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Review

Determination of parabens in shampoo using high performance liquid chromatography with amperometric detection on a boron-doped diamond electrode

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ABSTRACT

Methylparaben (MePa), ethylparaben (EtPa) and propylparaben (PrPa) have been widely used, among others, as chemical preservatives in cosmetics, drugs and foods. As these compounds are linked with allergies, dermatitis and estrogenic properties, it is necessary to control the concentration of these substances in different matrices. The aim of this paper are: to evaluate the electrochemical behavior of parabens on the boron-doped diamond (BDD) electrode and the development of a chromatographic method, with electrochemical detection (HPLC-ED), for determination of parabens in shampoo. A BDD (8000 ppm) electrode was adapted in a thin layer mode analytical cell consisting of a stainless steel and a platinum wire as reference and auxiliary electrodes, respectively. Chromatographic separations were obtained with a reversed phase C8 analytical column and a mobile phase of 0.025 mol L^{-1} disodium phosphate, pH 7.0, and acetonitrile (40:60, v/v), delivered at a flow rate of 1.0 mL min^{-1}. Sample preparation was performed by solid phase extraction using C18 cartridges and acetonitrile for elution. Benzylparaben was employed as internal standard. The HPLC-ED method developed, using the BDD electrode, was validated for the determination of parabens in shampoos and presented adequate linearity (>0.999), in the range of 0.0125–0.500% (w/w), detectability 0.01% (w/w), precision (RSD of 2.3–9.8%) and accuracy (93.1–104.4%) and could be applied for routine quality control of shampoos containing MePa, EtPa and PrPa.

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1. Introduction

Preservatives are often added to pharmaceutical and cosmetic formulations to manage microbial contamination. Alkyl esteres of *p*-hydroxybenzoic acid (parabens), are the most widely employed preservatives in cosmetic products due to their broad antimicrobial spectrum and effectiveness. The most common parabens used in cosmetic products are methylparaben (MePa), ethylparaben (EtPa), propylparaben (PrPa) and butylparaben (BuPa). They are often used in combination, since they have synergistic effects, in a wide variety of products such as cosmetics, ointments, and suspensions [1–3], which allows the use of lower levels while increasing preservative activity. Furthermore, parabens are often used in combination with other types of preservatives. Parabens have multiple biological actions, but it is generally related that their inhibitory effects on membrane transport and mitochondrial function processes are keys for their actions [1].

Since the presence of parabens was detected in human breast tumors by Darbre [4,5], the use of these preservatives in cosmetics has been discussed worldwide. It was also reported that parabens have estrogenic activity, since the compounds have been shown to bind to estrogen receptors from different sources.

The use of parabens in cosmetic products as a preservative is permitted in several countries, including Brazil, up to a maximum concentration of 0.4% (w/w) in the finished product for one ester and up to 0.8% (w/w) for mixtures of esters expressed as *p*-hydroxybenzoic acid [6].

Several analytical methods have been reported for the determination of parabens in a variety of matrices, among others, high performance liquid chromatography (HPLC) and capillary electrophoresis [2,3,7–15], micellar electrokinetic chromatography [16] and mass spectrometry [17–20].

Nevertheless, only a few electroanalytical methods have been reported for the determination of parabens [21]. Electrochemical methods may offer certain advantages, such as requiring easier sample preparation, being less time-consuming and offering detectivity and dynamic range comparable to other analytical methods [22,23].

Boron-doped diamond (BDD) electrodes have recently received a great deal of attention, owing to their unique electrochemical properties, e.g., high stability because of their inertness with respect to adsorption of chemical species and easy of cleansing of the surface compared with the glassy carbon electrode. Compared to classical carbon electrodes and other metallic solid electrodes, diamond electrodes open up new opportunities for working under extreme conditions, such as extremely high anodic potentials, or extremely aggressive media and its use has been proposed for many applications [21–29].

Radovan et al. [22] reported a study employing the BDD electrode for the determination of total parabens in hydroalcoholic solutions and water using cyclic voltammetry and chronoamperometry. The proposed method does not allow the individual determination of each paraben and in samples where more than one paraben is present, a preliminary separation of the target compounds must be carried out.

