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Determination of parabens in cosmetic products using multi-walled carbon nanotubes as solid phase extraction sorbent and corona-charged aerosol detection system

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ABSTRACT

The potential of carbon nanotubes for the solid phase extraction of parabens in cosmetic products and the detection using a corona-charged aerosol detector (C-CAD) is presented in this work. The analytical procedure is based on a conventional solid phase extraction step for which 20 mg of multi-walled carbon nanotubes were packed in a 3-mL commercial SPE cartridge. Methylparaben, ethylparaben, propylparaben and butylparaben were thus isolated and preconcentrated from the pre-treated samples and subsequently separated on a RP-C18 column using acetonitrile:water, 50:50 (v/v) as mobile phase. The analytical signals for the individual parabens were obtained using C-CAD. The experimental variables affecting the extraction procedure and the instrumental detection have been deeply studied. Limits of detection were in the range of 0.5–2.1 mg L^{-1}, while the linear range was extended up to 400 mg L^{-1}. The average precision of the method varied between 3.3–3.8% (repeatability) and 4.3–7.6% (reproducibility). Finally, the optimized procedure was applied to the determination of the target preservatives in a variety of cosmetic products with satisfactory results.

1. Introduction

Parabens are alkyl esters commonly used as preservatives to prevent foods, cosmetics and pharmaceuticals from microbial and fungal attack. These compounds, including methylparaben (MP), ethylparaben (EP), propylparaben (PP) and butylparaben (BP) are often found in combinations of two or more substances in almost all types of cosmetics (e.g. facial make-ups, deodorants, gels, creams or skin lotions) [1,2]. Recent investigations state that the super-scale use of these preservatives in cosmetics can result in potential health risks due to their estrogenic activity, modulating and disrupting the endocrine system. Moreover, their potential contribution to the incidence of breast cancer has been highlighted recently [3–6]. The European Union permits the use of parabens with a maximum concentration for each compound of 0.4% (w/w) and a total maximum concentration of 0.8% (w/w), expressed as p-hydroxybenzoic acid (EU cosmetics directive 76/768/EEC) [7]. Therefore, the simultaneous determination of the most commonly employed parabens in cosmetic products is desirable. Taking the sample complexity into account, highly selective methods are required for this purpose.

Various analytical techniques have been used for the determination of parabens in different matrices, including gas chromatography [8–10], high performance liquid chromatography (HPLC) [11–15], capillary zone electrophoresis [16,17] micellar electrokinetic chromatography (MEKC) [18–20] or ultra performance liquid chromatography [21]. HPLC techniques are more commonly used for parabens determination since gas chromatographic separation requires a prior derivatization of the compounds. In any case, sample treatment steps are mandatory before analyte injection into the chromatographic system [22]. Different sample preparation methods have been proposed for determining parabens in cosmetic samples. Solid phase extraction (SPE) [19,23,24] and solid phase microextraction [25–28] are the commonest alternatives of choice for this determination due to their simplicity and effectiveness of extraction. Besides, these techniques allow high selectivity and sensibility, reducing or eliminating the volume of organic solvent employed.

The application of carbon nanotubes in the analytical field as potential SPE sorbents is gaining importance in the recent years because of their special chemical and physical properties. These nanometric materials have a high hydrophobic surface area and exhibit strong interaction capabilities for various compounds. The described adsorption mechanisms involve the establishment of weak interactions, more precisely, π–π stacking, Van der Waals forces, other hydrophobic interactions and electrostatic forces [29]. This fact facilitates the adsorption of analytes in a selective and

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reproducible manner. As a result, multi-walled carbon nanotubes (MWCNTs) have been used as sorbent material for the determination of a variety of organic compounds in different samples [30–33]. However, the extraction performance of MWCNTs for parabens has not been previously utilized.

