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Polarographic determination of sunscreen agents in cosmetic products in micellar media

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Abstract

This paper introduces a simple, fast and reliable electroanalytical method for differential-pulse polarography based on electrochemical reduction at a dropping mercury electrode. The method was validated for the determination of 2-ethylhexyl-4-methoxycinnamate (EHMC) alone and in association with 4-methylbenzylidene camphor (MBC) or 2-hydroxy-4-methoxybenzophenone (BENZ-3) in samples of commercial cosmetic preparations. The supporting electrolyte that provided the best-defined and most intense peak current for EHMC determination was Britton-Robinson buffer (pH 4.0) in the presence of a cationic surfactant. Under optimized conditions, EHMC exhibited one single peak of reduction at −1.49 V versus Ag/AgCl. A limit of detection of 3.76×10^{-8} mol L^{-1} and a limit of quantitation of 1.25×10^{-7} mol L^{-1} were found for the pure EHMC standard. A good average recovery rate was reached for all the samples analyzed.

Keywords: Cinnamates; Benzophenone; 2-Ethylhexyl-4-methoxycinnamate; 4-Methylbenzylidene camphor; Micelles; Polarography

1. Introduction

Because skin cancer and photoaging appear to be related to excessive sunlight exposure and because the atmospheric layer of ozone that provides protection against UV radiation is reported to be decreasing, the use of sunscreen products is becoming ever more popular [1]. It is well known that the most dangerous UV radiation is UVB (290–320 nm), whose short wavelength and considerable energy can lead to damage to human skin, making protection a pressing issue. Of the various UVB sunscreen agents approved for inclusion in sunscreen products, 2-ethylhexyl-4-methoxycinnamate (EHMC) is the most widely used [2]. In addition to being effective in absorbing UVB, EHMC is insoluble in water, has a good safety record and is relatively inexpensive. Because they are categorized as drugs, sunscreen preparations must be analyzed for their sunscreen agent content. The availability of a simple, fast analytical method for quality control of sunscreen preparations is thus highly desirable [3].

The published procedures for the isolation of sunscreen agents from cosmetic matrices prior to chromatographic analysis require several sample manipulations that include solvent extraction, liquid–liquid extraction, sonication, centrifugation and filtration [4–6]. These processes are laborious and time-consuming and therefore are not suitable for routine analysis of cosmetic preparations. Moreover, large volumes of hazardous solvents have to be handled and disposed of [6].

Different techniques such as high-performance liquid chromatography (HPLC) [7–12] gas chromatography [13], Raman spectroscopy [14], thin-layer chromatography [15] and nuclear magnetic resonance [16] have been used to determine EHMC content.

Recently, methods that make use of mercury film electrodes in strongly alkaline media [17] and carbon-epoxy composite electrodes in non-aqueous solvents [18] have been applied to the determination of sunscreen agents by differential-pulse voltammetry (DPV). Nonetheless, no

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methods have been reported in the literature for the voltammetric determination of sunscreen agents in micellar media.

The concentration and nature of surfactants can affect not only the shape of electrochemical waves but also parameters such as half-wave potential, electron-transfer rates at the electrode, diffusion and transfer coefficients and the stability of intermediate species [18–20]. For this reason, micellar solutions have been extensively studied. Particularly, redox reactions of micelle-solubilized organic compounds have been the focus of many electrochemical studies, both in polarography and in voltammetry.

The optimal experimental conditions for the determination of EHMC alone and in the presence of 2-hydroxy-4-methoxybenzophenone (BENZ-3) or 4-methybenzylidene camphor (MBC) in samples of cosmetics are described in this paper. The results of this determination were also compared with those obtained by HPLC, chosen as reference for validating the method proposed here.

2. Experimental

2.1. Apparatus

The electrochemical measurements were made with a Princeton Applied Research (PAR) Model 303 potentiostat/galvanostat combined with a PAR Model 303A dropping mercury electrode (DME). The three-electrode system was completed by means of a platinum-wire auxiliary electrode and an Ag/AgCl reference electrode. A 50-mV pulse amplitude was adopted for differential-pulse polarography (DPP), with a scan rate of 5 mV s^{-1} and interval of 1 s.