High-performance liquid chromatography with electrochemical detection (HPLC-ED), using the BDD electrode, has been employed for the determination of benzodiazepines [30].

In this paper, the potentiality of the boron-doped diamond electrode in an amperometric detector for HPLC for the determination of methyl-, ethyl- and propylparabens in shampoos is evaluated. A method was developed and validated and applied for the analysis of shampoo samples commercialized in Brazil.

2. Experimental

2.1. Chemicals, materials and solutions

Methyl-(MePa), ethyl-(EtPa), propyl-(PrPa) and benzyl-(BzPa) parabens, purity >99%, were from Sigma–Aldrich® (St. Louis, USA). Analytical grade disodium hydrogenphosphate, sodium hydroxide, phosphoric acid were purchased from Merck (Darmstadt, Germany). Acetonitrile (HPLC-grade) was purchased from Tedia (Fairfield, USA). The SPE study was performed on a Vac-Elut vacuum manifold obtained from Supelco® (Bellefonte, USA). Bond Elut C-18 cartridges (500 mg/3 mL) were supplied by Varian® (Bellefonte, USA).

Standard stock solutions of MePa, EtPa and PrPa were prepared by dissolving 100 mg (± 0.1 mg) of each compound in 100 mL of water:acetonitrile (50:50, v/v). The solutions were stored at −18 °C between experiments.

Standard working solutions were prepared daily by diluting the standard stock solutions in water:acetonitrile (50:50, v/v) to concentrations of 0.05, 0.1, 2.5, 5.0, 10.0, 15.0, 25.0 $\mu g\,mL^{-1}$. Benzylparaben (internal standard) was prepared in the same way as described for the other parabens, however, the concentration of the standard working solution was 15.0 $\mu g\,mL^{-1}$.

Throughout the study, water was obtained from a Milli-Q system from Millipore (Bedford, USA). Before analysis, all the solutions were filtered through 0.22 μm membrane filters from Millipore (São Paulo, Brazil).

2.2. Conditioning of the boron-doped diamond electrode

Before first use the BDD-electrode was submitted to an anodic treatment (polarization by +3.0 V vs Ag/AgCl for 10 min) to remove the hydrophobic film that covers its surface. After that, the electrode was cathodically polarized for 10 min at −3.0 V vs Ag/AgCl, for the activation and conditioning of the surface. When necessary, after the initial treatment, the electrode was submitted only to the cathodic treatment (−3.0 V) for 30 s for the recuperation of the electrodic surface.

2.3. Cyclic voltammetry study

Cyclic voltammetry (CV) was employed to evaluate the electrochemical behavior of the parabens on the BDD electrode. The voltammetric study was carried out with an AutoLab®/PGSTAT30 potentiostat/galvanostat, interfaced with a personal computer. The AutoLab software GPES (General Purpose Electrochemical System) was used for data acquisition. The experiments were carried out in a single compartment three electrode cell, at room temperature (21 ± 1 °C), under nitrogen atmosphere. The counter electrode and the reference electrode were a platinum wire and a Ag/AgCl, KCl 3 mol L^{-1} electrode, respectively. A BDD disk (8000 ppm) was used as the working electrode. Cyclic voltammetric scans were carried out at different scan rates (10–400 mV s^{-1}), in the potential range of 0.0 to +1.5 V, using a step potential of 0.01 V. As supporting electrolyte, 0.010 mol L^{-1} and 0.10 mol L^{-1} phosphate buffer, pH 7, and Britton–Robinson buffer (BR) in a range of pH 2–12, were evaluated. A volume of 25 mL of the supporting electrolyte was transferred to the electrochemical cell and the oxygen was removed by purging with N_2 for 10 min.