Corona-charged aerosol detector (C-CAD) has been recently introduced as a new universal detection system for HPLC [34]. Its performance can be compared with that of others detectors of universal response such as the evaporative light scattering detector (ELSD) [35], refractive index (RI) [36], low-wavelength ultra-violet (UV) [37], and mass-spectrometer [38]. The operating principle of C-CAD is based on the detection of charged particles with a selected range of mobility instead of measuring individual gas-phase ions with different m/z ratio. Consequently, the signal obtained depends primarily on the particle size while, in comparison to UV or RI detectors, individual spectroscopic analyte properties negligibly affect the instrumental response obtained. As well as the ELSD, the response is not dependent on the analyte structure, being only limited by the fact that they can detect compounds provided that they have lower volatility than the mobile phase. C-CAD is characterized by a robust, sensitive, reproducible response and can be afforded at adequate acquisition and maintenance expenses. In addition, it boasts a wide dynamic range, ease of use and has been previously employed for the determination of non- or semivolatile compounds encountered in pharmaceutical, food, consumer product, industrial chemical and life science applications [39–41].

The research study presented in this work is focused on the development of a new application of MWCNTs as sorbent material for parabens extraction, preconcentration and sample clean-up step. Moreover, for the first time the evaluation of the applicability of the C-CAD in this context with a systematic study of the instrumental variables affecting the analytical response has been accomplished. Finally, the developed and optimized procedure for parabens has been applied to the analysis of a series of cosmetic products, demonstrating the feasibility of the novel system for a wide range of matrix complexities.

2. Experimental

2.1. Reagents and samples

All reagents were of analytical grade or better. Acetonitrile (Scharlab, Barcelona, Spain) and Milli-Q ultrapure water (Millipore, Madrid, Spain), were employed as components of the chromatographic mobile phase. Methanol and acetone (Panreac, Barcelona, Spain) were used in the solid phase extraction procedure. Hydrochloric acid, purchased from Panreac, was employed to adjust the pH of samples and aqueous standards.

The analytes (methylparaben, ethylparaben, propylparaben and butylparaben) were obtained from Sigma–Aldrich (Madrid, Spain). Stock standard solutions of each analyte were prepared in methanol at a concentration of 5 g L^{-1} and stored in glass-stoppered bottles in the dark at 4 °C. Working solutions containing all the analytes were prepared by dilution of the stocks in mobile phase or ultrapure water depending on the purpose.

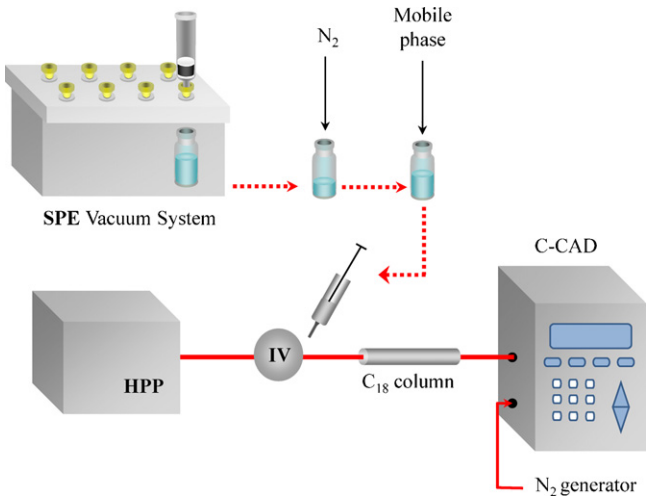

Fig. 1. Schematic description of the analytical procedure developed for parabens determination in cosmetic products: HPP, high pressure pump; IV, high pressure injection valve.

Multi-walled carbon nanotubes, purity 95%, were purchased from Sigma–Aldrich and used as sorbent materials for the preconcentration of the selected analytes. The external and internal diameters were in the range 20–30 and 5–10 nm, respectively, whereas the length varied between 0.5 and 200 μm.

Samples of different types of cosmetic products were purchased from local commercial stores and kept at room temperature until their analysis.

2.2. Apparatus

Analytes detection was carried out using a C-CAD, purchased from ESA Biosciences (Chelmsford, MA, USA). A Mistral 4 nitrogen generator was obtained from Clan Tecnológica (Seville, Spain). Signals were acquired using a HPChem Station software interfaced via an HP 35900C A/D converter, both from Agilent Technologies (Madrid, Spain). The detector settings were kept constant in all experiments using a gas pressure of 37 psi.

The chromatographic separation of the analytes was performed using a Hewlett Packard 1050 high pressure pump (Agilent Technologies) for the mobile phase delivery and a high pressure injection valve (Rheodyne 7725, Cotati, CA, USA) fitted with a 20-μL stainless steel sample loop. Chromatographic separation was carried out at room temperature on a RP-C18 column (250 mm × 4.6 mm) obtained from Análisis vínicos (Tomelloso, Spain). Besides, an ultrasonic bath (J.P. Selecta, Barcelona, Spain) was employed for the mobile phase degasification. The mobile phase composition was acetonitrile:water 50:50 (v/v) and the flow rate was fixed at 0.5 mL min^{-1}.

