GC-MS analytical methods for the determination of personal-care products in water matrices

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This article discusses the more recent methods combining gas chromatography and mass spectrometry (GC-MS) for analysis of personal-care products (PCPs) in water matrices. We describe different procedures for sample extraction and preparation as well as different instrumental methods commonly used for these compounds. GC-MS and GC-tandem MS (GC-MS^2), which are complementary to liquid chromatography combined with MS (LC-MS), allow identification and quantification of PCPs belonging to different classes with the sensitivity and the selectivity necessary for environmental monitoring. The compounds investigated include fragrances (e.g., nitro and polycyclic musks), antimicrobial compounds (e.g., triclosan), ultraviolet blockers (e.g., methylbenzylidene camphor), antioxidants and preservatives (e.g., phenols and p-hydroxybenzoic acid (parabens)) and insect repellents (e.g., N,N-diethyl-m-toluamide (DEET)). We critically review data in the literature by focusing attention on analytical methods devoted to simultaneous detection and quantification of structurally diverse pharmaceuticals and PCPs.

Keywords: Antimicrobial; Antioxidant; Emerging contaminant; Gas chromatography; GC-MS; Insect repellent; Mass spectrometry; Nitro musk; PCP; Personal-care product

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1. Introduction

Personal-care products (PCPs) are synthetic organic chemicals derived from usage by individuals in soaps, lotions, toothpaste, cosmetics and other PCPs. Together with various pharmaceuticals, they constitute the class of pharmaceuticals and PCPs (PPCPs) that form a wide variety of important ''unrecognized'' or ''emerging'' pollutants in everyday urban activities [1–4]. Following the precautionary principle, the EU Water Framework Directive has identified some PPCPs as future emerging priority candidates for monitoring and regulation [5,6].

The principal pathway by which PPCPs enter the environment is disposal in urban receiving waters from individual households, after showering and bathing. A variety of PPCPs have been detected everywhere at the nL-concentration level in effluents of wastewater-treatment plants (WWTPs), since conventional water-treatment processes do not seem to be sufficient to remove PPCPs from sewage water (30–90% efficiency) [2,3,7–12].

The occurrence of PPCPs in municipal sewage effluent and other environmental samples could negatively impact the health of the ecosystem and the health of humans, due to persistent, long-term chronic exposure of aquatic organisms to concentrations of PPCPs [1,2]. Moreover, there is some evidence of potential interactive effects of PPCPs, so that low doses may lead to cumulative stress and synergic toxicity effects in exposed organisms [1,2,13]. Some PCPs (e.g., ultraviolet (UV) screens, insect repellents (e.g., N,N-diethyl-m-toluamide (DEET)), p-hydroxybenzoic acid (parabens), and some synthetic musk fragrances) have been suspected endocrine-disrupting compounds (EDCs) (i.e. compounds that can mimic the natural hormones of animals) [1,9,11,12,14,15].

The issue of emerging contaminants is closely related to analytical capabilities of monitoring their occurrence in the various environmental compartments. With the development of sophisticated and sensitive analytical procedures – more efficient extraction techniques and better detectors – more and more PPCPs can be detected at trace levels in the environment [1,16]. Consequently, a number of new or previously ignored and/or unrecognized contaminants have been brought under scrutiny.

There is therefore the need for further improvements to develop quick and sensitive analytical procedures, in particular in two directions:

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1. high sensitivity at trace levels (up to ng/L); and,
2. versatility in simultaneous screening for a wide variety of compounds with large differences in physicochemical properties (e.g., log K_{ow}, water solubility, pK_a, M_w).

A single method for the analysis of different classes of target analytes would be convenient, since it would reduce the overall analysis time, field sampling and costs. Moreover, comprehensive information about multiple classes of PPCPs coinciding in an environmental sample is required for contaminant-monitoring planning and risk-assessment studies, since chemicals may interact to yield synergic toxicity effects on exposed organisms [1,13]. Even if most of the available methods are specifically devoted to a few contaminants or a single PPCP class, some multi-residue methods have been developed for determining organic pollutants in aqueous environment.

This article discusses the more recent methods combining gas chromatography and mass spectrometry (GC-MS) for the analysis of several GC-amenable compounds (e.g., potential PCPs in various water matrices); in particular, we critically review data in the literature by focusing attention on analytical methods for the simultaneous detection and quantification of structurally diverse PPCPs as representative molecular markers of water pollution.

2. PCP classes

PCP compounds in this article belong to the following chemical classes:

- fragrances (e.g., nitro and polycyclic musks);
- antimicrobial compounds (e.g., triclosan);
- UV blockers (e.g., methylbenzylidene camphor);
- antioxidants and preservatives (e.g., phenols and parabens); and,
- insect repellents (e.g., DEET).

These compounds were selected from the large number of chemical possibilities based upon usage, toxicity, potential hormonal activity, and persistence in the environment.

2.1. Synthetic musk fragrances

Two types of synthetic musk fragrances are widely used in Europe and North America: polycyclic and nitro musks (PNMs). They can be found in almost all consumer products (e.g., perfumes, deodorants, cosmetics and soaps) and are released into wastewater after use of the consumer products, so they are present in the environment due to wastewater discharges and land application of biosolids [1,2,17–20].

2.2. Antimicrobial compounds

Triclosan (5-chloro-2-[2,4-dichloro-phenoxy]-phenol, TCS) is one of the antimicrobial compounds used most in many consumer products (e.g., toilet soaps, toothpaste, detergents, deodorants, and sports clothing). It has been detected in surface waters and sewage plants (at a concentration level ≈1 μg/L) in various countries, and it has been found to be acutely and chronically toxic to aquatic organisms. A TCS derivative, methyl-triclosan (M-TCS), is a more lipophilic and environmentally persistent metabolite than the parent compound [1,7,9,21,22].

2.3. Sunscreen agents

Sunscreen agents are increasingly added (in relative amounts of 0.1–10%) to cosmetics and lotions as protection against harmful UV radiation. Though the high hydrophobicity of many of these compounds ($\log K_{ow} = 5 - 8$) indicates the potential for bioaccumulation, relatively little is known about the occurrence and the fate of UV filters in the environment. Several of these compounds show estrogenic activity [23–25].

2.4. Insect repellents

DEET and the more recent Bayrepel (1-piperidinecarboxylic acid, 2-(2-hydroxyethyl), 1-methylpropyl ester) are the insect repellents used most [11,26]. They have been widely detected in aquatic systems; from limited toxicity data, it can be inferred that DEET is slightly toxic to aquatic invertebrates, fish, and birds [9,14].

2.5. Preservatives

Parabens are the most common preservatives used in PCPs, pharmaceuticals and food products. Methylparaben and propylparaben are the most widely used and are normally used together due to their synergistic preservative effects [1,15,27]. Parabens exhibit estrogenic behavior [27].

3. Analytical methods

To analyze complex mixtures, such as water samples, a pretreatment procedure is required to provide a sample fraction enriched with all the target analytes and as free as possible from other matrix components [16]. Fig. 1 shows the general analytical procedure for analysis of PCPs in aqueous samples.

A variety of sample preparation methods is available for extraction and concentration of contaminants in water: liquid–liquid extraction (LLE); solid-phase extraction (SPE); solid-phase microextraction (SPME); and, semi-permeable membrane devices (SPMDs) [16,28].

Detection and quantification are based on GC paired with MS (Pathway A, Fig. 1), high-performance liquid chromatography (HPLC) coupled with MS, immunoassays, or a combination of techniques [16].

Choosing between GC and HPLC is generally based on the physiochemical qualities of the target analyte. HPLC-MS is usually used to determine more polar and less