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Pressurized liquid extraction-gas chromatography-mass spectrometry analysis of fragrance allergens, musks, phthalates and preservatives in baby wipes☆

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ABSTRACT

Baby wipes and wet toilet paper are specific hygiene care daily products used on newborn and children skin. These products may contain complexes mixtures of harmful chemicals. A method based on pressurized liquid extraction (PLE) followed by gas chromatography-mass spectrometry (GC-MS) has been developed for the simultaneous determination of sixty-five chemical compounds (fragrance allergens, preservatives, musks, and phthalates) in wipes and wet toilet paper for children. These compounds are legislated in Europe according Regulation EC No 1223/2009, being twelve of them banned for their use in cosmetics, and one of them, 3-iodo-2-propynyl butylcarbamate (IPBC), is banned in products intended for children under 3 years. Also, propyl-, and butylparaben will be prohibited in leave-on cosmetic products designed for application on the nappy area of children under 3 years from April 2015. PLE is a fast, simple, easily automated technique, which permits to integrate a clean-up step during the extraction process reducing analysis time and stages. The proposed PLE-based procedure was optimized on real non-spiked baby wipe samples by means of experimental design to study the influence on extraction of parameters such as extraction solvent, temperature, extraction time, and sorbent type. Under the selected conditions, the method was validated showing satisfactory linearity, and intra-day, and inter-day precision. Recoveries were between 80–115% for most of the compounds with relative standard deviations (RSD) lower than 15%. Finally, twenty real samples were analyzed. Thirty-six of the target analytes were detected, highlighting the presence of phenoxyethanol in all analyzed samples at high concentration levels (up to 0.8%, 800 $\mu g\,g^{-1}$). Methyl paraben (MeP), and ethyl paraben (EtP) were found in 40-50% of the samples, and the recently banned isobutyl paraben (iBuP) and isopropyl paraben (iPrP), were detected in one and seven samples, respectively, at concentrations between 0.093 and 247 $\mu g\,g^{-1}$. In the case of phthalates, the forbidden phthalates dibutyl phtalate (DBP) and di(2-ethylhexyl)phthalate (DEHP) were also found in thirteen samples at low levels. All the samples contained fragrance allergens in many cases at high levels (up to 2400 $\mu g\,g^{-1}$) and three musks were detected in the samples. Excluding the banned compounds, all samples complied with the concentration limits established by the European Regulation although 25% of them did not fulfill the labeling requirements for fragrance allergens.

1. Introduction

In last years, there is an increasing use of disposable wet tissues due to their commodity; makeup remover, suntan cream, deodorants or moisturizing lotions among others, are offered as wipes. Child specific care products such as baby wipes are usually employed for the cleansing of newborns, babies and children [1–3]. Children under three years are daily exposed to this product (up to sixteen units per day), mainly applied in the sensitive diaper zone including the genital area. This zone has a higher pH and is usually irritated due to the prolonged contact of the skin with urine and feces, which may damage the skin barrier and increase its permeability [4]. The skin barrier development in babies remains incomplete until 12 months of age, and the trans epidermal water loss in an infant is much higher than in an adult [5]. Therefore, skin is more susceptible to microbial and contaminants invasion. It has

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been reported that around 25% of babies develop atopic dermatitis, and 50% show napkin dermatitis [6,7]. In addition, babies and children are most susceptible to exposure to certain chemicals due to the immaturity of their physiological functions. Infants are more vulnerable due to the lack of enzymes to break down and remove toxins, and particularly sensitive to harmful substances that can affect endocrine, immune or nervous systems [8,9].

Fragrance allergens, preservatives, plasticizers, and synthetic musks are common ingredients in personal care products. Fragrances provide nice and attractive scents to make the product more attractive. Preservatives are essential to deliver a safe product to consumers; they are intended to actively prevent microbial growth within cosmetic products. In the case of baby wipes, the wet tissue liquids are aqueous; the storage temperature and the hard surface wipe (commonly cellulose) create an optimal medium for microbial growth. Plasticizers (phthalates and adipates) are mainly employed as fragrance solvents. Synthetic musks and plasticizers do not appear as such in the cosmetics label; musks are present under the terms “fragrance” or “parfum”.

These families of chemicals are regulated in Europe by the Regulation (EC) No 1223/2009 and its subsequent amendments [10]. In this way, 26 fragrances must be monitored, the so-called suspected allergen substances or fragrance allergens. Their presence must be indicated in the list of ingredients when their concentrations exceed 0.01% for rinse-off products, and 0.001% for leave-on products. One of these fragrances, lyral®, was recently proposed to be transferred from Annex III (list of substances allowed in cosmetics with restrictions) to Annex II (list of substances prohibited in cosmetic products).