Solid phase extractions were performed using a VacElut-20 sample-processing station (Scharlab), equipped with a vacuum-control valve and PTFE cartridge adapters (Varian, Barcelona,

Table 1
Figures of merit of the proposed method.

Analyte	Linear range (mg L^{-1})	R	LOD[a] (mg L^{-1})	LOQ[b] (mg L^{-1})	t_r[c] (min)
Methylparaben	5.3–400	0.996	2.1	5.3	8.6
Ethylparaben	4.6–400	0.990	1.5	4.6	11.3
Propylparaben	3.0–400	0.998	0.7	3.0	15.9
Butylparaben	2.0–400	0.997	0.5	2.0	24.0

[a] Limit of detection.
[b] Limit of quantification.
[c] Chromatographic retention time.

Spain). Three milliliters commercial SPE cartridges were packed with an appropriate amount of sorbent using frits to avoid losses of material.

A high speed centrifuge with a microprocessor control (J.P. Selecta) was used in the sample treatment step.

2.3. Procedure

The experimental setup employed is given in Fig. 1. An accurately weighed amount of sample (1.0 g) was properly diluted in ultrapure water (between 1:20 and 1:100, v/v); then, the sample solution was treated with ultrasounds for 30 min and was centrifugated for 15 min. The pH of the supernatant was adjusted to pH 3 using HCl 0.1 M and 1 mL of this liquid phase was subjected to the SPE procedure. This sample treatment facilitates the subsequent extraction process.

The solid phase extractions were performed in laboratory-packed cartridges containing 20 mg of MWCNTs. The cartridges were preconditioned with 5 mL of methanol and equilibrated with 5 mL of Milli-Q water prior to each extraction procedure. Then, 1 mL of the pre-treated sample, obtained as foregoing explained, was passed through the sorbent at a flow rate of 1 mL min^{-1}. Subsequently, a washing step was conducted using 4 mL of Milli-Q water at pH 3 and the cartridges were dried for 2 min. Finally, the analytes were eluted with 2 mL of acetone at a flow rate of 1 mL min^{-1}. The extracts were evaporated to dryness under a nitrogen stream at room temperature and redissolved in 500 μL of the mobile phase before their injection in the chromatographic system. The peak area was used as the analytical signal. The cartridge can be reused for ca. 200 extractions by including a washing step with water between samples analysis.

3. Results and discussion

3.1. Chromatographic separation and detection

The optimization of the chromatographic separation of the target analytes was influenced by the detection system. The response of the C-CAD depends on the amount of organic solvent in the mobile phase as it influences the transport efficiency of the nebulizer and the generated signal. A high organic content in the mobile phase leads to an increase in the transport efficiency of the nebulizer, which results in a greater number of particles reaching the detector chamber and a higher signal. An empirical solution to this problem is the so-called mobile phase gradient compensation [42,43]. Therefore, it would be desirable to establish chromatographic conditions that avoid the variability in the solvent composition without the need of a gradient compensation. Taking this fact into account, the chromatographic separation of parabens was optimized using an isocratic composition of the mobile phase to generate stable baselines, working with fixed mixtures of solvents and constant flow rates during each run. From the different mixtures evaluated, acetonitrile:water (50:50, v/v) was chosen for the analytes separation since it offered the best resolution of the peaks and a stable baseline. The flow rate was maintained at 0.5 mL min^{-1}. Under these chromatographic conditions each run needs about 30 min to be completed. The retention times of the parabens assayed are listed in Table 1. The analytes selected are efficiently separated in 25 min. However, 5 min were added to the run in order to prepare the system for the following injection. It should be mentioned that this time can be shorten for standards to 15 min without affecting peak resolution by reducing the water content in the mobile phase to 25%. Nevertheless, the analysis of samples with a high content of hydrophilic components (i.e. sugars) leads to interferences for the quantification of MP. A typical chromatogram obtained for an aqueous standard containing the four compounds at a concentration of 200 mg L^{-1} is shown in Fig. 2.

