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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

Simona Gherghel[a,b,c,d,*], Ruth M. Morgan[a,b], Javier Arrebola-Liébanas[c], Roberto Romero-González[c], Chris S. Blackman[d], Antonia Garrido-Frenich[c], Ivan P. Parkin[d]

[a] UCL Department of Security and Crime Science, 35 Tavistock Square, London WC1H 9EZ, United Kingdom
[b] UCL Centre for the Forensic Sciences, 35 Tavistock Square, London WC1H 9EZ, United Kingdom
[c] Research Group "Analytical Chemistry of Contaminants", Department of Chemistry and Physics, Research Centre for Agricultural and Food Biotechnology (BITAL), University of Almería, Agrifood Campus of International Excellence, ceiA3, E-04120 Almería, Spain
[d] UCL Department of Chemistry, 20 Gordon Street, London WC1H 0AJ, United Kingdom

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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

* Corresponding author at: UCL Department of Security and Crime Science, 35 Tavistock Square, London WC1H 9EZ, United Kingdom.
E-mail address: simona.gherghel.14@ucl.ac.uk (S. Gherghel).

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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 m × 0.25 mm, 0.25 μm film thickness) from Varian (Palo Alto, California, USA). The carrier gas was helium (99.9999% purity) and the column flow was maintained at 1 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

temperature ranged between 21 and 23 °C and the humidity ranged between 25 and 48%.

2.3. GC–MS conditions

The GC oven temperature was programmed from 35 °C (held for 1 min) to 180 °C (held for 1 min) at 5 °C/min rate, and then to 300 °C (held for 2 min) at 25 °C/min rate. The total chromatographic run was 37.8 min, with the start of the acquisition time at 2.2 min to avoid the elution of the solvent, methanol. The transfer line and the ion source temperatures of the mass spectrometer were set to 280 °C. The thermal desorption of the SPME fibre was carried out using an injector temperature of 250 °C in splitless mode for 3 min, and a further 6 min of purging in split mode was used to help prevent carryover effects. A SPME specific inlet liner with a diameter of 0.8 mm was purchased from Agilent Technologies to improve GC resolution and to minimise peak broadening. The mass spectrometer was operated in Electron Ionisation (EI) mode at −70 eV. Data acquisition rate was of 5 spectra/s and the mass range was scanned from m/z 40 to 250. EI mass spectrum of compounds eluted from the GC column was compared to EI mass spectra from the National Institute of Standards and Technology (NIST) v 2.2 g (2014) database for identification.

2.4. Selection of the SPME fibre

For the selection of the optimal fibre towards five VOCs of interest, and also towards VOCs from a commercial perfume, five different SPME fibres, described in Section 2.1, were investigated. First, the ability of SPME to recover the five VOCs was studied by analysing in triplicate 10 μL of a 200 μM solution made of limonene, linalool, geraniol, eugenol, and coumarin in methanol. Second, 10 μL of a men's perfume was analysed in duplicate.

2.5. Optimisation of the HS-SPME extraction of fragrance mixtures

After determining the optimal SPME fibre, the main extraction factors (incubation time, extraction time, and extraction temperature) were optimised using a face-centred cube central design ($\alpha = 1.682$), based on a 2^3 full factorial design plus six axial points and six replicates in the centre of the design. Therefore, 20 experiments were carried out, including six replicates, where 10 μL of a 50 μM of a fragrance mixture (FM) made of α-pinene, limonene, linalool, geraniol, eugenol, coumarin, and ethylene brassylate in methanol was pipetted straight into a vial. Additionally, four empty vials used as blanks were analysed throughout the analysis sequence. The values for the incubation time varied from 1.6 to 18.4 min, for extraction time from 4.8 to 55.2 min, and for extraction temperature from 33.2 to 66.8 °C. The results were plotted using the Minitab 18 statistical software (Minitab, State College, USA).

2.6. Optimisation of the HS-SPME extraction of fragrance mixtures from garments

After the optimisation of an extraction method for fragrance mixtures, the next step was the optimisation of a method for the extraction of fragrances mixtures from garments. For this purpose, pieces of 100% cotton swatches of approximately 2 cm × 2 cm and 0.2 g were employed. Each swatch was placed on a Petri dish and spiked in the centre with 10 μL of the 50 μM fragrance mixture used in Section 2.5. Similar to the optimization of the extraction from fragrance mixtures (Section 2.5), a 2^3 full factorial CCD was created, where 20 samples were analysed in random order. However, the values varied from 4.9 to 30.1 min for incubation time, from 9.8 to 60.2 min for extraction time, and from 39.9 to 70.1 °C for extraction temperature.