All pH measurements were made with a Micronal (São Paulo, Brazil) Model B474 pH-meter. Supporting electrolytes and stock solutions were prepared in demineralized water from a Milli-Q system (Millipore, Bedford, MA).

2.2. Chromatography

The HPLC analyses were performed with a Model 320 Varian-ProStar equipped with a UV–vis detector (ProStar/Dynamax). A 250.00-mm long, 4.60-mm i.d. reverse-phase C-8 column (Microsorb-MV 100-5, Varian) packed with 5.00-μm particles was used. The mobile phase was 1.00% methanol:acetic acid (90:10, v/v). All chemical reagents were chromatography grade. Elution was monitored in the visible portion of the spectrum and quantitations were performed with a UV detector operating at 285, 300 and 310 nm for BENZ-3, MBC and EHMC, respectively. Chromatography was carried out at room temperature with a mobile-phase flow rate of 1.00 mL min^{-1}.

2.3. Reagents

EHMC, MBC and BENZ-3 (all from Galena, Brazil) and cetyltrimethylammonium chloride (Sigma) were used as received. All other chemicals were of analytical-reagent grade. Stock solutions (1.00×10^{-3} mol L^{-1}) of EHMC were prepared daily by dissolving the solid substance in methanol. Britton-Robinson (BR) buffer solutions with methanol (50%) were used as supporting electrolytes. The buffers were prepared by mixing 0.04 mol L^{-1} acetic acid, 0.04 mol L^{-1} orthophosphoric acid, 0.04 mol L^{-1} boric acid and an appropriate volume of 0.20 mol L^{-1} sodium hydroxide.

2.4. Preparation of sample solutions

Sunscreen content was evaluated in the following commercial sunscreen products: sunblock lotions A (SPF 20 and SPF 6) and B (SPF 20 and 8), anti-wrinkle cream (SPF 15), hand moisturizing cream and foot moisturizing cream. Samples of the products were prepared by using a one-step dilution procedure. For each product a 0.10 to 1.00-g amount was dissolved in 15 mL of absolute methanol and mixed with vertex treatment for 15 min. After centrifuging at 1000 rpm for 10 min, the supernatant was transferred into a 25-mL calibrated flask and made up to that volume with methanol. Appropriate volumes of the resulting solutions were placed in the voltammetric cell.

2.5. Measurement procedures

2.5.1. Polarography

The general procedure for obtaining polarographic curves was as follows. A 10-mL aliquot of BR buffer with 1.60×10^{-3} mol L^{-1} cetyltrimethylammonium chloride (CTAC) was placed in the voltammetric cell and the required aliquot of the standard solution of EHMC or sample was added by means of a micropipette. The solution was purged with nitrogen for 15 min and the polarographic curves were recorded.

2.5.2. Chromatography

Stock solutions of the standards were prepared by dissolving appropriate amounts of BENZ-3, MBC and EHMC in methanol. Sets of standard solutions were produced by diluting aliquots of the stock solutions with methanol to 10 mL in calibrated flasks, to obtain final concentrations ranging from 3.00 to 15.00 mg L^{-1}. Each sample of commercial sunscreen preparation (approximately 3.60–4.60 mg) was accurately weighed in a 15-mL beaker, dissolved in methanol and centrifuged. The supernatant was transferred into a 25-mL calibrated flask and diluted to the mark with methanol. An aliquot of the resulting solution was filtered through a 0.45-μm membrane filter prior to HPLC analysis. By means of the injection value, 50 μL of the prepared sample solutions and standard solutions were chromatographed under the operating conditions described in Section 2.2. Quantitation was based on the peak area of the sample.

3. Results and discussion

3.1. *Influence of surfactants on EHMC reduction*

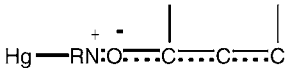
EHMC is not reduced in BR buffer in the 3.0–9.0 pH range. The use of a non-ionic surfactant such as Triton X-100 or an anionic surfactant (lauryl sulfate) in the electrolyte did not lead to changes in the polarograms. In contrast, the presence of a cationic surfactant (1.60×10^{-3} mol L^{-1} CTAC) led to the appearance of a DPP peak for EHMC. The differential-pulse curves in pH 4.0 BR buffer for the absence (a) and presence (b) of a cationic surfactant are shown in Fig. 1. EHMC gave rise to one single wave between −1.49 and −1.68 V versus Ag/AgCl in the pH range investigated. The cationic surfactant induced a great shift in the peak potentials toward more positive values (curve B), a feature that has also been observed for cinnamic acid under similar conditions [21]. For this compound the behavior of the peak potential as a function of pH was similar both in the presence and absence of surfactant.