2.4. High performance liquid chromatography with electrochemical detection (HPLC-ED)

The HPLC system comprised a 709 IC pump (Metrohm®), a 20 μL injection loop and a electrochemical detector, model 871 Advanced Bioscan system (Metrohm®) with a BDD (8000 ppm) adapted in a

thin layer mode as analytical cell, interfaced with a personal computer with the IC Net software for data acquisition. The geometric area of the electrode was 78 mm^2. The thin layer flow cell consisted of a stainless steel and a platinum wire as reference and auxiliary electrodes, respectively. The amperometric detector, in pulse working mode, was the electrochemical technique applied to carry out the analysis, with the following parameters: initial potential +1.2 V; medium potential −0.5 V and end potential −2.0 V; pulse repetition time 0.4 s, range 10 μA, polarity positive. Chromatographic separations were obtained with a Waters XTerra™ C8 analytical column (250 mm × 4.6 mm, 5 μm) and mobile phase of 0.025 mol L^{-1} disodium phosphate, pH 7.0:acetonitrile (40:60, v/v) delivered at a flow rate of 1.0 mL min^{-1}. Before starting the analyses, mobile phase was percolated through the column until the cell current reached a stable level.

2.5. High performance liquid chromatography with diode array detector (HPLC-DAD)

High performance liquid chromatographic analyses were also performed using a Waters chromatographic system (Milford, USA), composed of a binary pumping system, model 1525, a diode array detector (DAD) model 2996 and a Rheodyne 7725 injector, with sample loop of 50 μL. Chromatographic separation was achieved using a XTerra™ C8 column (250 mm × 4.6 mm, 5 μm) with a similar guard-column (4.0 mm × 4.0 mm, 5 μm), purchased from Waters (Milford, USA). The mobile phase consisted of a mixture of water:acetonitrile. Gradient elution of 60:40 (v/v) water:acetonitrile to 45:55 (v/v) water:acetonitrile (0–10 min), then to 60:40 (v/v) water:acetonitrile (10–15 min) was used. Flow rate was 1.0 mL min^{-1}. All analyses were performed at room temperature and at λ = 254 nm.

2.6. Sample preparation

For development and for application of the HPLC methods (with the ED and DAD dectectors), shampoo samples with and without parabens were purchased from retail markets in Campinas, SP, Brazil. A sample of 1.0 g of the shampoo was accurately weighed, diluted to 25 mL in a volumetric flask with water and the mixture was sonicated for 5 min. An aliquot of 1 mL of this sample solution was applied to a preconditioned (with methanol and water) C18 SPE cartridge. The sorbent was washed with 5 mL of water and the elution of the analytes was performed with 3 mL of acetonitrile, at a constant flow rate of 1 mL min^{-1}. The eluate was collected in a 10 mL volumetric flask and diluted to volume with water. This solution was filtered (0.22 μm membrane filter) and 50 μL and 20 μL was injected into the HPLC-DAD and HPLC-ED systems, respectively.

2.7. Validation

The method was in-house validated using the following performance criteria: linearity and linear range, sensitivity, detectability, intra-assay and inter-assay precision, recovery and accuracy [31].

The linearity, linear range, sensitivity and detectability were established through the analytical curve, using benzylparaben as internal standard. The analytical curve was obtained through fortification of a blank shampoo sample (without parabens) at seven concentration levels of 0.0125, 0.0250, 0.0625, 0.125, 0.250, 0.375, and 0.500% (w/w). All analyses were performed in triplicate. The sensitivity is the slope of the analytical curve.

The detectability (detection limit of the instrument) was calculated, using the following expression: detectability = $ks_{y/x}/m$, where $k = 3$, $s_{y/x}$ is the standard deviation of the residuals and m is the slope of the analytical curve.

The intra-assay precision (repeatability) of the method, expressed as the relative standard deviation of peak area measurements ($n = 5$), was evaluated through the results obtained with the method operating over 1 day, under the same conditions, using blank shampoo samples fortified with the parabens under study at 0.125% and 0.250% (w/w). The inter-assay precision was determined for the same levels and the analyses were performed for 3 days, in triplicate.

Accuracy was evaluated through recovery tests. For this purpose, a blank shampoo sample was fortified at 0.125% (w/w) and 0.250% (w/w) and analyzed ($n = 6$) according to Section 2.6, by the HPLC-ED method. Accuracy was also evaluated by comparing the HPLC-ED to the HPLC-DAD method. Six commercial products containing parabens were then analyzed, in triplicate.

The matrix effect was evaluated through comparison of the response obtained from the analysis of a fortified blank shampoo sample and a fortified extract obtained after the SPE procedure, using a blank shampoo sample.