2.7. Validation of the HS-SPME extraction of fragrance mixtures from garments

For the validation of the optimised method using garments, the parameters studied were linearity, working ranges, LOD, LOQ, sensitivity, trueness (intraday and interday relative recoveries), repeatability (intraday precision) and reproducibility (interday precision). The samples for the interday study were freshly prepared on the day of the analysis. The linearity was assessed by studying the determination coefficient (R^2) of the calibration curves. Calibration curves were constructed in cotton and in polyester. Seven different concentrations of the studied VOCs were prepared in triplicate in methanol, ranging from 0.5 to 100 μM, whilst the concentration of the internal standards in the calibrants was 20 μM. Sensitivity was determined as the slope of the calibration straight-line. The LOD and LOQ for each analyte were calculated as the concentration for which the signal-to-noise ratio was 3 and 10, respectively. The working ranges were determined by the minimal value of the LOQ and the highest concentration tested with good linearity. Trueness of the method was evaluated by studying the relative recoveries of analytes from the gas phase when 10 μL of the FM was spiked on fabrics at two different concentrations (2.5 and 25 μM) within the same day (n = 3) and on different days (n = 4). Precision was based on repeatability (evaluated as intraday precision) and reproducibility (evaluated as interday precision), and expressed as relative standard deviation (RSD).

2.8. Analysis of commercial perfumes from garments using the validated HS-SPME method

Using the optimised and validated method, cotton and polyester swatches were spiked with 10 μL of a number of different commercially available perfumes diluted between 500 and 1500 times in methanol. The diluted perfume solution also contained 20 μM of 1,4-dibromobenzene and methyl nonanoate as internal standards. When present in the perfume, the concentration in the headspace of the analytes with available calibration curves was calculated.

2.9. Analysis of commercial perfumes from garments using liquid extraction

For the comparison of HS-SPME extraction with liquid extraction, similar to Section 2.8, a cotton swatch was spiked with 10 μL of a commercially available men's perfume diluted in methanol 500 and 100 times, and also undiluted. Following the sample preparation from Gherghel et al. [24], the swatch was added to a 2 mL GC vial, to which 1 mL of methanol was added for the liquid extraction. The vial was shaken using a Vortex for 2 min, after which 50 μL of the liquid were transferred to a 50 μL GC vial insert. For each sample, 1 μL was injected to the GC, a five-time increase compared to Gherghel et al. [24].

3. Results

3.1. Selection of the SPME fibre

Various fibres with different coating materials were investigated to check their extraction ability specifically towards a fragrance solution made of popular perfume ingredients, and also towards a commercially available men's perfume.

For the analysis of the fragrance solution, 10 μL of a 200 μM solution of limonene, linalool, geraniol, eugenol, and coumarin in methanol were analysed in triplicate as representative compounds. For each fibre type, the mean peak area and relative standard deviations of each of the five compounds were determined, allowing in turn to calculate the sum of the mean peak areas and the average of the relative standard deviations, respectively. Whilst the sum allows an evaluation of the amounts of compounds extracted, the average of the relative standard deviations, expressed as coefficient of variation (CV), provides information about the repeatability performance.

These two parameters enabled the determination that for the fragrance solution, the DVB/CAR/PDMS fibre performed the best over the entire range of compounds analysed, producing the highest peak areas with the best repeatability (CV = 4.6%) (Table SM-1, Supplementary Material). Similar extraction rates were also obtained for the PDMS/DVB fibre, especially for lower volatility compounds, such as eugenol and coumarin (Fig. 1). However, the PDMS/DVB fibre produced on average approximately three times poorer repeatability compared to the DVB/CAR/PDMS fibre (Table SM-1).

For the analysis of a real perfume, 10 μL of a commercially available men's perfume was analysed in duplicate for all fibres examined. The CAR/PDMS fibre extracted the highest amounts of compounds from the perfume; however, it also produced the highest variation between the duplicates (CV = 9.5%) (Table SM-1). The DVB/CAR/PDMS fibre produced the second highest recovery, whilst providing a low CV of 1.5%.