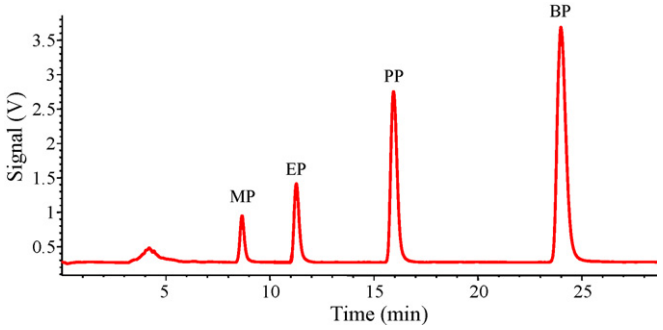

Fig. 2. Chromatogram of a standard solution of parabens at a concentration of 200 mg L^{-1} working at 50 pA.

The principal variables affecting the C-CAD response were the evaporative chamber temperature and the nebulizing gas pressure. Other instrumental parameters to consider were the attenuation of the signal and the final filter applied. The C-CAD employed works at a fixed evaporative chamber temperature of 60 °C in order to evaporate the mobile phase in the column effluent. In comparison with the new generation of C-CAD detectors, the system used in this research does not allow this temperature to be changed. Nevertheless, the results obtained under this working temperature were adequate for the present application. An important instrumental parameter in this type of detectors is the nebulizer gas pressure, which affects the uniformity and size of the droplets formed. Nitrogen is the nebulizer gas recommended for a proper functioning of the detector and the optimum gas pressure is in the range of 35–40 psi. Therefore, an intermediate pressure of 37 psi, provided by a nitrogen gas generator (purity 99.99%), was employed. A critical parameter to consider was the attenuation rate of the signal, which is inversely related to the sensitivity of the detection. The attenuation range of the detector varies from 1 to 500 pA. This parameter was changed taking into account the different concentration levels of the parabens assayed. The highest responses correspond to 1 pA (lower attenuation) while for higher concentrations it was set at 200 pA in order to obtain an adequate instrumental response. The lower attenuation (1 pA) was selected for the first analysis of diluted commercial samples with unknown concentrations in order to detect the presence of analytes using the highest gain of the detector. When some of the analytes' signals were saturated, the attenuation was increased as required. Finally, the detector allows establishing a filter for the application of a smooth of the signal. A medium filter was selected for the present application.

3.2. Optimization of the solid phase extraction procedure

According to the literature, MWCNTs have obvious advantages as SPE sorbents for the isolation and preconcentration of organic compounds. The interaction of carbon nanotubes with the aromatic ring of organic substances through π–π interactions has been previously described [29]. Taking into account the chemical structure of the target analytes (see Fig. 3), MWCNTs were selected as sorbent material for the preconcentration and separation of parabens in cosmetic products. No references dealing with the application of MWCNTs as sorbent in this context have been reported up to date. Therefore, a systematic study of the variables potentially affecting the sorption process was deeply conducted.

The experimental variables evaluated were the following: sample pH, eluent and clean-up reagents, sample volume and dilution, and amount of sorbent. For this study, an aqueous standard solution

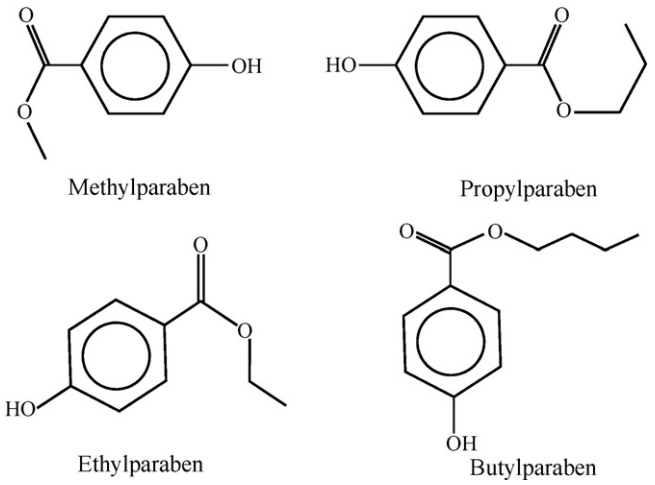

Fig. 3. Molecular structures of the parabens assayed.

with the parabens most commonly employed in cosmetics (MP, EP and PP) at a final concentration of 0.5 μg mL^{-1} was used. After each extraction, the extracts were evaporated to dryness under a nitrogen stream and reconstituted in 500 μL of the mobile phase acetonitrile:water (50:50, v/v) for chromatographic analysis.