3. Results and discussion

The BDD-electrode exhibits many advantages in relation to other solid state electrodes, including wide potential window, low background current, high sensitivity and reproducibility. However, its surface termination has a strong influence on its electrochemical properties. Nevertheless, the electrode is not selective to the determination of organic compounds of the same class and prior separations are mandatory. In order to establish a method for the determination of parabens in shampoo two main subjects were addressed: study of the electrochemical behavior of the parabens on the BDD-electrode, using cyclic voltammetry, and separation of the compounds using reverse phase liquid chromatography.

3.1. Cyclic voltammetry study

All parabens under study (MePa, EtPa, PrPa and BzPa) presented an anodic peak in BR-buffer (2 < pH < 12) with irreversible characteristics at the scan rate of 50 mV s^{-1} (Fig. 1). The overall process is diffusion controlled, since a linear relationship between peak current intensity and the square root of the scan rate was verified.

The peak potential is shifted towards positive potentials with decreasing pH-values, showing that the oxidation of the parabens is more difficult in an acidic medium. Between pH 8 and 12 the process is no longer proton dependent. Although it was verified that the peak current intensity is higher in BR at pH > 7, the parabens undergo hydrolysis in alkaline medium forming 4-hydroxybenzoic acid, and therefore pH values higher than 7 are not suitable for quantitative analyses. Therefore, for the subsequent studies a pH of 7 was chosen. In order to verify the influence of the supporting electrolyte on the paraben oxidation, studies using phosphate buffer were carried out and the results compared with those obtained with the BR-buffer. Two concentrations were evaluated (0.010 and 0.10 mol L^{-1}) and the results are shown in Fig. 2.

It was verified that the peak current intensity depends on the concentration of the supporting electrolyte, which is explained by the increase of the ionic strength of the solution. Even though the maximum peak current intensity was obtained in 0.10 mol L^{-1} BR-buffer, pH 7, the phosphate buffer was chosen for the development of the HPLC-ED method, due to the fact that this medium is more compatible with the chromatographic system. It was verified later that a phosphate concentration of −0.025 mol L^{-1} was enough to provide selectivity and sensitivity to the HPLC-ED method.

Considering that parabens are hydrophobic compounds and that in reverse phase chromatography an organic modifier needs to be used in the mobile phase to promote the separation of the