3.2. Optimisation of the HS-SPME extraction of fragrance mixtures

After the selection of the SPME fibre, the following step was the determination of the optimal SPME variables for the extraction of VOCs of interest. To investigate the effect of different extraction parameters and their optimal values, a central composite design was used where the effect of incubation time, extraction time, and extraction temperature was tested at five different levels for seven different VOCs.

Generally, the sum of the chromatographic peak areas is used as a response in CCD for SPME optimisation [40,42]. However, because of the large differences in the intensity of the analytes extracted, the sum of the normalised peaks was considered a better CCD response. The peak area of each analyte was normalised by using the maximum peak area for that analyte from the analysis sequence. Hence, the maximum possible CCD response in this case was 7, one for each analyte investigated. The conditions for the twenty experiments and the experimental responses, that is the sum of the normalised peak areas, are provided in Table SM-2.

Analysis of variance (ANOVA) provides the significance of each factor and of the interactions between factors. Based on ANOVA's analysis of the CCD results, the model's linear coefficient extraction temperature and the quadratic term coefficient of extraction temperature had a significant impact on the extraction of the VOCs investigated from the fragrances mixture by SPME ($p < 0.05$) (Table SM-3).

The value of the R^2 indicates the percentage of the total variations in the experimentation that is not explained by the model. A R^2 of 70.08% was obtained. The lack-of-fit test is not significant (p-value = 0.784), where generally a p-value lower than 0.05 shows that the model does not accurately fit the data.

Fig. SM-1 represents the three-dimensional representation surface plots with the response (normalised peak area) on the Z-axis against two independent variables at a time. It can be observed how with an increase in extraction temperature there is an increase in the peak areas of the target analytes (Fig. SM-1 top right and bottom).

The experimental study concluded that the optimal conditions predicted for the HS-SPME extraction of all fragrance compounds investigated were 18.4 min of incubation and 55.2 min of extraction time at 56 °C, where the extraction temperature was the only significant factor ($p = 0.013$).

3.3. Optimisation of the HS-SPME extraction of fragrance mixtures from garments

Having optimised the HS-SPME extraction parameters for analysis of fragrance mixtures, the next step was to ensure optimal relative recoveries of VOCs when the perfume was extracted from garments. Using the optimised extraction variables, a sample of the FM and samples of the FM spiked on various garments were analysed. The peak area results for each VOCs in the FM are plotted individually in Fig. 2 due to the scale variation.

Especially for high volatility compounds, polyester and acrylic provided a similar VOCs profile compared to the one in the fragrance mix itself, showing only a limited matrix interaction. On the other hand, for cotton, the high volatility compounds such as α-pinene and limonene were largely extracted, whilst a decrease (of linalool, geraniol) or an absence (of eugenol, coumarin, ethylene brassylate) in the extraction of higher volatility compounds was observed. These results were consistent with those obtained for a second different 100% cotton material. It was generally observed that the extraction of the VOCs containing alcoholic groups was

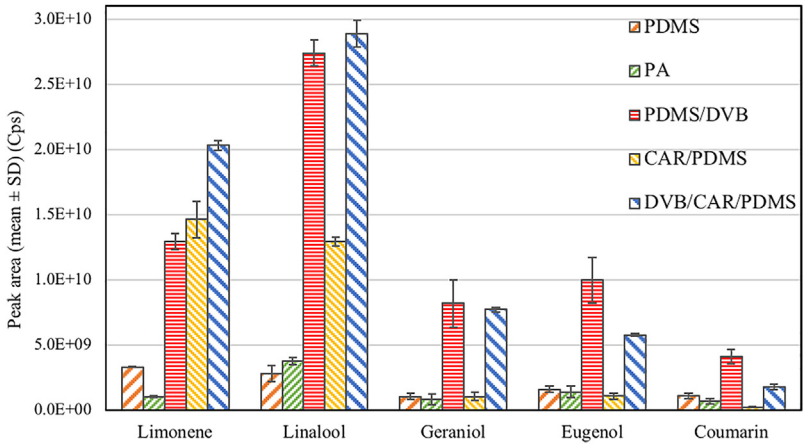

Fig. 1. Average peak area of five fragrance compounds by five different SPME fibre types. Cps (Counts per second).