CTAC is a cationic surfactant that belongs to the group of quaternary ammonium compounds. In suitable solvents it forms spherical micelles above the critical micellar concentration (CMC), which in water occurs at 0.90 mmol L^{-1} (25 °C). In the presence of electrolytes the CMC is lowered because of increased micellization from free ions [22].

CTAC is adsorbed onto the electrode surface by hydrophobic attraction and by electrode electrostatic attraction at negative potentials. At concentrations lower than the CMC, the surfactant acts as an ion-pairing agent, and monomers are adsorbed onto the electrode surface, though only to a very small extent [23]. At concentrations higher than the CMC, a strong adsorption is observed at negative potentials, which can lead to an extraordinary enhancement in the sensitivity of voltammetric measurements [22,23].

The existence of a conjugated system in α,β-unsaturated carbonyl compounds allows a resonance-stabilized anion to be formed, which enables interactions to occur with the cationic surfactant [24].

According to our results and the general mechanism for similar compounds, the effect of a cationic surfactant on the polarographic reduction of EHMC might be explained on the basis of a model suggested by Missan et al. [25]. In the presence of a layer of adsorbed cationic surfactant on the mercury surface, EHMC reduction (usually a 1,2-addition of electrons to the double bond) is replaced by a two-electron step involving a 1,4-addition across the ion pair.



$$\mathrm{Hg}{-}\overset{+}{\mathrm{R}}\mathrm{N}{:}\overset{-}{\mathrm{O}}\cdots\overset{|}{\mathrm{C}}\cdots\mathrm{C}\cdots\overset{|}{\mathrm{C}}$$

The unnecessary re-orientation of the molecule with respect to the electrode surface—usually required, however, for a 1,2-addition (or the negatively charged oxygen atom would be repelled from the electrode surface)—might be at least partly responsible for the reduction of the EHMC-surfactant ion pair at less negative potentials.

The effect of CTAC concentration on the EHMC polarographic peak was studied within the range of 2.70×10^{-5} to 1.90×10^{-3} mol L^{-1} at an EHMC concentration of 1.60×10^{-3} mol L^{-1} in 0.04 mol L^{-1} BR medium (pH 4.0). As shown in Fig. 2, the height of the EHMC reduction peak increased with the surfactant concentration up to 1.60×10^{-3} mol L^{-1} approximately. A pronounced decrease was observed for the highest concentration tested, as a result of the surfactant competing at a higher degree with EHMC for the electrode surface adsorption sites.

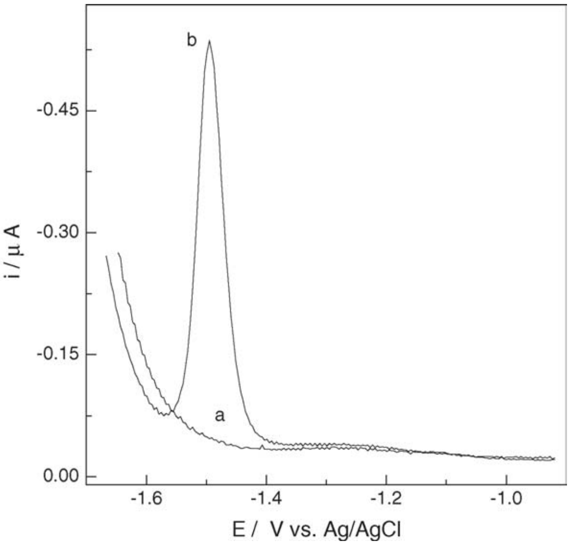


Fig. 1. Differential-pulse polarograms for 1.90×10^{-5} mol L^{-1} EHMC in BR buffer (pH 4.0): (a) without surfactant and (b) with 1.60×10^{-3} mol L^{-1} cetyltrimethylammonium chloride (CTAC). Parameters: drop time = 1.0 s; scan rate (ν) = 5 mV s^{-1}; pulse amplitude (ΔE) = 50 mV.