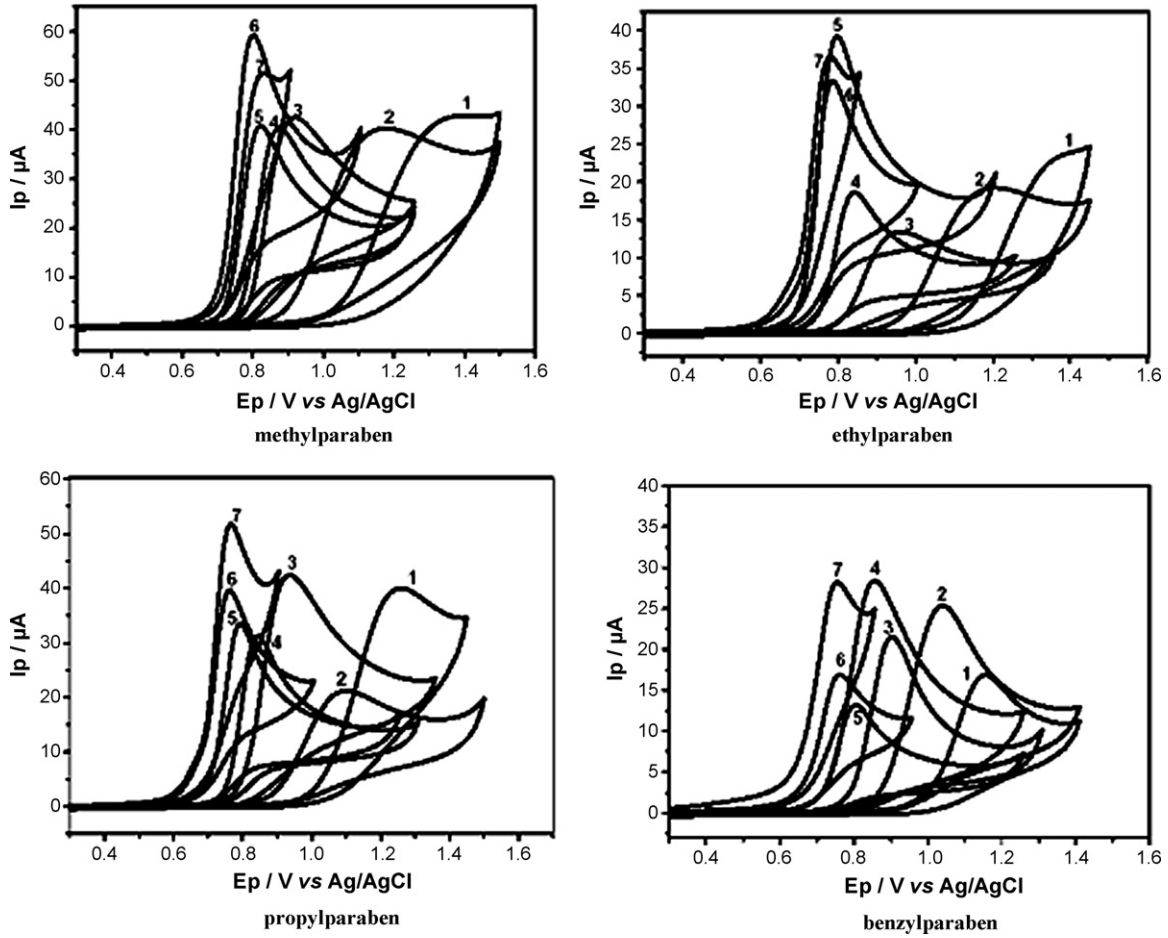

Fig. 1. Cyclic voltammogram, using a BDD working electrode (8000 ppm) and platinum wire and Ag/AgCl, KCl 3 mol L^{-1} as counter and reference electrodes, respectively. Paraben concentrations: 50 μg mL^{-1}; scan rate: 50 mV s^{-1}; supporting electrolyte: 0.10 mol L^{-1} Britton–Robinson buffer (1) pH 2.0; (2) pH 4.0; (3) pH 6.0; (4) pH 7.0; (5) pH 8.0; (6) pH 10.0 and (7) pH 12.0. (A) Methylparaben; (B) ethylparaben; (C) propylparaben; and (D) benzylparaben

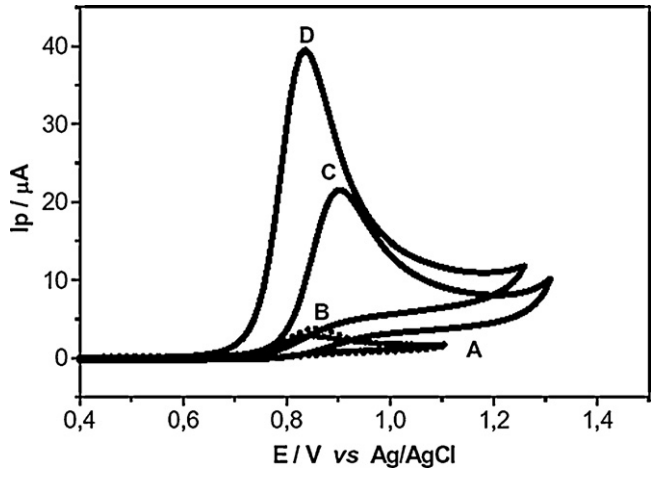

Fig. 2. Cyclic voltammogram using a BDD working electrode (8000 ppm) and platinum wire and Ag/AgCl, KCl 3 mol L^{-1} as counter and reference electrodes, respectively. Benzylparaben concentration: 50 μg mL^{-1}; supporting electrolyte: (A) 0.010 mol L^{-1} phosphate buffer, pH 7.0; (B) 0.010 mol L^{-1} BR-buffer, pH 7.0; (C) 0.1 mol L^{-1} phosphate buffer, pH 7.0; (D) 0.10 mol L^{-1} BR-buffer, pH 7.0; scan rate: 50 mV s^{-1}