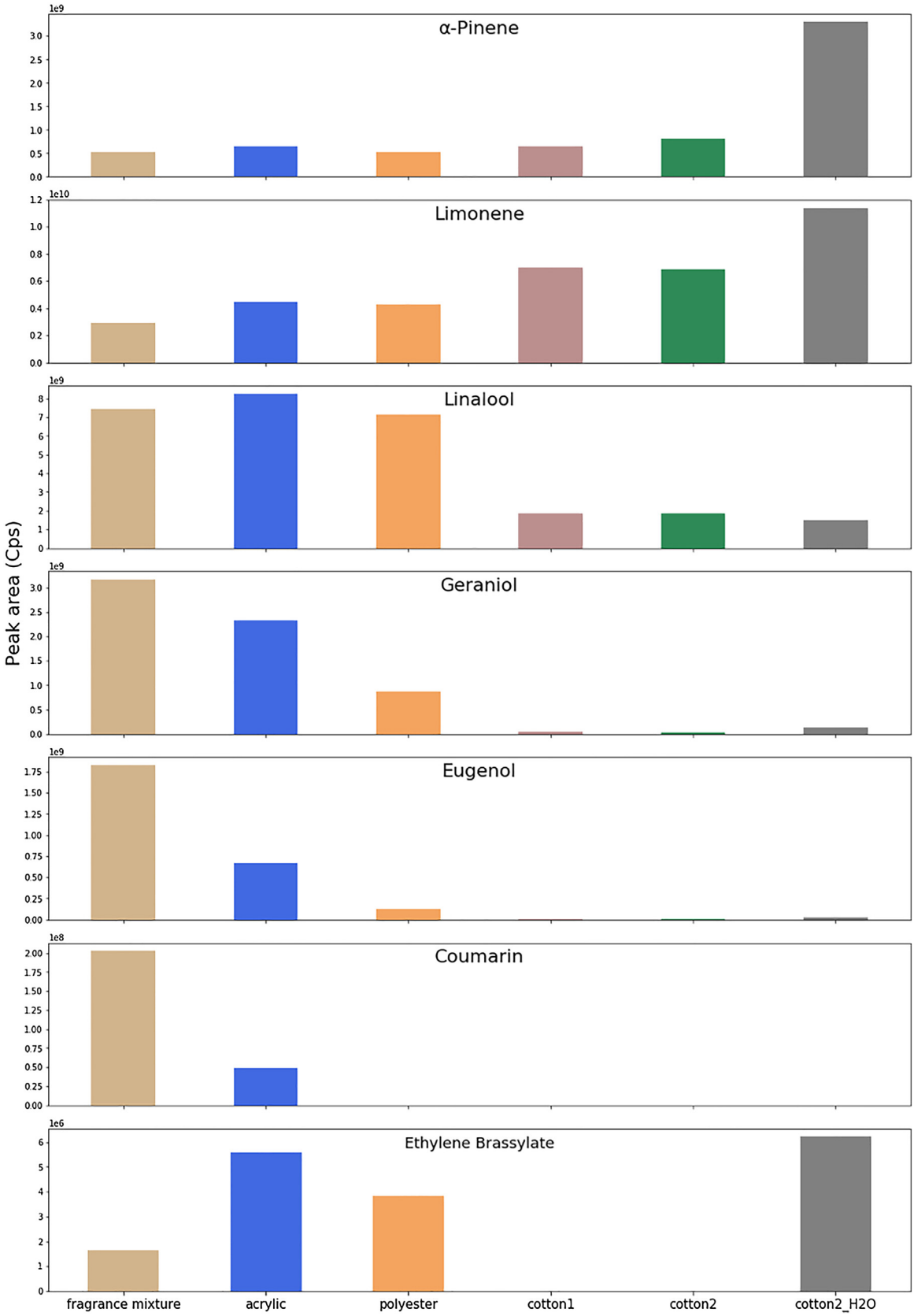

Fig. 2. Extraction of the seven individual VOCs from a fragrance mixture and from a fragrance mixture recovered from acrylic, polyester, cotton #1, cotton #2 and lastly from cotton #2 to which 10 mL of water were added (cotton2_H2O). Cps (Counts per second).

highly affected by the cotton swatches compared to the polyester and acrylic swatches.