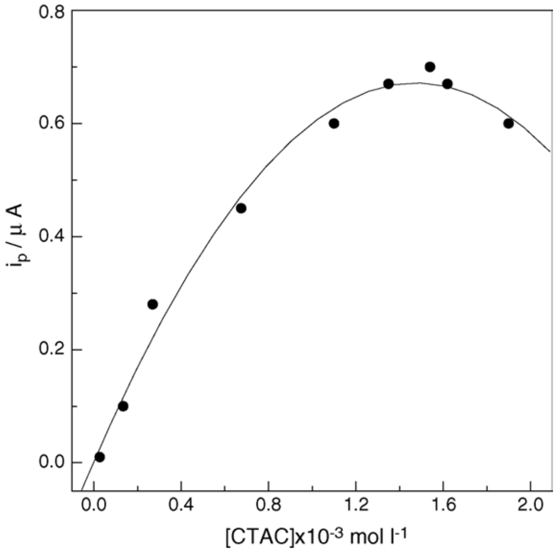


Fig. 2. Influence of CTAC concentration on differential-pulse polarograms for 1.00×10^{-4} mol L^{-1} EHMC in BR buffer (pH 4.0). Other conditions as in Fig. 1.

At 1.60×10^{-3} mol L^{-1}, CTAC induced the greatest shift in the peak potential toward more positive values (180 mV from the electrolyte discharge), improving the shape of the differential-pulse peak and extending the applicability of the proposed method for the determination of EHMC in cosmetic preparations.

3.2. Polarographic behavior of sunscreens

The effect of pH on the reduction process was investigated by recording polarograms of 1.00×10^{-4} mol L^{-1} EHMC at pH values ranging from 3.0 to 9.0. In Fig. 3 (curve A), which shows the influence of pH on the peak current, three zones can be distinguished. At pH values from 3.0 to 5.0 the peak current decreases gradually, to remain nearly constant until pH 6.0. A new decrease is observed from pH 6.0 to 7.0, after which the current again remains nearly constant until pH 9.0. From pH 7.0 to 9.0 the peak current is practically independent of pH. The variations in peak current with the increase of pH indicate a simultaneous presence of different ionic species in the solution.

The variations in peak potential as a function of pH are shown in Fig. 3(curve B). The peak potential shifted toward more negative values with the increase in pH and the slope of linear variation was of 36 mV pH^{-1}, indicating that a chemical reaction (proton-transfer reaction) precedes the process that takes place at the electrode [26]. Two linear-variation portions can be seen intersecting at approximately pH 4.0.

This behavior is analogous to that observed for cinnamic acid. According to Brand and Fleet [27], similarities in overall behavior suggest that the acid and cinnamate esters are reduced in protonated form. Therefore, the greatest peak potential shift observed for EHMC above pH 4 is indicative of slow step protonation.

For analytical purposes, the medium chosen to conduct our further studies was 0.04 mol L^{-1} BR buffer at pH 4.0.

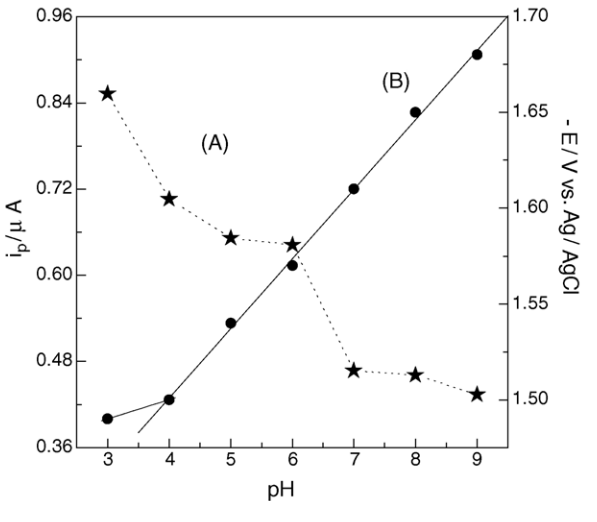


Fig. 3. Effect of pH on the peak current (A) and peak potential (B) for 1.00×10^{-4} mol L^{-1} EHMC. Other conditions as in Fig. 1.