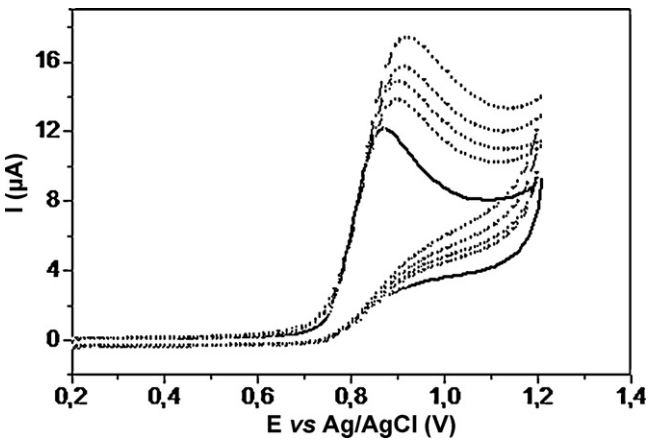

Fig. 3. Cyclic voltammogram using a BDD working electrode (8000 ppm) and platinum wire and Ag/AgCl, KCl 3 mol L^{-1} as counter and reference electrodes, respectively. (A) 30 μg mL^{-1} benzylparaben in 0.10 mol L^{-1} phosphate buffer. Addition of acetonitrile (v/v): (B) 6%; (C) 8%; (D) 10%; and (E) 14%. Scan rate: 50 mV s^{-1}

compounds, the influence of acetonitrile on the electrochemical behavior of the parabens using the BDD-electrode was studied. For this purpose different proportions of acetonitrile:phosphate buffer were prepared and the voltammograms recorded. It was verified that the organic modifier enhances the peak current intensity in 50% after addition of 14% of acetonitrile to the 0.10 mol L^{-1} phosphate buffer, pH 7, without modifying the shape of the voltammetric peak (Fig. 3). This result suggests that the diffusion of the species is enhanced when acetonitrile is added to the supporting electrolyte.

3.2. Chromatographic separation of the parabens using HPLC-ED

In the present study, a thin layer amperometric detector, in the pulsed mode, was used to carry out the detection of the parabens after separation in the chromatographic column. Pulse mode was chosen as optimal condition to obtain a compromise between peak intensity and no production of passive films on the electrode surface. This information is given in the text. A BDD-disk was inserted in a Teflon® bar and adapted to the thin layer cell of the amperometric detector. Chromatographic separations were carried out with a C8 analytical column and a mobile phase of 0.025 mol L^{-1} phosphate buffer, pH 7.0, and acetonitrile (40:60, v/v) delivered at a flow rate of 1.0 mL min^{-1}.

The required potential for the oxidation of the parabens was re-evaluated due to the fact that the reference electrode in the amperometric cell coupled to the HPLC was a stainless steel instead of the Ag/AgCl, KCl 3 mol L^{-1} electrode used in the earlier cyclic voltammetric studies. The optimum conditions, considering sensitivity and repeatability of the active electrode surface, were pulse mode potential 1.2 V, −0.5 V and −2.0 V, with a repetition time of 0.5 s. It is well known that solid state electrodes, including the BDD-electrode, undergo passivation during successive scans. In order to verify this effect, a sample solution containing all parabens, at a concentration of 50 μg mL^{-1}, was injected five times into the chromatographic system. The results showed that the variation in peak area observed were lower than 2% and could not be attributed to electrode fouling. However, when the signal obtained for a same paraben concentration changed more than 10%, the electrode was cleaned cathodically (−3.0 V) for 30 s.

The chromatographic system suitability parameters were all in the acceptable range: plate counts ($N > 2000$), resolutions ($Rs > 2$) and asymmetry factors ($As < 1.2$) [31]. The retention times obtained were: 4.5 min (MePa), 5.1 min (EtPa), 5.9 min (PrPa) and 7.2 min (BzPa), with a total run time of 10 min. The addition of the internal standard to the samples is essential to obtain adequate between-run precision using the BDD-electrode. Benzylparaben was chosen as internal standard, due to the fact that it presents similar electrochemical response and is not used in shampoo products.

3.3. Sample preparation

Shampoo is a complex matrix and requires previous treatment before HPLC analyses. For extraction and clean-up, solid phase extraction was chosen, using C18 cartridges. A chromatogram of a commercial shampoo sample after sample preparation (described in Section 2.6) is shown in Fig. 4. No interferences were observed at the retention times of the analytes using the BDD detector.