In order to evaluate a potential influence of the headspace volume, a further experiment studied the addition of 10 mL of water to a vial containing cotton swatch spiked with the FM (Fig. 2 last bar). Higher extraction efficiencies were obtained for the majority of the compounds when water was used compared to the spiked cotton on its own. Moreover, the addition of water enabled the extraction of eugenol and ethylene brassylate, compounds that were not previously extracted. This is probably due to the ability of water to draw out chemicals, especially polar compounds, from cotton. It should be noted that coumarin was not recovered from any of the cotton samples or from the polyester sample.

Knowing that the addition of water improves the extraction of the fragrance compounds from fabric (see Fig. 2), a further CCD was designed for incubation time (from 5 to 30 min), extraction time (from 10 to 60 min), and extraction temperature (from 40 to 70 °C). The levels of the variables studied, and the experimental responses are given in Table SM-4. Once again, the peak area of each analyte was normalised, and the sum of the normalised peak areas was used as the CCD response.

Based on ANOVA's analysis of this second CCD experiment (Table 1), the model's linear coefficient extraction time was the only coefficient that had a significant impact on the extraction of the targeted VOCs from cotton by SPME ($p < 0.05$). Thus, the model equation can be rewritten to: $y = -5.6 + 0.1156X_2$, where y = summed normalised areas of VOCs.

The 3D response surface models (Fig. SM-2) show an increase in the extraction of the analytes with an increase in the extraction time. The optimal values for the SPME extraction of the seven VOCs from cotton was an incubation time of 5 min, an extraction time of 60 min, and an extraction temperature of 58 °C, where the extraction time was the only significant factor ($p = 0.001$).

Once the extraction variables were optimised, two additional trials were carried out. The first trial involved the addition of organic modifiers to the water solvent, and the second trial involved an investigation of the desorption parameters, namely desorption temperature and the splitless desorption time.

In the first trial, cotton swatches spiked with 10 μL of 50 μM FM were analysed in 10 mL of either water on its own, water with 2.5% or 5% of acetone or methanol (Fig. SM-3). Overall, the addition of acetone to water decreased the extraction of the VOCs. The addition of methanol at 5% lead to slightly lower or similar extraction rates compared to water on its own, therefore further HS-SPME experiments were continued by using only 10 mL of water.

In the second trial, desorption temperature and splitless time, i.e. the time when the analytes are desorbed from the SPME fibre to the injector, were investigated. When increasing the desorption time from 250 to 270 °C using a constant desorption time of 0.5 min, a decrease in the recovery of most compounds was observed (Fig. SM-4). When increasing the splitless time from 0.5 to 1.5, and to 3 min, an increase in the extraction rates for most compounds was observed. Therefore, further studies were conducted using a splitless time of 3 min and an injector temperature of 250 °C.

Table 1
Analysis of variance (ANOVA) of the central composite design experiment for the extraction of VOCs by SPME from a fragrance mixture applied on a cotton swatch.

Term	Coefficient	Degree of freedom	Sum of squares	F-value	p-value
Model		9	9.112	3.55	0.031
Intercept	−5.6	1			
X_1	0.149	1	0.136	0.48	0.506
X_2	0.1156	1	7.169	25.13	0.001*
X_3	0.137	1	0.386	1.35	0.272
X_1^2	−0.00182	1	0.121	0.54	0.484
X_2^2	−0.000126	1	0.005	0.04	0.844
X_3^2	−0.00121	1	0.138	0.48	0.503
X_1X_2	−0.00335	1	1.133	3.95	0.074
X_1X_3	0.0082	1.63 1	0.024	0.09	0.776
X_2X_3	0	1.69 1	0	0	0.999
Residual		10	2.852		
Lack of fit		5	2.222	3.53	0.096
Pure error		5	0.630		
Total		19	11.964		
R^2	0.762				
Adj R^2	0.547				

X_1: incubation time (min); X_2: extraction time (min); X_3: extraction temperature (°C).
* The ANOVA results indicate that the X_2 term is the only significant factor (0.05 probability level according to Duncan test) affecting the extraction of the analytes.

3.4. Validation of the HS-SPME extraction of fragrance mixtures from garments

The optimised HS-SPME extraction method developed for the extraction of VOCs from fabric swatches was validated for two different fabrics, cotton and polyester. To ensure adequate quantification of the analytes of interest, an evaluation of the linearity, working ranges, LOD and LOQ, relative recoveries (intraday and interday), repeatability, reproducibility, and sensitivity of the method was carried out.