3.2.1. Sample pH

According to their chemical structure, the charge of the parabens studied can be affected by the pH of the sample (pK_a values varying from 8.27 and 8.45 for MP and BP, respectively). Therefore, their retention on the sorbent could be influenced by this variable. The sample pH was investigated in the range 2–10 by adding appropriate volumes of HCl 0.1 M or NaOH 0.1 M to the aqueous standards. According the results, the signals remained almost constant from 2 to a pH value of 3. Then, a considerable decrease of the extraction happened when the pH varied between 3 and 7, leading to a less marked reduction of the signal at higher pH. Therefore, pH 3 was selected as the optimum value of this variable. It should be noted that these results are not concordant with the expected behavior when the analytes pK_a values are taken into account, which would lead one to anticipate only a lower interaction of the analytes with the sorbent due to their ionization when their pK_a is reached. A possible interpretation of the data obtained would be that the MWCNTs employed have some type of acid impurities that are in their neutral form at the lower pH values assayed, leading to the maximum hydrophobic interactions with the analytes. This fact is more relevant than the influence of the pK_a of the selected parabens, which can be detected in a lower extent in a basic media.

3.2.2. Eluent and clean-up reagents

Different solvents (acetonitrile, methanol and acetone) were evaluated for their use as eluents of the retained analytes. The worst result was that obtained with acetonitrile, whereas acetone provided quantitative elution of the three parabens assayed and therefore, it was chosen as optimum. Finally, the eluent volume was studied and it was found that no carry over between samples was obtained for 2 mL of acetone. For the clean-up step to be implemented between samples, 4 mL of distilled water were found to be enough for an adequate interference removal and cartridge conditioning.

3.2.3. Sample volume and amount of sorbent

The volume of sample that can be subjected to the solid phase extraction without reaching the breakthrough value is directly related to the sorbent capacity and, consequently, to the quantity of MWCNTs used for the extraction. Moreover, the sorbent amount affects the quantity of analyte that can be retained and the volume of eluent required. The studies conducted demonstrated that 20 mg of MWCNTs allowed a quantitative retention of all the parabens at the concentrations evaluated (50 mg L^{-1}) when 1 mL of the standard solution was passed through the cartridge. When the extraction was applied to cosmetic samples, the chromatographic signals of MP and EP were overlapped by those coming from matrix compounds. In order to reduce this negative effect, the sample was diluted in ultrapure water. A dilution factor of 1:10 (v/v) was enough to minimize this effect. However, higher dilution factors were applied as required in order to adequate the initial concentration of the parabens in the sample to the dynamic calibration range of the method.

The maintenance of the sorbent capacity was checked by the regular extraction of a control standard solution with all the analytes at 50 mg L^{-1}, which also permits to control the reusability of the cartridge. The sorbent was replaced when a variation higher than 10% was obtained for the peak areas.

By including the clean-up step between samples, the cartridge can be reused for ca. 200 extractions with negligible variations on the sorbent capacity.

Table 2
Intra- and interday precisions of the proposed method.

Analyte	Intraday precision (RSD%, n = 5)	Interday precision (RSD%, n = 3)
Methylparaben	3.8	7.0
Ethylparaben	3.7	7.6
Propylparaben	3.6	6.3
Butylparaben	3.3	4.3

3.3. Figures of merit

The figures of merit of the method are summarized in Table 1. The calibration graphs were constructed for six aqueous standards containing the analytes used in the optimization step plus BP since some of the samples to be analyzed contained this compound as indicated in the label. The standards were subjected to the whole procedure under the optimized conditions previously described. The lowest detectable concentrations were obtained using the S/N = 3 ratio. According to the results, the sensitivity of the method increases with the alkyl chain of the analyte, this property being better for BP. This is in accordance with the fact that the response in C-CAD depends on the particle size. The precision (repetitivity and reproducibility) of the method (Table 2), expressed as relative standard deviation, was evaluated for five and three replicates of a working aqueous standard prepared at a low concentration of the calibration curve (15 mg L^{-1}). The values calculated for intraday