3.4. Validation

Analytical test method validation is required to ensure that an analytical methodology is accurate, specific, repetitive and robust over the specified range that an analyte will be analyzed.

The method developed was in-house validated using the following performance criteria: linearity and linear range, sensitivity, selectivity, intra-assay and inter-assay precision, detectability and accuracy. The limits of detection and quantitation were not established, due to the fact that the parabens are present in the sample in high concentrations. The linearity, linear range and sensitivity were established through the calibration curve obtained by fortification of blank shampoo samples (without parabens) at seven concentration levels of 0.0125, 0.0250, 0.0625, 0.125, 0.250, 0.375, and 0.500% (w/w). All analyses were performed in triplicate and

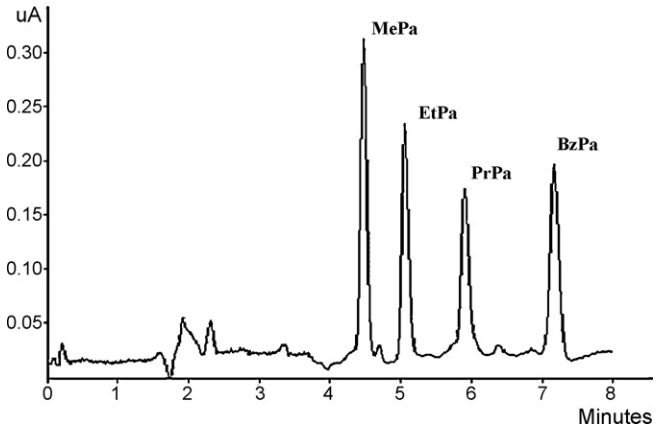

Fig. 4. Chromatogram of 0.0125% (w/w) MePa, EtPa and PrPa on a XTerra™ C8 column (250 mm × 4.6 mm, 5 μm). BzPa was used as internal standard. Mobile phase: 0.025 mol L^{-1} disodium phosphate, pH 7.0:acetonitrile (40:60, v/v) delivered in a flow rate of 1.0 mL min^{-1}. HPLC-ED, using a BDD-working electrode in an amperometric thin layer flow cell in pulse mode: initial potential +1.2 V; medium potential −0.5 V and end potential −2.0 V; pulse repetition time 0.4 s, range 10 μA, polarity positive

BzPa was used as internal standard. The results are shown in Table 1.

Linearity was expressed as the linear correlation coefficient and tested using a pure error lack-of-fit test with simple regression, which was not significant at the 5% level. The sensitivities, expressed as the slope of the analytical curves, were similar for all compounds due to the fact that all have the same oxidizing group in the molecule. The detectability, estimated through the calibration curve, was 0.4 μg mL^{-1}, corresponding to 0.01% (w/w) parabens in the shampoo sample and is adequate to the main purpose of the method. This limit is similar to those obtained with other techniques, such as capillary electrochromatography [10].

Intra- and inter-day assays were performed to verify the precision of the proposed method. These parameters are expressed by the relative standard deviation and presented in Table 1.

The intra-assay precision of the method, lower than 6.3%, was evaluated through the results obtained with the method operating over 1 day under the same conditions, using a blank shampoo sample fortified at two concentration levels, 0.125% and 0.250% (w/w). The inter-assay precision, lower than 9.8%, was determined at the two concentration levels over a 3 days period. These results, although higher than 5%, could be accepted for the purposes of the method. The accuracy was evaluated through recovery tests, by the analysis ($n = 6$) of blank shampoo samples fortified at two levels (0.125% and 0.250%, w/w). The results are shown in Table 1 and were in the range of 93.1–104.4%.

Accuracy was also evaluated by comparing the results obtained through sample analysis using the proposed HPLC-ED method with an earlier in-house validated HPLC-DAD method. Commercial shampoo samples containing parabens were analyzed, in triplicate. The results are shown in Table 2; *t*-tests were carried out in order to check the validity of the data obtained. At the 95% confidence level all *t* values demonstrated no significant differences, using both chromatographic methods. It is worth emphasizing that, in all samples, the presence of MePa and PrPa were declared, and confirmed by our results (Table 2). Ethylparaben was detected in two samples and is also in agreement with the product label.