Due to the diversity in the chemical structure of the VOCs analysed, two different internal standards were added at a concentration of 20 μM to all calibration standards and spiked samples. Within the concentration range investigated, coumarin showed a non-linear response, for both fabrics studied. At this point, coumarin was eliminated from the study because of the low affinity of SPME fibre and experimental conditions tested.

The validation results for the extraction of VOCs in cotton and polyester are displayed in Table 2. With the exception of α-pinene and limonene which showed linearity in cotton in the range of concentrations tested, for the rest of the analytes two different concentration ranges were required. Although it was possible to fit the calibration curves to a polynomial equation, it was more desirable to split the calibration range into two different sections, as fragrance traces are expected to be found at very low concentrations when they have transferred onto a secondary piece of fabric.

Linearity was evaluated based on coefficients of determination (R^2). Most analytes provided a R^2 value above 0.99 and a number of analytes provided a R^2 between 0.98 and 0.99 (see Table 2). The LOD varied between 0.44 and 45 nM for cotton, and between 0.06 and 7 nM for polyester. The LOQ varied between 1.47 and 151 nM for cotton, and between 0.21 and 20 nM for polyester. Big differences for LOD and LOQ were observed for ethylene brassylate between cotton and polyester, so that in cotton the LOD was approximately 6 times higher and the LOQ approximately 11 times higher than in polyester. Generally, the sensitivity, in terms of slope, varied from 0.0005 to 0.017 for cotton, and from 0.002 to 0.064 for polyester.

The intraday relative recovery values varied from 85 to 114% at a concentration of 2.5 μM, and between 89 and 102% at a concentration of 25 μM. The interday relative recoveries ranged from 83 to 123% at a concentration of 2.5 μM, and between 75 and 133% at a concentration of 25 μM.

All repeatability values (evaluated as intraday precision) were below 15% at 2.5 μM, and below 9% at 25 μM. Good reproducibility values (evaluated as interday precision) were obtained for most compounds, with no RSD value higher than 21%, with the exception of α-pinene at 25 μM in polyester (RSD = 26%).

Table 2
Validation parameters of the validated method in cotton and polyester sample.

Compound	m/z[b]	Rt[a]	Matrix	R^{2c}	Calibration curve	Wr[d]	LOD[e]	LOQ[f]	Intraday relative recovery %[g]		Interday relative recovery %[h]	
									2.5 μM	25 μM	2.5 μM	25 μM
α-Pinene	77.1, 91.1, 93.1	9.48	Cotton	0.995	Y = 0.00396*X + 0.00004	0.5–50	0.95	3.16	105 (6)	97 (5)	123 (12)	105 (7)
			Polyester	0.990	Y = 0.01259*X – 0.00086	0.5–2.5	2.07	6.90	100 (7)	102 (4)	113 (12)	133 (26)
				0.989	Y = 0.00753*X + 0.01143	2.5–50						
Limonene	67.1, 68.2, 93.1	12.47	Cotton	0.997	Y = 0.01748*X + 0.01214	0.5–50	0.44	1.47	103 (3)	94 (5)	117 (11)	96 (7)
			Polyester	0.992	Y = 0.06395*X + 0.16199	0.5–10	0.06	0.21	101 (7)	91 (1)	115 (21)	95 (12)
				0.981	Y = 0.02803*X + 0.48115	10–50						
Linalool	55.2, 71.1, 93.1	14.63	Cotton	0.998	Y = 0.00259*X + 0.00063	0.5–10	3.42	11.39	95 (8)	89 (2)	118 (20)	91 (8)
				0.995	Y = 0.00191*X + 0.00222	10–100						
			Polyester	0.997	Y = 0.00422*X – 0.00085	0.5–10	2.77	9.24	88 (7)	94 (3)	100 (13)	92 (5)
				0.993	Y = 0.00331*X – 0.00292	10–100						
Geraniol	41.2, 67.1, 69.1	19.04	Cotton	0.994	Y = 0.00320*X – 0.00112	0.5–10	12.10	40.32	90 (8)	90 (3)	95 (9)	90 (3)
				0.987	Y = 0.00290*X – 0.01590	10–100						
			Polyester	0.998	Y = 0.00402*X – 0.00022	0.5–10	6.28	20.92	92 (4)	92 (2)	93 (10)	91 (12)
				0.985	Y = 0.00225*X + 0.01285	10–50						
Eugenol	77.1, 103.1, 164.1	21.87	Cotton	0.991	Y = 0.00108*X + 0.00018	0.75–10	1.68	5.61	88 (12)	90 (1)	111 (21)	91 (7)
				0.990	Y = 0.00096*X – 0.00419	10–100						
			Polyester	0.987	Y = 0.00205*X + 0.00187	0.5–10	1.96	6.53	114 (1)	101 (5)	112 (11)	86 (17)
				0.997	Y = 0.00177*X + 0.00417	10–50						
Ethylene brassylate	55.1, 86.1, 98.1	34.10	Cotton	0.992	Y = 0.00088*X – 0.00018	0.5–10	45.45	151.52	85 (8)	94 (1)	93 (4)	75 (21)
				0.982	Y = 0.00055*X – 0.00012	10–100						
			Polyester	0.991	Y = 0.00209*X – 0.00068	0.75–10	7.11	13.70	98 (15)	99 (9)	83 (12)	82 (16)
				0.982	Y = 0.00197*X – 0.00813	10–100						