The effects of surfactant and pH were not studied for MBC or BENZ-3 reduction; instead, the conditions identified for EHMC reduction were used for these compounds.

Because EHMC and MBC are α,β-unsaturated carbonyl compounds, the behavior of the voltammetric reduction of these agents might be very similar to that of unsaturated carbonyl compounds. When an electroreducible group is conjugated with olefinic groups, the resulting molecule becomes more easily reducible under comparable conditions, a feature that is well illustrated for α,β-unsaturated carbonyl compounds. The double C═C bond is almost certainly reduced before the carbonyl group. The reduction involves the protonated form of the molecule, with participation of two electrons [27–29].

The electroreduction of benzophenone and substituted benzophenone in both aqueous and non-aqueous media on mercury and glassy carbon electrodes is well known. Studies have shown that steric as well as electronic effects and pH influence the redox potential of substituted benzophenone. At pH 4.0 the reduction peak of BENZ-3 is attributed to two-electron reduction of the carbonyl group [30–32].

3.3. Calibration graph

The calibration curve for EHMC in pH 4.0 BR buffer with 1.60×10^{-3} mol L^{-1} CTAC was measured by DPP. The following parameters were regarded as most suitable for EHMC determination: drop time = 1 s, pulse amplitude = 50 mV, scan rate = 5 mV s^{-1}, pulse width = 50 ms. The differential-pulse polarograms of various concentrations of EHMC shown in Fig. 4 exhibited good linearity. The linear segment increased from 1.80×10^{-6} to 7.00×10^{-5} mol L^{-1} according to the regression equation i_p (μA) = 0.0192 + 0.1397C

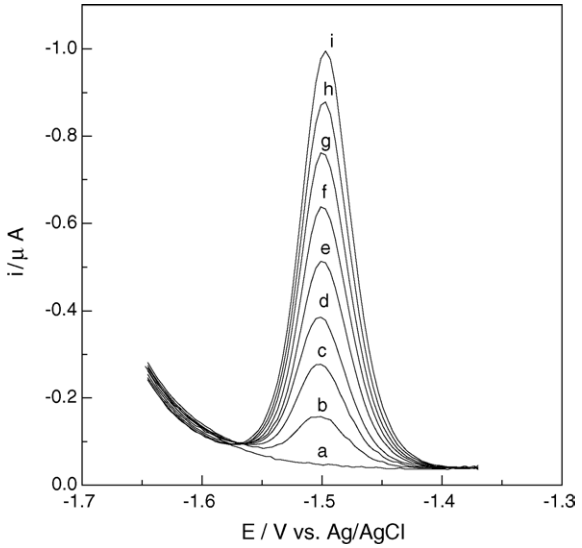


Fig. 4. Differential-pulse polarograms obtained with increasing concentrations of EHMC in the presence of 1.60×10^{-3} mol L^{-1} CTAC in BR buffer (pH 4.0). (a) Blank, (b) 0.50; (c) 1.00; (d) 2.00; (e) 3.00; (f) 4.00; (g) 5.00; (h) 6.00 and (i) 7.00×10^{-5} mol L^{-1}, respectively. Other conditions as in Fig. 1.

(mol L^{-1}) ($r = 0.999$). The relative standard deviation (R.S.D.) of 2.30% for 1.00×10^{-5} mol L^{-1} EHMC ($n = 5$) revealed good repeatability. The limits of detection (LOD) and of quantitation (LOQ) were 3.76×10^{-8} mol L^{-1} and 1.25×10^{-7} mol L^{-1}, respectively, and were calculated with the relations $3s/b$ and $10s/b$ for LOD and LOQ, respectively, where s is the standard deviation of the arithmetic average of 10 voltammograms of blank performed at the same potential as EHMC and b is the slope of the calibration curve. The sensitivity of the method proposed is high enough for the determination of EHMC added as sunscreen agent to cosmetic preparations. In order to further verify the suitability of the method proposed, it was also applied with known amounts of standard EHMC being added to the analytical solutions of cosmetics.