Parabens (esters of p-hydroxybenzoic acid) are the preservatives most frequently used due to their broad antimicrobial spectrum and low cost. It is estimated that 75–90% of cosmetics contain parabens at levels between 0.01 and 0.3% [11]. Their maximum permitted concentration is 0.4% for a single ester and 0.8% for mixture of esters. Isopropyl-, isobutyl-, phenyl-, benzyl-, and pentylparaben have been recently banned for their use in cosmetics [10], and ethyl-, methyl-, propyl- and butylparaben are categorized as potential endocrine disrupters. In addition, propyl- and butylparaben have been banned in Denmark in products for children under 3 years [12]; they will be banned in all Europe from April 2015 for their use in the diaper area for children below 3 years, and their maximum permitted concentration in other cosmetic products will be 0.14% (instead 0.8%). Phenoxyethanol is one of the most commonly used preservatives and its maximum permitted concentration is 1%. The France National Agency of Security of Medicaments (ANSM) has recently proposed to avoid the use of phenoxyethanol in products intended for children under 3 years, and to reduce the maximum permitted concentration to 0.4% in other personal care products [13]. Maximum permitted concentration for triclosan, was recently decreased to 0.2–0.3% in several products. 3-Iodo-2-propynyl butylcarbamate (IPBC) is banned in products for children under 3 years, except in bath products, shower gels and shampoos (0.02%); for leave-on products its maximum permitted concentration is 0.01%. The bromine-containing preservative bronidox can also be present in personal care products at a maximum concentration of 0.1%. The antioxidants butylated hydroxyanisole (BHA) and butylated hydroxytoluene (BHT) can be used without restrictions.

Concerning synthetic musks and phthalates, European legislation on cosmetics banned the use of musk ambrette, moskene and tibetene since 1995 due to their bioaccumulative properties. Other musks (phantolide, tonalide and ketone) are allowed with restrictions. Diethyl phthalate (DEP) is widely used in personal care products; however, the European Commission on Endocrine Disruption has listed DEP as a priority substance. Other six phthalates: dibutyl phtalate (DBP), dimethoxyethyl phthalate (DMEP), diisopentyl phthalate (DIPP), dipentyl phthalate (DPP), benzyl butyl phthalate (BBP) and di(2-ethylhexyl)phthalate (DEHP) have been linked to endocrine disruption and they are forbidden in cosmetics and personal care products.

In last years, some efforts have been made to determine all these target families of cosmetics ingredients, and several analytical methods based in traditionally procedures (liquid–liquid, and solid–liquid extractions), and current sample preparation (stir-bar sorptive extraction, matrix-solid phase dispersion, or pressurized liquid extraction, among others) have been proposed [14–19]. Nevertheless, there is a lack of studies devoted to the simultaneous determination of several families of cosmetic ingredients, and there are not specific analytical studies for this particular cosmetic product: the baby wipes. Most literature only includes aspects related with allergies [20–22] and only two studies include the determination of a reduced number of parabens [23,24]. Nevertheless, the analytical control of this product is essential to guarantee product safety for babies and children. Pressurized liquid extraction (PLE) is a very suitable technique to extract cosmetic ingredients, being analytes efficiently extracted from the samples at high pressure, minimizing sample preparation time [19,25,26].

The aim of this study is the development of a PLE and gas chromatography-mass spectrometry (GC-MS) method for the rapid (25 min) simultaneous determination of sixty-five chemicals belonging to four families of cosmetic ingredients in baby wipes and wet toilet paper.

2. Experimental

2.1. Chemicals, materials and samples

The studied compounds, their purity, suppliers, CAS numbers, retention time and quantification and identification ions are summarized in Table 1. Also, European legislation restrictions are included. Deuterated methyl-4-hydroxybenzoate-2,3,5,6-d_4 (MeP_d_4; 98atom% D), benzyl_d_7 alcohol (98atom% D) and bis(2-ethylhexyl)phthalate-3,4,5,6-d_4 (DEHP_d4; 98atom% D) used as surrogate standard, were obtained from C/D/N Isotopes (Quebec, Canada), Aldrich (St. Louis, MO, USA), and Fluka Chemie GmbH (Steinheim, Germany), respectively.

Acetone, ethyl acetate, n-hexane, methanol and acetonitrile were provided by Sigma–Aldrich Chemie GmbH (Steinheim, Germany). Sand (200–300 μm mesh particle size) was provided by Scharlau (Barcelona, Spain). Florisil (60–100 mesh) was purchased from Supelco Analytical (Bellefonte, PA, USA) and anhydrous sodium sulphate (99%) from Panreac (Barcelona, Spain).

Individual stock solutions were prepared in acetone, isooctane or methanol. Further dilutions and mixtures were prepared in acetone or ethyl acetate. All solutions were stored in amber glass vials at −20 °C. All solvents and reagents were of analytical grade.

Metallic, and glass material; sorbents (Florisil and sodium sulphate anhydrous) were baked at 230 °C for 12 h before use to eliminate possible phthalate contamination. All materials were allowed to cool down wrapped with aluminum foil and Florisil and sodium sulphate anhydrous in desiccator.

Baby wipes and wet toilet paper samples intended for children under 3 years of age from national and international brands were obtained from local sources. The samples were kept in their original containers at room temperature, until their analysis.

2.2. PLE procedure

Extractions were performed on an ASE 150 (Dionex, Co., Sunnyvale, CA, USA), equipped with 10 mL stainless steel cells and 60 mL collection vials. Two cellulose filters (Dionex, 27 mm) were