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Development of a HS-SPME/GC–MS method for the analysis of volatile organic compounds from fabrics for forensic reconstruction applications

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ABSTRACT

An analytical method for the determination of trace amounts of volatile organic compounds (VOCs) relevant to the cosmetics industry was optimised, validated and employed for the analysis of commercial perfumes. The method used a combination of headspace solid phase microextraction (HS-SPME) and gas chromatography–mass spectrometry (GC–MS). In addition to fibre type, three different HS-SPME extraction conditions were investigated simultaneously, namely incubation time, extraction time and extraction temperature, using a central composite design in order to determine the optimal conditions for the extraction of VOCs of interest. The main figures of merit of the proposed method (calibration range, limits of detection and quantification, trueness and precision) were evaluated for six different VOCs in both natural and synthetic fibres in order to validate it and verify its capability for the proposed application. The validated method was applied for the analysis of traces of commercial perfumes from fabrics, and the VOCs of interest were successfully quantified. This simple, highly sensitive, and robust method has the potential to represent a powerful approach for forensic reconstructions where perfumes have transferred between individuals, such as during assaults and sexual assaults.

1. Introduction

The interest in the detection and quantification of both natural and synthetic volatile organic compounds (VOCs) has been increasing in the last few decades across various economic and scientific sectors, including the food industry [1,2], the perfume and cosmetic industry [3,4], the environmental sector [5,6], and forensic sciences [7,8]. In the forensic field, the focus has been mainly on the analysis of VOCs emanated by body odour [9–11], human remains [12–14], animal remains [15,16], explosives [17,18], and drugs [19,20].

Despite the wide popularity of perfumes and fragrances, the analysis of VOCs from cosmetic products for forensic applications has been limited. Clothing recovered from a crime scene, such as the clothing of a sexual assault victim, can be analysed for traces of fragrance VOCs. Trace material that has transferred can offer valuable information in forensic reconstruction to help identify contacts between objects, people, or locations [21]. Studies such as those by Scott et al. [22] and Bull et al. [23] have provided data that can begin to provide an empirical evidence base to understand the dynamics of various trace particulates, such as diatoms and pollen grains, in terms of how they can transfer and persist on clothing under forensic conditions. Despite the popularity of fragrances in modern societies, analysis of fragrance VOCs from clothing is not currently used in forensic analysis, but it could potentially be a useful tool to assess the likelihood of a contact between individuals.

In a proof of concept study evaluating the potential value of VOCs from fragrances to act as a form of trace evidence, Gherghel et al. [24] investigated the transfer dynamics of fragrance between fabrics by using gas chromatography–mass spectrometry (GC–MS) to analyse methanol extracts of fabrics that had been in contact with fragranced fabrics under two different time variables. This

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previous study showed that both the period of time that two cotton swatches are in contact for, and the period of time that a perfume is left to dry prior to transfer, affect the amount of fragrance recovered from the recipient fabric. However, the authors highlighted the need for further investigation into methods for extracting fragrances from fabrics to overcome instrumental sensitivity. As a result, the current paper seeks to improve the extraction of traces of VOCs specific to the perfume industry from fabrics.

Various techniques have been applied for the extraction of VOCs from a diverse range of matrices, such as plants [25,26], foods [27,28], and soils [29–31]. However, there is limited published research investigating the extraction of VOCs from fabrics, despite its applicability. A notable application of VOCs is in the textile industry, especially for processes that involve microencapsulation, a technique where tiny particles or droplets (of lasting fragrances, skin softeners, disinfectants, insect repellents, and many more) are enclosed within a capsule that allows the substance to be readily released [32]. For example, to determine the fragrance durability on clothing of two different types of microcapsules containing lemon essential oils, Miro Specos et al. [33] extracted the VOCs from treated and laundered fabrics in ethanol at various intervals after the wash cycle.

Solvent extraction is traditionally one of the most routinely used extraction methods, particularly for organic analytes [34]. This simple method uses the solubility properties of VOCs for selective extraction. The structure of the analytes determines their solubility into solvents of various polarities, thus solvent polarity can influence the extraction profile [35]. In addition to diluting the sample, one of the main disadvantages of solvent extraction is that it is generally a very laborious technique, especially compared to the solid phase microextraction (SPME) sampling technique that can be automated.

SPME is a solvent free method that integrates sampling, extraction, and concentration of analytes. Compared to solvent extraction, SPME is a non-exhaustive extraction technique, where only a small proportion of the target analyte is extracted from the sample matrix [36]. This technique has the benefit of portability, the possibility of automation, and increased sensitivity, in addition to a passive sampling approach that does not interfere with the sample when used in headspace (HS) mode [37]. Such benefits are highly valuable in forensic sciences, as mirrored by the increase in popularity of this extraction technique among forensic scientists in the last decade [38].