3.4. Determination of EHMC in cosmetic preparations

The proposed DPP method was applied to determining the EHMC content in sunblock lotions (brand A, SPF 20 and 6; brand B, SPF 20 and 8), anti-wrinkle cream, foot moisturizing cream and hand moisturizing cream. Determination of EHMC content in the preparations was performed by using the standard addition method. Each sample of cosmetic was treated as described in Section 2.3 and appropriate volumes were placed in the electrochemical cell for analysis.

Fig. 5 illustrates the differential-pulse polarograms of successive additions of EHMC to anti-wrinkle cream in the presence of 1.60×10^{-3} mol L^{-1} CTAC.

Table 1 shows the nominal content of EHMC and the average of three determinations of this agent for each sample. The third row shows the differences between EHMC contents determined by the electroanalytical method and the values stated by the manufacturers of the preparations. When the results obtained by DPP were compared with those obtained by HPLC (Table 1), a good agreement was found between both methods.

The recovery rate of EHMC from the preparations, calculated as the average of three measurements for each sample, ranged from 94.00 to 102.20% (Table 2), indicating that the proposed voltammetric method has good accuracy and repeatability.

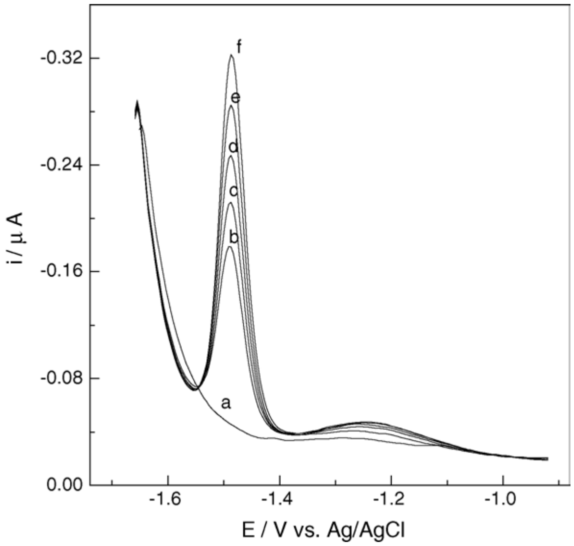


Fig. 5. Differential-pulse polarograms obtained for the determination of EHMC in anti-wrinkle cream in the presence of 1.60×10^{-3} mol L^{-1} CTAC in BR buffer (pH 4.0). (a) Blank; (b) anti-wrinkle cream sample; (c–f) successive additions of standard EHMC (mol L^{-1}). Other conditions as in Fig. 1.

3.5. Simultaneous determination of two sunscreen agents

The method proposed was also successfully applied to the simultaneous determination of two sunscreen agents in the preparations. For MBC, the response was linear in the presence of EHMC concentrations within the range of 1.00×10^{-6} to 8.00×10^{-6} mol L^{-1}, according to the regression equation i_p (µA) $= 3.88 \times 10^{-4} + 0.011C$ (mol L^{-1}) ($r = 0.999$). A LOD of 4.73×10^{-7} mol L^{-1} and a LOQ of 1.58×10^{-6} mol L^{-1} were obtained. For BENZ-3, the response was linear in the presence of EHMC concentrations within the range of 1.00×10^{-6} to 8.00×10^{-6} mol L^{-1} according to the regression equation i_p (µA) $= 0.003 + 0.009C$ (mol L^{-1}) ($r = 0.999$). A LOD of 5.60×10^{-7} mol L^{-1} and a LOQ of 1.88×10^{-6} mol L^{-1} were obtained. In the presence of each sunscreen agent, EHMC exhibited linearity in the concentration range of 1.00×10^{-6} to 8.00×10^{-6} mol L^{-1}, according to the regression equation i_p (µA) $= 0.006 + 0.026C$ (mol L^{-1}) ($r = 0.999$),

Table 1
Determinations of 2-ethylhexyl-4-methoxycinnamate (EHMC) in selected commercial cosmetic preparations using the proposed polarographic method and HPLC