[a] Retention time (min).
[b] Quantification ions.
[c] Regression coefficient.
[d] Working range (μM).
[e] Limit of detection (nM).
[f] Limit of quantification (nM).
[g] Repeatability is given in brackets (n = 3).
[h] Reproducibility is given in brackets (n = 4).

3.5. Analysis of commercial perfumes from garments using the validated SPME method

Four different commercial perfumes, one marketed for women and three for men, were analysed using the optimised and validated method in both cotton and polyester. As the method was validated for determination of perfume traces, the samples were diluted between 500 and 1500 times in methanol prior to spiking. Additionally, blank samples of cotton and polyester were tested.

Fig. 3 shows the chromatograms of the cotton blank sample and of a 500 times diluted men's perfume recovered from cotton by HS-SPME. Various chromatographic peaks originating from the cotton, such as those detected at 14.8, 17.8, 24.9, 25.7 and 27.6 min RT (numbered from 1 to 5 in Fig. 3 top) were observed in all spiked cotton samples. However, their retention times do not interfere with those of the analytes of interest, highlighted in the chromatogram of the diluted men's perfume (Fig. 3 bottom). These cotton originating analytes were tentatively identified by high resolution mass spectrometry (Q-Exactive Orbitrap) as nonanal, decanal, 1-undecanol, 2,4-di-tert-butyl-phenol, and 2,2,4-trimethyl-1,3-pentanediol diisobutyrate.

Moreover, Fig. 4 with a narrow RT window from 11.1 to 11.5 min, illustrates how certain VOCs were found in all four fragranced samples (11.2 min RT), albeit at various concentrations, whilst some VOCs (11.37 min RT) are present in only certain perfumes.

Similarly, Fig. SM-5 represents the chromatograms of the polyester blank sample and of the diluted perfumes recovered from polyester. As observed with cotton, some of the compounds present in the perfume traces samples were originating from the fabric itself.

Using the calibration curves constructed during validation, the concentration of each analyte in both cotton and polyester, when available, was determined in the diluted perfumes analysed (n = 2) (Table 3). All RSD values were below 22%. Eugenol was not found in the four perfumes analysed.

3.6. Analysis of commercial perfume from garments using liquid extraction

Following the sampling procedure developed by Gherghel et al. [24], one of the perfumes marketed for men was additionally analysed using liquid extraction. In a similar fashion to the HS-SPME analyses of real perfumes, the sample was diluted 500 times prior to extraction. The resulting chromatogram of the cotton swatch spiked with the diluted men's perfume and extracted using methanol (Fig. 5(a)) revealed very poor sensitivity of the method. A further test with this perfume diluted 100 times showed no major improvements (Fig. 5(b)). Next, the perfume was spiked undiluted and the results obtained (Fig. 5(c)) were comparable to the HS-SPME extraction where the perfume was diluted 500 times (Fig. 5(d)). The sensitivity between the different experiments is readily seen in the scale and units of y-axis in Fig. 5.

