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Development of a solid phase microextraction gas chromatography tandem mass spectrometry methodology for the analysis of sixty personal care products in hydroalcoholic gels – hand sanitizers – in the context of COVID-19 pandemic

Lua Vazquez [a], Maria Celeiro [a], Ana Castiñeira-Landeira [a], Thierry Dagnac [b], Maria Llompart [a, *]

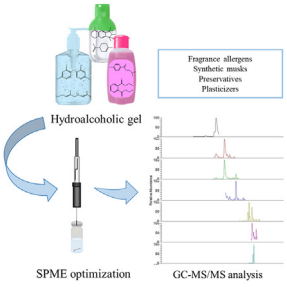
[a] CRETUS, Department of Analytical Chemistry, Nutrition and Food Science, Universidade de Santiago de Compostela, E-15782, Santiago de Compostela, Spain

[b] Galician Agency for Food Quality - Agronomic Research Centre (AGACAL-CIAM) – Unit of Organic Contaminants, Apartado 10, E-15080, A Coruña, Spain

HIGHLIGHTS

- SPME-GC-MS/MS is proposed to analyze 60 personal care products in hydroalcoholic gels
- Target compounds include fragrance allergens, musks, preservatives and plasticizers
- The most critical parameters affecting SPME were optimized by experimental design
- The green, simple and fast method demonstrated suitability and high throughput
- The analysis of real hand sanitizers revealed a high number of target compounds

GRAPHICAL ABSTRACT



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ABSTRACT

Because of the coronavirus pandemic, hydroalcoholic gels have become essential products to prevent the spread of COVID-19. This research aims to develop a simple, fast and sustainable microextraction methodology followed by gas chromatography tandem mass spectrometry (GC-MS/MS) to analyze simultaneously 60 personal care products (PCPs) including fragrances allergens, synthetic musks, preservatives and plasticizers in hand sanitizers. Micro-matrix-solid-phase dispersion (μMSPD) and solid-phase microextraction (SPME) were compared with the aim of obtaining high sensitivity and sample throughput. SPME demonstrated higher efficiency being selected as sample treatment. Different dilutions of the sample in ultrapure water were assessed to achieve high sensitivity but, at the same time, to avoid or minimize matrix effect. The most critical parameters affecting SPME (fibre coating, extraction mode and temperature) were optimized by design of experiments (DOE). The method was successfully validated in terms of linearity, precision and accuracy, obtaining recovery values between 80 and 112% for most compounds with relative standard deviation (RSD) values lower than 10%. External calibration using standards prepared in ultrapure water demonstrated suitability due to the absence of matrix effect.

* Corresponding author. CRETUS, Department of Analytical Chemistry, Nutrition and Food Science, Faculty of Chemistry, University of Santiago de Compostela, E-15782, Santiago de Compostela, Spain.
E-mail address: maria.llompart@usc.es (M. Llompart).

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Experimental design
Fragrance allergens

Finally, the simple, fast and high throughput method was applied to the analysis of real hydroalcoholic gel samples. Among the 60 target compounds, 39 of them were found, highlighting the high number of fragrance allergens, at concentrations ranging between 0.01 and 217 μg g^{-1}. Most of the samples were not correctly labelled attending cosmetic Regulation (EU) No 1223/2009, and none of them followed the World Health Organization (WHO) recommendation for hand sanitizers formulation.

1. Introduction

Hydroalcoholic gels have become essential products, being one of the basic tools to prevent and mitigate transmission of COVID-19 [1,2]. The World Health Organization (WHO) published a protocol to homogenise the hydroalcoholic gel formulation and fabrication, assuring their antimicrobial properties. In this context two aqueous formulations were established, containing: (i) ethanol, hydrogen peroxide, and glycerol and (ii) isopropyl alcohol, hydrogen peroxide, and glycerol [3]. This protocol strongly recommended that no ingredients other than those specified above be added and especially fragrances because of the risk of allergic reactions. Attending the classification of these daily consumer products, if the main purpose of the hydroalcoholic gel is cleaning or cleansing the skin they are considered cosmetics by the EU [4].

The world increasing consumer's demand for cosmetics and personal daily care products imply rigorous controls to assure their safety. All cosmetics products marketed on the European Union must comply with the Regulation (EU) No 1223/2009 [4] and this compliance must be analytically verifiable. Fragrances, synthetic musks, preservatives, antioxidants, or plasticizers are among the compounds more frequently found in cosmetic formulations [5–7].

