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Review

Analytical methods for the determination of personal care products in human samples: An overview

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ABSTRACT

Personal care products (PCPs) are organic chemicals widely used in everyday human life. Nowadays, preservatives, UV-filters, antimicrobials and musk fragrances are widely used PCPs. Different studies have shown that some of these compounds can cause adverse health effects, such as genotoxicity, which could even lead to mutagenic or carcinogenic effects, or estrogenicity because of their endocrine disruption activity. Due to the absence of official monitoring protocols, there is an increasing demand of analytical methods that allow the determination of those compounds in human samples in order to obtain more information regarding their behavior and fate in the human body. The complexity of the biological matrices and the low concentration levels of these compounds make necessary the use of advanced sample treatment procedures that afford both, sample clean-up, to remove potentially interfering matrix components, as well as the concentration of analytes. In the present work, a review of the more recent analytical methods published in the scientific literature for the determination of PCPs in human fluids and tissue samples, is presented. The work focused on sample preparation and the analytical techniques employed.

Contents

1. Introduction

Personal care products (PCPs) comprise different groups of compounds that are currently used as additives in different common products such as cosmetic, household, food or pharmaceutical

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products, among others. Considerable amounts of PCPs are used in everyday human actions, so they are produced in large quantities (thousands of tons per year). Although these compounds are used in some products intended for direct ingestion, the main route of exposure is the absorption through the skin, being further metabolized and eventually bioaccumulated and/or excreted [1–3]. This dermal absorption may result in adverse health effects as dermatitis but also in more serious effects, such as mutagenic, carcinogenic and estrogenic activity [4–7]. Because of their adverse effects on human health and their potential bioaccumulation, PCPs are regarded as emerging organic contaminants [8]. The development of accurate methods for simultaneous determination of more than one group of these contaminants and their degradation products, which in some cases are more harmful that the parents compounds, in human fluids (urine, plasma, breast milk or semen) or tissues (adipose tissue, placenta), is consequently of major interest. As a result of this growing need for analytical methodologies, in recent years there has been a notable increase in the publication of validated analytical methods concerning to the determination of different PCPs in human samples.

Regarding experimental issues, due to the complexity of the biological matrices and the low concentration levels of these compounds in samples, certainly it is of essential importance the optimization of new sample treatment procedures. In this way, a sample clean-up to remove the interference of matrix components in the analysis and stages for concentration of analytes, are both required to achieve a selective and sensitive determination of PCPs in human samples. Although the most widely analyzed matrix is urine, other more complex samples, such as placental tissue, have also been analyzed [9–11].

The validation of single methods for multiresidue analysis of different families of those compounds is convenient, since it would reduce the overall analysis time, field sampling and total costs. Moreover, comprehensive information about multiple classes of PCPs is required for risk assessment studies, since chemicals may interact to yield synergic toxicity effects on exposed organisms [12].

In this context, the aim of the present review is to provide a comprehensive overview of the recent developments related to the determination of PCPs in human fluids and tissues, with special emphasis on sample preparation and analytical techniques as well as the achieved detection limits (LODs).

2. Personal care products

The PCPs selected for review in the present work belong to four different chemical families: preservatives; antiseptics/disinfectants; benzophenone UV-filters and fragrances. These compounds were selected based on production/usage, toxicity and potential hormonal activity.

2.1. Preservatives

A preservative is a substance that is added to final products such as personal hygiene products, foods and beverages, pharmaceuticals, wood, biological material, etc., to prevent decomposition by microbial growth or by undesirable chemical changes. Parabens (PBs), the alkyl esters of *p*-hydroxybenzoic acid, are widely used for this purpose, especially against mold and yeast. Methylparaben (MPB), ethylparaben (EPB), propylparaben (PPB), butylparaben (BPB) and benzylparaben (BzPB) are the most commonly used compounds, and individually or in combination, they are used in over 13,200 different commercial formulations [13]. The widespread use of parabens arises from their low toxicity, broad inertness, worldwide regulatory acceptance and low cost. However, nowadays there is an increasing trend to avoid using parabens because of growing evidence that they act as endocrine disrupters [14,15].

2.2. Antiseptics/disinfectants

Antiseptics are antimicrobial substances that are applied to living tissue/skin to reduce infections, sepsis or putrefaction. Antiseptics are generally distinguished from disinfectants, which destroy microorganisms found on non-living objects. Because of their properties, antiseptics and disinfectants are widely used in PCPs, thus, they are common ingredients in soaps and cosmetics. Triclosan (TCS) and triclocarban (TCC) are the most commonly used. In Europe about 350 t of TCS are produced annually for commercial applications [16]. Nowadays, concerns have been raised about them because of their pronounced microbial and algal toxicity, and their potential for fostering antimicrobial resistance [17,18].

2.3. Organic UV-filters

Organic UV-filters are often used to protect skin against UV radiation damage. They are constituents of many daily products such as skin creams, body lotions, hair sprays, hair dyes, shampoos and sunscreen. The European Union (EU) Regulation 1223/2009 – Cosmetics Regulation – provides a robust, internationally recognized regime, which reinforces product safety. It stipulates the compounds that are able to be used as UV-filters in cosmetics and their maximum concentrations [19]. The family of benzophenones (BPs) is one of the most frequently used groups of UV-filters. BPs consists of 12 main compounds, called from benzophenone-1 (BP-1) to benzophenone-12 (BP-12), as well as, other less known as 2-hydroxybenzophenone (2-OH-BP), 3-hydroxybenzophenone (3-OH-BP) and 4-hydroxybenzophenone (4-OH-BP). Other important families of UV-filters widely used are *p*-aminobenzoic acid and its derivatives, camphor derivatives, salicylates, methoxycinnamates and benzimidazoles. Despite their widespread use, there is increased concern about some of these compounds because of their possible estrogenic activity [20,21]. Because most of these compounds have been carefully studied in a recent review paper published by Chisvert et al. [22], the majority of them have not been studied in the present review. However, BPs are included since the cited review only develops the determination of benzophenone 3 and 4 as target compounds in biological fluids and it has been estimated that it is important to complete and expand the valuable information provided.

2.4. Musk fragrances

Synthetic musk fragrances (SMs) have been widely used to replace the natural ones and they can be found in a large amount of manufactured products such as laundry detergents, softeners, soaps and cosmetics. The main groups of SMs are nitro and polycyclic musk compounds. The most commonly used nitro musks are musk xylene (MX) and musk ketone (MK) whereas musk ambrette (MA), musk moskene (MM) and musk tibetene (MT) are less frequently used [23]. The use of nitro musks is being limited due to their environmental persistence and potential toxicity to aquatic environments [24]. Polycyclic musks are currently used in higher quantities than nitro musks being celestolide (ADBI), galaxolide (HHCB) and toxalide (AHTN) the most commonly used and traseloide (ATII), phantolide (AHMI) and cashmeran (DPMI) less usual. However, some polyciclic musks are being studied because of they are suspected to act as selective estrogen receptor modulators [24].