Measurements	Sunblock lotion A SPF 20	Sunblock lotion A SPF 6	Sunblock lotion B SPF 20	Sunblock lotion B SPF 8	Anti-wrinkle cream	Foot moisturizing cream	Hand moisturizing cream
Nominal conc. (%, w/w)	7.00	4.50	7.00	5.50	7.50	1.90	1.90
Electroanalytical method: measured (%, w/w) ± %R.S.D.	6.70 ± 1.70	3.80 ± 2.00	6.94 ± 2.20	4.90 ± 1.50	7.60 ± 3.10	1.86 ± 1.50	1.80 ± 2.70
Relative error (%)	−4.28	−15.56	−0.86	−10.90	1.33	−2.10	−5.80
HPLC measured (%, w/w) ± %R.S.D.	6.72 ± 1.50	4.20 ± 3.00	6.50 ± 1.30	5.35 ± 2.50	7.65 ± 3.50	1.85 ± 1.60	1.80 ± 2.50
Relative error (%)	−4.00	−6.70	−7.00	−2.70	2.00	−2.63	−5.26

Measured values are the average of three determinations; conc., concentration; R.S.D., Relative standard deviation.

Table 2
Recovery of EHMC added to selected commercial cosmetic preparations by differential-pulse polarography

Samples	Added (mol L^{-1})	Found (mol L^{-1})	Recovered (%)	R.S.D. (%)
Sunblock lotion A SPF 20	1.81×10^{-6}	1.78×10^{-6}	99.00	1.50
Sunblock lotion A SPF 6	1.90×10^{-6}	1.87×10^{-6}	98.00	1.70
Sunblock lotion B SPF 20	1.90×10^{-6}	1.93×10^{-6}	102.10	2.20
Sunblock lotion B SPF 8	1.90×10^{-6}	1.91×10^{-6}	101.00	1.70
Anti-wrinkle cream	1.90×10^{-6}	1.77×10^{-6}	94.00	2.20
Foot moisturizing cream	1.90×10^{-6}	1.95×10^{-6}	100.50	1.20
Hand moisturizing cream	1.90×10^{-6}	1.93×10^{-6}	102.20	2.50

Measured values are the average of three determinations. R.S.D., relative standard deviation.

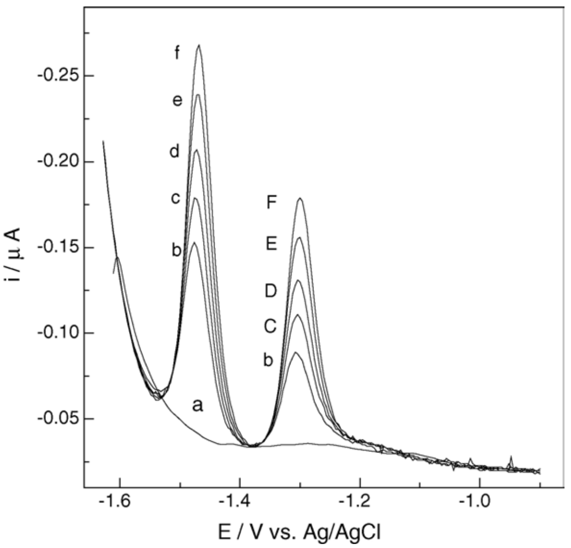


Fig. 6. Differential-pulse polarograms obtained for the simultaneous determination of EHMC and MBC in the presence of 1.60×10^{-3} mol L^{-1} CTAC in BR buffer (pH 4.0). (a) Blank; (b) sunblock lotion A (SPF 20) sample; (c–f) successive additions of standard EHMC (mol L^{-1}); (C–F) successive additions of standard MBC. Other conditions as in Fig. 1.

with a LOD of 2.10×10^{-7} mol L^{-1} and a LOQ of 6.84×10^{-7} mol L^{-1}.

Fig. 6 shows the polarograms of mixtures of MBC and EHMC at various concentrations for one of the preparations. Table 3 shows the results for the determination of EHMC, MBC and BENZ-3 for two preparations, along with the results obtained by HPLC. A good agreement between both methods was achieved, indicating that the method proposed can be applied to the simultaneous determination of EHMC alone or in combination with MBC or BENZ-3 in cosmetic preparations.