Cosmetics analysis is a challenge task due to the complexity of the samples formed by a high number of chemical substances, from highly lipophilic to moderately polar, exhibiting basic, acidic, or neutral properties, in a wide range of concentrations from trace levels to thousands of μg g^{-1}. For this reason, a previous sample pre-treatment before analytical determination is required. Solid-liquid extraction (SLE) and liquid–liquid extraction (LLE), have been the most employed procedures for cosmetics analysis. However, multiple extraction steps and considerable organic solvent volumes are often required to obtain an optimum extraction yield. Other drawback is that further steps such as centrifugation, concentration, evaporation and reconstitution or solid-phase extraction (SPE) clean-up are required after extraction [6,8,9]. The analytical determination that is usually accomplished by gas chromatography (GC) or liquid chromatography (LC), depending on the chemical nature of the target analytes. The combination with mass spectrometry (MS) or tandem mass spectrometry (MS/MS) detection became the most suitable option, improving analytical selectivity and sensitivity [9,10]. In last years, green analytical chemistry (GAC) principles have been increasingly implemented for cosmetics analysis through the miniaturization of classical extraction procedures, as well as the substitution of hazardous chemicals and solvents by environmentally friendly alternatives, with the main objective of improving the environmental friendliness without compromising method performance [11,12]. In this way, the use of ultrasound-assisted extraction (UAE), pressurized liquid extraction (PLE) or micro-matrix solid-phase dispersion (μMSPD) has been successfully proposed [8,9]. However, most of the methods have been focused on the determination of individual compounds or a small number of compounds belonging to the same family [6,8,13–15] and only few of them, mainly based on μMSPD, include multianalyte determination [16,17].

Solid-phase microextraction (SPME) is a well-established green solvent-free extraction technique with a large number of applications in different fields such as food, forensic, biomedical, and the environment [18]. The combination of SPME-GC-MS results in a valuable analytical tool. Despite this, a low number of applications for cosmetics analysis are reported, being all of them focused on the determination of few compounds from the same families. SPME has been applied to determine allowed ingredients such as preservatives or fragrances, as well as forbidden substances such as nitrosamines or formaldehyde in cosmetics [19–23]. However, to the best of our knowledge, it has never been applied to simultaneously determine multianalytes from different families in cosmetics.

The main goal of this work is the development of a simple, green, miniaturized, high throughput and easy to implement in worldwide laboratories methodology based on SPME-GC-MS/MS to simultaneously determine a high number of compounds including fragrance allergens (23), synthetic musks (11), preservatives (10) and plasticizers (16) in hydroalcoholic gels. The control of these products is essential since they are massively employed several times every day for many people all around the world. The main experimental parameters affecting SPME have been optimized by experiments design to obtain the high extraction efficiency for the 60 target analytes. Finally, the validated SPME-GC-MS/MS methodology was applied to real hand sanitizers samples demonstrating its suitability. This methodology can be easily implemented in any routine laboratory and automated using a SPME autosampler. Target compounds were quantified in the real samples and the compliance with the applicable legislation, as well as WHO recommendations were discussed.

2. Materials and methods

2.1. Chemicals, reagents and materials

The 60 target compounds (23 fragrance allergens, 11 synthetic musks, 10 preservatives and 16 plasticizers), their CAS number, the retention time, the molecular mass and the MS/MS transitions are depicted in Table S1. Methanol, ultrapure water MS grade and ethyl acetate were supplied by Scharlab (Barcelona, Spain) and acetone by Sigma Aldrich Chemie GmbH (Steinheim, Germany). Individual stock solutions were prepared in methanol and further dilutions and mixtures in acetone (spike solutions). All solutions were stored in amber glass vials and protected from light at −20 °C. All solvents and reagents were of analytical grade.

Commercial 65 μm polydimethylsiloxane/divinylbenzene (PDMS/DVB), 50/30 μm divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS) and 85 μm polyacrylate (PA) fibres and manual SPME holders were obtained from Supelco (Bellefonte, PA, USA). Prior the first use, the fibres were conditioned as recommended by the manufacturer, inserting them in the GC injector under helium flow at 250 °C (PDMS/DVB), 270 °C (DVB/CAR/PDMS) and 280 °C (PA) for 30 min.