Cosmetic products containing parabens may contact the skin, hair and scalp, lips, mucosae, axillae and nails, and are used from an occasional to a daily basis. The potential harm of parabens to consumers increases especially when consumption is in large quantities. Recently, parabens in cosmetic products have received keen attention, because the elevated amounts of parabens in topical

Table 1
Validation data for the HPLC-ED method.

Validation parameter	Methylparaben	Ethylparaben	Propylparaben
Linear range (%, w/w)	0.0125–0.500	0.0125–0.500	0.0125–0.500
Linearity (r)	0.9989	0.9997	0.9996
Sensitivity (μA/%, w/w)	3.67	3.42	3.12
Intercept	0.0561	−0.082	−0.018
Detectability (%, w/w)	0.01	0.01	0.01
Intra-day precision (% RSD)			
0.125% (w/w)	4.6	3.2	4.4
0.250% (w/w)	6.9	6.3	2.3
0.500% (w/w)	2.4	2.0	0.4
Inter-day precision (% RSD)			
0.125% (w/w)	4.1	9.8	4.3
0.250% (w/w)	7.2	4.9	2.7
0.500% (w/w)	2.4	1.6	6.7
Accuracy (recovery test), (%)			
0.125% (w/w)	93.1	95.1	96.8
0.250% (w/w)	104.1	104.4	104.3
0.500% (w/w)	93.4	89.3	92.1

Table 2
Average paraben concentrations (%, w/w) in commercial shampoo samples, determined through the HPLC-ED and HPLC-DAD methods. The estimated standard deviation (n = 3) is presented in parentheses.

Sample	Methyparaben (%, w/w)		Ethylparaben (%, w/w)		Propylparaben(%, w/w)	
	HPLC-ED	HPLC-DAD	HPLC-ED	HPLC-DAD	HPLC-ED	HPLC-DAD
1	0.081(±0.005)	0.069 (±0.001)	ND[a]	ND[a]	0.028 (±0.001)	0.038 (±0.001)
2	0.208 (±0.02)	0.167 (±0.01)	0.039 (±0.003)	0.032 (±0.001)	0.032 (±0.003)	0.049 (±0.001)
3	0.067 (±0.003)	0.072 (±0.001)	ND[a]	ND[a]	0.012 (±0.001)	0.011 (±0.001)
4	0.220 (±0.009)	0.181 (±0.001)	ND[a]	ND[a]	0.094 (±0.002)	0.091 (±0.001)
5	0.107 (±0.007)	0.088 (±0.001)	ND[a]	ND[a]	0.077 (±0.005)	0.059 (±0.001)
6	0.025 (±0.009)	0.037 (±0.004)	0.011 (±0.002)	0.009 (±0.001)	0.031 (±0.008)	0.018 (±0.001)

[a] Not detected by either methods studied and not declared in the product label.

products have been shown to induce allergic contact dermatitis [8]. The use of parabens is permitted in cosmetic products as a preservative at a maximum concentration of 0.8% (w/w) and the maximum concentration limit set for any single ester is 0.4% [1,8–11]. The data of Table 2 show that all samples analyzed presented a content of total parabens lower than 0.31% (w/w). Although the values of parabens in these samples are not labeled by the producers, the amounts of parabens determined do not exceed the maximum limit.

4. Conclusions

The results obtained in the present study show that boron-doped diamond is adequate for the quantitation of parabens and suitable to be used in flow cells. The BDD showed adequate response when inserted in a thin layer amperometric detector cell. However, the BDD electrode is not able to differentiate between the parabens and a prior chromatographic separation is required to achieve selectivity.

The main disadvantage of the BDD electrode is possible surface passivation. Therefore, the use of an internal standard is mandatory. In addition, it is important that an efficient sample clean-up is performed prior to introduction of the sample in the HPLC-ED system. Solid phase extraction, using C18 sorbents, is appropriate for this purpose and with this procedure electrode fouling could be reduced. Another important aspect that should be considered is that the elution needs to be carried out under isocratic conditions. Changes in the composition of the mobile phase during the chromatographic run introduce baseline drifts.

The method developed is an alternative method to the HPLC-DAD method and shows adequate validation parameters and is therefore suitable for the determination of parabens in shampoo.

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