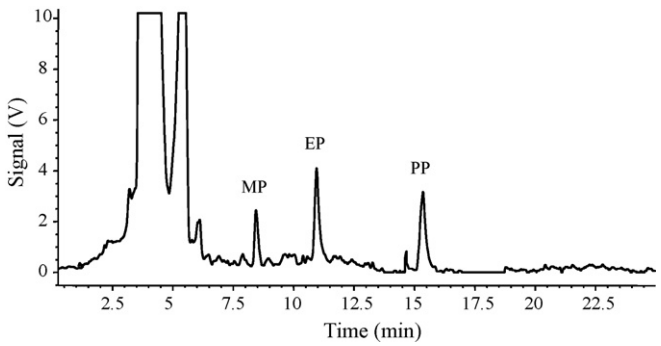

Fig. 4. Exemplary chromatogram obtained for a sample of moisturizing cream with a dilution rate of 1:100 (v/v) working at 50 pA.

Table 3
Determination of parabens in cosmetic products.

Samples	Dilution	Concentration (mg L^{-1})			
		Methylparaben	Ethylparaben	Propylparaben	Butylparaben
Moisturizing cream 1	1:100	1490 ± 45	1150 ± 40	590 ± 20	–
Moisturizing cream 2	1:60	504 ± 19	–	348 ± 15	–
Moisturizing cream 3	1:25	858 ± 29	208 ± 6	125 ± 4	270 ± 9
Antiwrinkle cream	1:60	1476 ± 45	–	616 ± 20	–
Make-up	1:50	1109 ± 35	–	–	–
Lotion	1:50	615 ± 21	320 ± 11[a]	290 ± 10	–
Shampoo	1:50	1210 ± 38	310 ± 10	125 ± 4	75 ± 3
Hands cream	1:20	190 ± 6	154 ± 5	46 ± 2	30 ± 1
After sun	1:20	308 ± 12	–	112 ± 4	–

–, not labeled and non-detected.
[a] Not labeled but found.

Table 4
Recoveries of parabens from different types of cosmetic products (n = 3). 300 mg L^{-1} of each analyte were spiked to the samples.

Sample	Methylparaben		Ethylparaben		Propylparaben		Butylparaben	
	Found ± SD[a]	Recovery (%)	Found ± SD[a] n = 3	Recovery (%)	Found ± SD[a] n = 3	Recovery (%)	Found ± SD[a] n = 3	Recovery (%)
Make-up	1292 ± 50	92 ± 4	244 ± 8	82 ± 3	301 ± 13	100 ± 1	308 ± 15	103 ± 2
Antiwrinkle cream	1563 ± 50	88 ± 1	283 ± 11	94 ± 4	870 ± 30	95 ± 1	288 ± 10	96 ± 2
Moisturizing cream 3	1041 ± 35	90 ± 1	475 ± 23	94 ± 5	418 ± 20	99 ± 2	564 ± 20	99 ± 2
Shampoo	1282 ± 35	85 ± 2	561 ± 26	92 ± 3	428 ± 20	101 ± 3	389 ± 15	104 ± 3

[a] SD, standard deviation.

experiments were lower than 4% in all cases, whereas the interday reproducibility ranged between 3.3% for BP and 7.6% for EP.

3.4. Analysis of samples

A series of samples of cosmetic products of different natures were obtained from local stores and analyzed using the proposed method following the procedure described in Section 2.3. A previous dilution of the samples in ultrapure water was necessary prior to their solid phase extraction. An exemplary chromatogram obtained for the sample "moisturizing cream 1" is depicted in Fig. 4. Since the concentration of the parabens was not specified in the products labels, a standard dilution of 1:10 (v/v) was initially applied to all the samples. A higher dilution ratio was used (up to 1:100, v/v) depending on the analytes concentration and the signals obtained. The maximum dilution rate that was finally applied and the concentration levels found for the parabens are shown in Table 3. The values found ranged from 30 mg L^{-1} for BP to 1490 mg L^{-1} for MP. On the other hand, MP and PP were detected in almost all the samples since they constitute the most commonly used preservatives due to their antimicrobial activity and solubility in water. The analytes were detected in all cases when their presence in the products was labeled. However, EP was found in the lotion sample despite not being specified in the product label.

