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Review

An overview of sample preparation for the determination of parabens in cosmetics

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ABSTRACT

The controversial and widespread use of parabens in cosmetics makes this group of compounds particularly interesting from an analytical point of view. This article provides an overview on analytical methodology for the determination of parabens in cosmetic products, placing special emphasis on sample preparation. First, we consider simple approaches such as dilution and homogenization or, to a lesser extent, direct analysis. Then, we discuss different extraction techniques used in a vast range of applications. In modern extraction strategies, the following sample pretreatments are of increasing interest and we address them in this review:

(1) new materials for solid-phase extraction;
(2) matrix solid-phase dispersion;
(3) dispersive micro-solid-phase extraction;
(4) solid-phase microextraction;
(5) stir-bar sorptive extraction;
(6) liquid-phase microextraction;
(7) supercritical fluid extraction; and,
(8) pressurized liquid extraction.

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Abbreviations: BP, Butyl-paraben; CAR/PDMS, Carboxen/Polydimethylsiloxane; CE, Capillary electrophoresis; CW/DVB, Carbowax/Divinylbenzene; CZE, Capillary-zone electrophoresis; DART-MS, Direct analysis in real time with mass spectrometry; DLLME, Dispersive liquid-liquid microextraction; D-SPE, Dispersive micro-solid-phase extraction; EP, Ethyl-paraben; FI, Flow injection; FIA-SPE-MEKC, Flow-injection analysis–solid-phase extraction–micellar electrokinetic chromatography; GC, Gas chromatography; GC-FID, Gas chromatography with flame-ionization detection; GC-MS, Gas chromatography with mass spectrometry; HF-LPME, Hollow-fiber liquid-phase microextraction; HPLC-UV, High-performance liquid chromatography with UV detection; IMS, Ion-mobility spectroscopy; LC, Liquid chromatography; LC-MS, Liquid chromatography with mass spectrometry; LC-UV, Liquid chromatography with UV detection; LLE, Liquid-liquid extraction; LOD, Limit of detection; LPME, Liquid-phase microextraction; MWCNT, Multi-walled carbon nanotube; MP, Methyl-paraben; MSPD, Matrix solid-phase dispersion; PA, Polyacrylate; PDMS, Polydimethylsiloxane; PDMS/DVB, Polydimethylsiloxane/Divinylbenzene; PLE, Pressurized liquid extraction; PP, Propyl-paraben; RSD, Relative standard deviation; SBSE, Stir-bar sorptive extraction; SDME, Single-drop microextraction; SFE, Supercritical fluid extraction; SFODME, Solidified floating organic-drop microextraction; SPE, Solid-phase extraction; SPME, Solid-phase microextraction; TLC, Thin-layer chromatography; USAEME, Ultrasound-assisted emulsification microextraction.

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1. Introduction

Parabens are antimicrobials used as preservatives in a wide variety of cosmetics. It is estimated that 75–90% of cosmetics contain parabens at levels typically 0.01–0.3% [1]. These compounds are esters derived from p-hydroxybenzoic acid that prevent fungal and microbial growth, but, in turn, can cause side effects to consumers and organoleptic alterations in the cosmetics [2]. Methyl-paraben (MP), ethyl-paraben (EP), propyl-paraben (PP) and butyl-paraben (BP) are the most common parabens found in cosmetics. Paraben mixtures are usually added to cover a wide antimicrobial spectrum due to their selective activity. Characteristics, such as being odorless and tasteless, and non-decolorizing action, explain their widespread application [3]. Additional information of these compounds and their salts, especially in relation to chemical characteristics and antimicrobial activity, is shown in Table 1.

Notwithstanding the above, the scientific literature indicates possible side effects associated with the use of paraben-containing cosmetics, since these are rapidly absorbed through the skin [5]. In particular, endocrine-disrupting effects have been pointed out. An increase in the paraben chain-length seems to increase estrogenic activity as receptors [6]. In addition, the application of cosmetics containing parabens to individuals with damaged or broken skin can cause sensitization [5]. In certain studies with animals, adverse reproductive effects have been reported [6]. Although not fully proved, a possible relationship between paraben-containing deodorants and breast cancer has also been suggested [7]. Different expert panels have recommended further evaluation in order to clarify to what extent parabens present in cosmetics are harmful [8].