Table 4 exhibits the values of EHMC, MBC and BENZ-3 recovery from two of the preparations. The precision and accuracy of the method were determined. In Table 3, precision is expressed as %R.S.D. and accuracy as mean relative error, both obtained with the standard addition method. Good values were found for precision and accuracy, indicating that the method can be applied to the analysis of preparations of similar formulas containing EHMC alone or in combination with MBC or BENZ-3.

3.6. Determination of sunscreen agents by HPLC

The chromatograms obtained for BENZ-3, MBC and EHMC exhibited well-resolved peaks and retention times of approximately 3.50, 5.00 and 8.00 min, respectively, under the experimental conditions (data not shown). The analytical system was tested for linearity in the range of 3.00 to 15.00 mg L^{-1} and was found to be linear, with a coefficient of correlation $r = 0.999$. LODs were 0.41 mg L^{-1} (1.80×10^{-6} mol L^{-1}) for BENZ-3, 0.76 mg L^{-1} (3.04×10^{-6} mol L^{-1}) for MBC and 0.99 mg L^{-1} (3.65×10^{-6} mol L^{-1}) for EHMC. These

Table 3
Simultaneous determination of 2-ethylhexyl-4-methoxycinnamate (EHMC), 2-hydroxy-4-methoxybenzophenone (BENZ-3) and 4-methybenzylidene camphor (MBC), in two commercial cosmetic preparations using the proposed polarographic method and HPLC

Methods and sunscreen agents	Sunblock lotion A (SPF 20)			Sunblock lotion B (SPF 20)		
	Nominal conc. (% w/w)	Measured conc. (% w/w) ± R.S.D. (%)	Error (%)	Nominal conc. (% w/w)	Measured conc. (% w/w) ± R.S.D. (%)	Error (%)
Proposed method						
EHMC	7.00	7.01 ± 2.20	0.14	7.00	7.00 ± 1.60	0
BENZ-3	–	–	–	3.50	3.66 ± 1.90	4.60
MBC	4.00	3.87 ± 1.60	−3.25	–	–	–
HPLC						
EHMC	7.00	6.80 ± 1.50	−2.86	7.00	6.50 ± 1.30	−7.00
BENZ-3	–	–	–	3.50	3.84 ± 1.20	9.70
MBC	4.00	3.50 ± 2.90	−12.50	–	–	–

Measured values are the average of three determinations.

Table 4
Recovery for the simultaneous determination by DPP of EHMC, BENZ-3 and MBC added to two commercial cosmetic preparations

Agent	Sunblock lotion A SPF 20			Sunblock lotion B SPF 20		
	Added (mol L^{-1})	Found (mol L^{-1})	Recovered ($x \pm$ R.S.D. %)	Added (mol L^{-1})	Found (mol L^{-1})	Recovered ($x \pm$ R.S.D. %)
EHMC	1.90×10^{-6}	1.86×10^{-6}	97.72 ± 0.82	1.90×10^{-6}	1.89×10^{-6}	99.65 ± 2.60
BENZ-3	–	–	–	1.90×10^{-6}	2.13×10^{-6}	112.10 ± 0.66
MBC	1.97×10^{-6}	2.03×10^{-6}	103.30 ± 0.35	–	–	–

Measured values are the average of three determinations; x, mean; R.S.D., relative standard deviation.

results indicate that HPLC is not as sensitive for determining sunscreen agents as the method proposed. The results of the quantitative analyses of sunscreen agents by HPLC are shown in Tables 1 and 3.

4. Conclusions

The study revealed that DPP is a suitable technique for the determination of EHMC in cosmetic preparations. The use of CTAC led to significant and desirable changes in the peak potentials and currents of the differential-pulse polarograms obtained for EHMC. The inclusion of CTAC in the supporting electrolyte was found to be a convenient procedure for the selective determination of low levels of EHMC in samples of cosmetics. The new methodology proposed provides a simple but precise determination of EHMC in preparations, involving a simple step of sample pre-treatment and resulting in short analysis times.

Acknowledgments

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