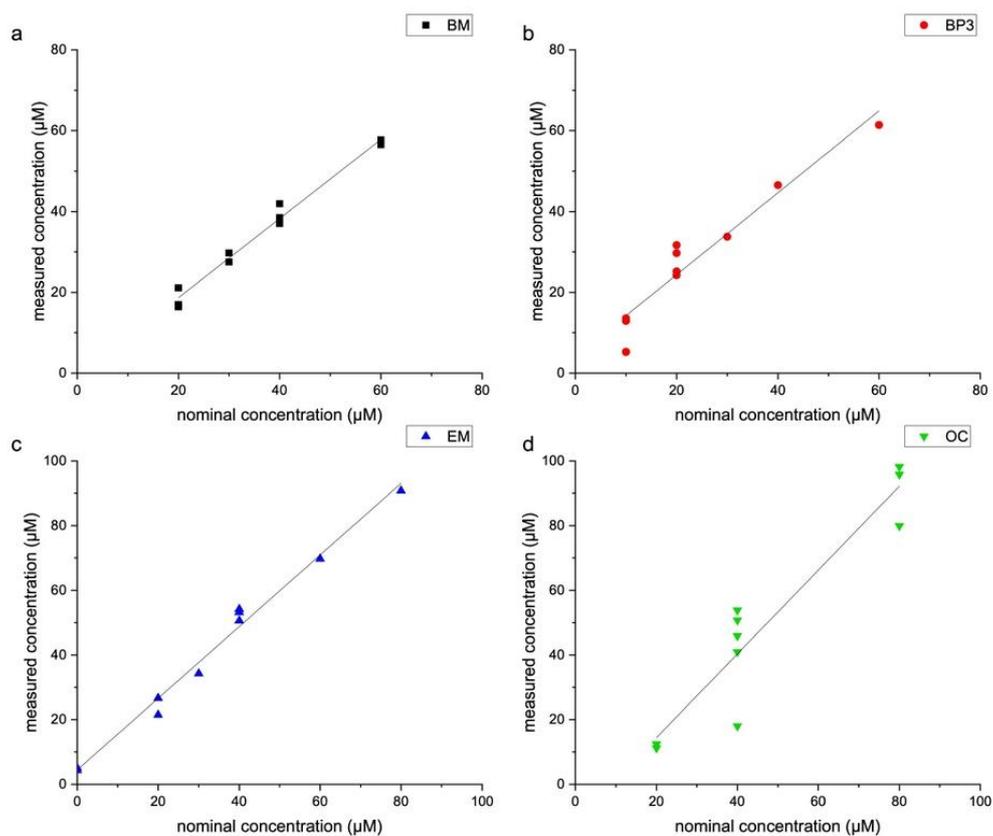


Figure 3: UV filter-measured concentrations using the spectroelectrochemistry-assisted deconvolution method vs. nominal concentrations in the model mixtures: (a) BM slope: 0.97, intercept: -0.89,  $r^2$ : 0.98; (b) BP3 slope: 1.01, intercept: 4.09,  $r^2$ : 0.92; (c) EM slope: 1.11, intercept: 4.42,  $r^2$ : 0.99; (d) OC slope: 1.30, intercept: -11.52,  $r^2$ : 0.89.

### 3.3 Quantification in commercial sun creams

Two commercial sun creams containing BP3, BM and OC as UV filters were analysed. HPLC analysis was used as the reference method. Spectroelectrochemical analyses were performed as described above. As the investigated ingredients were known thanks to the ingredient list, only BM, BP3 and OC concentrations were computed through the deconvolution method.

Table 3: Quantification of UV filters in commercial sun creams

Commercial	UV filter	Mass rate in the cream (%)	

sun cream		HPLC	Spectroelectrochemistry	Relative difference (%) spectroelectrochemistry vs HPLC
Sun cream 1	BP3	3.3 ± 0.0	3.3 ± 0.5	0.0
	BM	2.3 ± 0.0	2.3 ± 0.2	0.0
	OC	6.3 ± 0.1	6.1 ± 0.9	-3.2
Sun cream 2	BP3	4.4 ± 0.1	3.9 ± 0.3	-11.4
	BM	3.4 ± 0.1	3.0 ± 0.0	-11.8
	OC	4.9 ± 0.1	5.2 ± 0.5	+6.1

When quantifying UV filters in sun cream 1, both techniques gave very similar results, with a relative difference below 5% for all filters and even below 1% for BM and BP3. When working with sun cream 2, both techniques still gave similar concentrations. However, spectroelectrochemical quantification led to a slight underestimation of BP3 and BM, without exceeding a 15% relative difference. Both techniques gave the same preponderance order as the ingredient list, OC being dominant and followed by BP3 and BM in both sun creams. Overall, spectroelectrochemical-assisted deconvolution quantification gave a satisfactory quantification of the three UV filters in the tested sun cream.

## 4. Conclusion

Although spectral deconvolution enables the identification of UV–vis absorbing molecules present in a solution as well as the quantification of each isolated component, specific quantification of UV filters in complex solutions can be challenging, as UV filters tend to absorb in similar wavelength ranges. Some UV filters can be oxidized upon application of a positive potential, leading to changes in the solution absorbance. The different UV filter behaviours under these conditions allowed us to perform UV filter quantification by spectral deconvolution after and before the oxidation of mixtures of UV filters. Under the conditions that were developed in this work, it was possible to quantify four different UV filters in tertiary or quaternary mixtures. Overall, the quantification accuracy was very good for BM while the quantification results were slightly overestimated (20%) for BP3 and EM. The case of OC was more complex. The UV absorbance of OC extensively overlaps with those of EM and BP3. Since OC was not oxidised in the conditions used in our measurements, its

concentration could only be calculated from the initial absorbance spectrum. Eventually, we found that the quantification of OC was possible, but the standard deviations were somewhat higher than those of the other UV filters tested. We also demonstrated that UV filters could be extracted from commercial sunscreens and quantified using this technique. Although the accuracy of the method can be further improved, this preliminary study demonstrates that spectroelectrochemistry could become an interesting tool for the quantification of UV-active compounds either in finished products (cosmetics, for example) or in the environment. This approach has the advantage of not requiring a separation step and of using only very limited volumes of solvent.

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## Conflict of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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