This current study seeks to develop, optimise, and validate a HS-SPME GC–MS method for the extraction of fragrances from fabrics, which can allow further and improved research into the dynamics of fragrance traces. A two-step-strategy was carried out to determine the optimal levels of the most relevant factors that can improve the HS-SPME extraction: (i) optimisation of the extraction of VOCs from a fragrance mixture to understand the behaviour of the studied VOCs during a HS-SPME process and, (ii) optimisation of the extraction of VOCs from pieces of fabric previously spiked with VOCs to understand the process of desorption of the compounds from the fabric. For both optimisation steps, central composite design (CCD) was used [39,40]. Further, validation studies using the optimised SPME method provided the linearity, limits of detection (LOD), limits of quantification (LOQ), working ranges, trueness (intraday and interday relative recoveries), and precision (repeatability and reproducibility) values. Next, the validated method was used for the extraction of VOCs from fabric swatches spiked with commercial perfumes. Lastly, the SPME method was compared to the liquid extraction employed in Gherghel et al. [24]. The benefit of the optimised and validated method for the extraction of perfume compounds from fabrics presented here is a more sensitive and robust analytical method for obtaining insights into how these fragrance compounds have been transferred to and persisted on garments.

2. Materials and methods

2.1. Chemical and materials

Reference standards of seven VOCs, including (+)-α-pinene (98.5% purity), (R)-(+) limonene (97%), linalool (97%), geraniol (98%), eugenol (99%), coumarin (99%), and ethylene brassylate (97%) were purchased from Sigma Aldrich, Gillingham, UK. These reference standards were chosen based on their popularity in the fragrance industry, assuring the standards chosen covered a wide range of volatility. Two internal standards of analytical standard grade, 1,4-dibromobenzene and methyl nonanoate, as well as methanol (HPLC grade, 99.9% purity) were obtained from Sigma Aldrich, Gillingham, UK. Commercially available perfumes were purchased from a mainstream retailer, with a focus given to perfumes marketed for men as 99% of sexual assaults from U.K. in 2014 were committed by men according to the Office for National Statistics [41]. The reference standards, internal standards, stock solutions of each compound, and the perfumes were kept refrigerated ($T < 5\,^{\circ}C$). The stock solutions were prepared in methanol on a monthly basis at concentrations between 10–25 mM.

For the HS-SPME procedure, the fibres were purchased from Supelco (Bellefonte, Pa, USA). The five different fibres investigated were polydimethylsiloxane (PDMS), polyacrylate (PA), polydimethylsiloxane/divinylbenzene (PDMS/DVB), carboxen/polydimethylsiloxane (CAR/PDMS), and divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS). All fibres were 1 cm long. Prior to first use and daily when used, the fibres were conditioned according to the manufacturer's recommendations. After use, individual SPME fibres were kept in a closed 15 mL Falcon tube at room temperature in order to avoid undesired absorption of potential VOCs present in the laboratory environment. For all SPME analyses, 20 mL screw cap vials sealed with 18 mm pre-fitted PTFE-silicon septum were used.

The garments used in this study were purchased from a popular UK male clothing retailer, and were a white long sleeve T-shirt made of 100% cotton, a white T-shirt made of 100% cotton, a blue tank top made of 100% polyester, and a beige jumper made of 100% acrylic. Prior to the analyses, the garments were washed together in a conventional washing machine without adding any detergent. The dried garments were stored together in a closed plastic bag at ambient temperature.

2.2. Instrumentation

Samples were analysed on a Scion Gas Chromatography system coupled to a Scion QqQ-MS/MS instrument (Bruker Corporation, Freemont, CA, USA) and equipped with a Combi Pal autosampler (CTC Analytics, Switzerland). A Trace™ 1310 Gas Chromatography system coupled to a Q-Exactive™ hybrid quadrupole-Orbitrap mass spectrometer system (Thermo Fisher Scientific, Bremen, Germany) with Xcalibur 4.1 software (Thermo Fisher Scientific, Les Ulis, France) were employed for confirmation of unknown compounds. Chromatographic separation was achieved on a VF-5 ms capillary column ($30\,\mathrm{m} \times 0.25\,\mathrm{mm}$, $0.25\,\mu\mathrm{m}$ film thickness) from Varian (Palo Alto, California, USA). The carrier gas was helium (99.9999% purity) and the column flow was maintained at $1\,\mathrm{mL\,min^{-1}}$ using an electronic flow controller.

A portable thermometer–hygrometer (model 82021, VWR Scientific) was employed for measuring the laboratory temperature and humidity. Throughout this study, the laboratory ambient