Although parabens are authorized preservatives, legislation restricts their concentration in cosmetics in some cases (Table 2). European Union (EU) and USA legislation allows the use of 4-hydroxybenzoic acid (and its salts and esters) up to 0.4% (as acid) for a single paraben and 0.8% (as acid) for paraben mixtures. The Danish legislation is the most restrictive, with PP and BP banned in cosmetic products for children up to three years old. By contrast, Canada does not restrict the use of parabens in cosmetics.

There is no doubt that legislation lags behind the market. A large amount of paraben-free cosmetics have been marketed in recent years with a very positive response from the consumer. Labeling these products usually claims 0% parabens or paraben-free cosmetics. However, the lack of specific regulation facilitates labeling fraud.

Their controversial and widespread use makes parabens a group of molecules to be controlled from an analytical point of view. Fig. 1 shows the evolution of published works on determination of parabens in comparison with the total number of papers devoted to cosmetic analysis. Nowadays, parabens are the most popular compounds in the analytical control of cosmetics.

Information about some analytical methods published between 1980 and 2006 for paraben determination can be found in the book edited by Salvador and Chisvert [9]. A review by Wang and Liu [10] summarized sample preparation and instrumental techniques used in the determination of different preservatives in cosmetics. In the past year, different reviews related to this topic have been published. Current trends in liquid-liquid extraction (LLE) and solid-liquid extraction applied to cosmetic analysis have been reviewed by Cabaleiro et al. [11]. These authors also reviewed solid-phase extraction (SPE) and solid-phase microextraction (SPME) in cosmetic analysis [12]. Malika et al. [13] reviewed some methods for the identification of MP in cosmetics.

In general, the complexity of cosmetics matrices and their different physical states have led to the development of very different analytical methodologies. Sample dilution with conventional SPE and high-performance liquid chromatography with UV detection (HPLC-UV) or gas chromatography with mass spectrometry (GC-MS) detection are largely used for paraben determination in cosmetics. In recent years, the scientific literature has covered the development of methodologies by implementing different trends in analytical chemistry, and more concretely in analyte extraction [e.g., SPME and liquid-phase microextraction (LPME)].

This review article presents the state-of-the-art of determination of parabens in cosmetics with particular emphasis on the implementation of current techniques for extraction.

2. Official analytical methods for identification and quantification of parabens in cosmetics

Only the EU has established official methods for identification and determination of parabens in cosmetics [14] (Fig. 2). As can be seen, paraben identification is carried out after sample acidification, extraction in acetone, filtration, mixing with water, precipitation of fatty acids in basic medium, extraction with diethyl ether to remove the remaining lipophilic content, extract acidification and thin-layer chromatography (TLC).

With regard to quantitative determination (specified for 2-phenoxyethanol, 1-phenoxypropan-2-ol, MP, EP, PP, BP and benzyl 4-hydroxybenzoate or benzyl-paraben), the cosmetic sample is acidified and extracted with an ethanol/water mixture, vigorously shaken, heated in a water bath, cooled, filtered and subjected to HPLC-UV.

We see that very long, tedious procedures are required for both identification and quantification of parabens. Despite this, 4-hydroxybenzoic acid, MP, EP and benzyl 4-hydroxybenzoate are not separated in the identification procedure, and, in addition, co-elution of many other preservatives and cosmetic additives is possible in the quantification. In view of this, we strongly recommend the development of alternative analytical methods. In particular, sample treatment must be improved in order to enhance rapidity and simplicity and to achieve better analytical characteristics. Table 3 includes the list of different analytical methods published for parabens in cosmetics.

3. Simple strategies for sample preparation

The development of strategies aimed at simplifying sample preparation should be pursued, if not always possible due to the complex nature of the cosmetics matrix. In only one work was the sample directly analyzed for semi-quantitative determination of parabens (MP, EP, PP and BP) [15]. It was carried out by direct analysis in real time with MS (DART-MS). An open-air ionization source allows direct paraben determination in the cosmetics sample. Repeatability is a critical feature in this methodology (up to 40% of relative standard deviations, RSDs). When a simple

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