The carryover was evaluated by analyzing a blank of water after the extraction of standard and samples, leading to no signal in the detector. A washing step was conducted after each extraction in order to assure the SPE cartridge remains clean.

Finally, the recoveries for each analyte from a series of selected samples were evaluated under the optimum extraction conditions. Different types of cosmetic products (make-up, antiwrinkle cream, moisturizing cream and hair gel) were selected for this study in order to spread the range of matrices evaluated. The samples, previously analyzed, were spiked with 300 mg L^{-1} of each analyte and subjected to the whole procedure described in Section 2.3. The final concentrations were obtained using the calibration curves and the relative percentages of recuperation were calculated as the ratio between the concentration of the analyte found after the spiking process and the initial concentration of each analyte in the sample. The results obtained are shown in Table 4. The high recovery values obtained ensure the accuracy of the concentrations found in the non-spiked commercial samples.

3.5. Comparison with other methods

The present method can be compared with other alternatives described for parabens determination in cosmetic products. Table 5 summarizes the main analytical information of the com-

Table 5
Comparison of the proposed method with other developed alternatives for the determination of parabens in cosmetics.

Method	Cosmetic product	LOD	RSD (%)	Recovery (%)	Reference
SDME[a]-GC–MS	Mouthwash solution, gels	0.001–0.015 μg L^{-1}	<12.1	92–105	[8]
SFE[b]/HPLC–MS	Lanoline cream, skin milk	4.7–19.3 μg L^{-1}	<18.6	–	[12]
HPLC-CL[c]	Wash-off cosmetics	1.9–5.3 μg L^{-1}	<3.1	93–106	[13]
HPLC-UV	Foam shampoo	0.02–0.05 mg L^{-1}	<3.2	98–105	[15]
FIA[d]-SPE-MEKC	Gel, lotions, water/oil-based creams	0.07–0.1 mg L^{-1}	<2.3	93–102	[19]
SPE-HPLC-C-CAD	Creams, shampoo make-up, lotions	0.5–2.1 mg L^{-1}	<3.8	90–104	Proposed method

[a] SDME: single drop microextraction.
[b] SFE: supercritical fluid extraction.
[c] CL: chemiluminescence.
[d] FIA: flow injection analysis.

parable methods reported for this type of samples. It can be derived from the data that the proposed system presents similar recovery and repeatability values compared with the majority of the other approaches. On the other hand, the limits of detection achieved are higher. Nevertheless, it should be highlighted that the present method has been optimized for the concentration level at which the target analytes are expected to be found in cosmetic products and, therefore, a better sensitivity is not required. In contrast, the higher selectivity achieved with this alternative, making use of an uncomplicated sample treatment, is of special interest due to the complexity of the matrices. Compared with some of the methods [8,12], the costs of acquisition and maintenance of the system presented in this article are lower. Besides, the complexity of the analytical systems employed [13,19] and sample pretreatment requiring several steps [15,19] of other methods described, can be compared with the ease of operation and functioning of C-CAD and the SPE performance. In addition, a wider range of cosmetic samples with different complexity has been evaluated in the present in comparison with other applications [12,13,15].

4. Conclusions

The experimental work reported in this article has been aimed at the evaluation of the potential of two relatively new analytical tools, carbon nanotubes and C-CAD, in the field of cosmetics. The results obtained, in terms of sensitivity, precision and recovery values have demonstrated its applicability for the determination of parabens in such matrices. Concerning the SPE procedure, it is demonstrated for the first time that MWCNTs can be used as effective SPE material for the extraction of parabens. The π–π interaction established between the analyte and the carbon nanotubes surface simplified the isolation step due to the low retention of potential interferents, leading to a high selectivity and ruggedness of the extraction with clean extracts without chromatographic interferences. Moreover, the low amount of stationary phase and the reusability of the cartridge is a great advantage as it notably reduces the cost of the analysis. As far as the C-CAD is concerned, we have demonstrated its capability for the determination of parabens with very good analytical features without the need of a compensation gradient. The universal response of the detector allowed the determination of the target compounds, providing signals that are dependent on the analytes' particle size. Therefore, it could be stressed that the system described in this work meets the analytical requirements with a simple design that does not necessitate trained personnel, employing instrumentation with an easy functioning and a low cost of acquisition and maintenance. This makes the proposed method a valid alternative for the determination of parabens in cosmetic products.

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