A number of the validated fragrance compounds, such as α-pinene, limonene and linalool, were recovered from this perfume using the liquid extraction method. Even with a 500-dilution factor, HS-SPME showed greater affinity towards limonene (Fig. 6(a)). For α-pinene (Fig. 6(b)) and linalool (Fig. 6(c)) greater amounts were recovered using liquid extraction only when the perfume was undiluted.

4. Discussion

4.1. Selection of the SPME fibre

There are various factors known to affect the extraction of analytes by SPME fibres. One of the most important factors is the

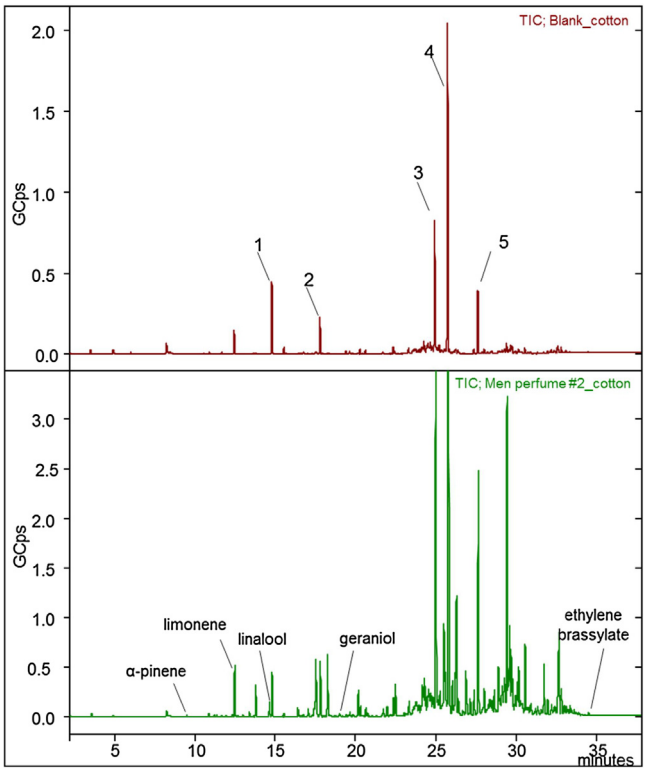

Fig. 3. Top: gas chromatogram of a blank cotton sample, where the peaks of some cotton originating compounds were tentatively indentified as: (1) nonanal; (2) decanal; (3) 1-undecanol; (4) 2,4-di-tert-butyl-phenol; (5) 2,2,4-trimethyl-1,3-pentanediol diisobutyrate. Bottom: gas chromatogram of a cotton sample spiked with men's perfume #2 diluted 500 times, where the peaks of the target compounds found in the perfume are highlighted. GCps (Giga Counts per second).

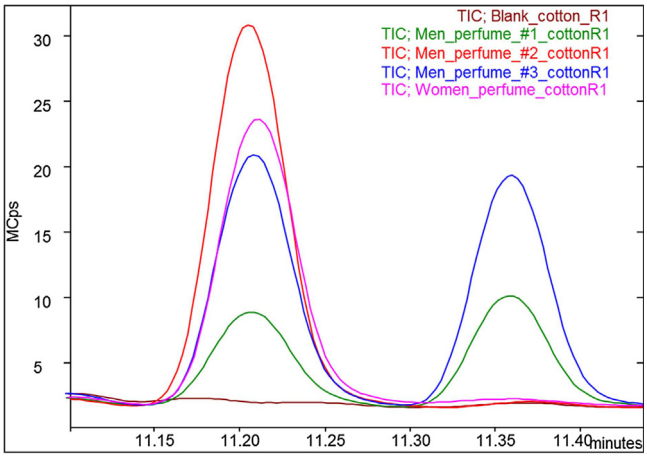

Fig. 4. Gas chromatograms (RT 11.1–11.5 min) of a blank cotton sample (bordeaux), of three cotton samples spiked with men's perfume (red, blue, and green), and of a cotton sample spiked with women's perfume (pink). MCps (Mega Counts per second). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

coating material on the fibre itself. Successful application of SPME analysis relies on the selection of a suitable fibre type for particular analytes. The five SPME fibres investigated in this study cover a wide range of analyte chemistries.

PDMS is the most typically employed coating phase in analytical applications. PDMS and PA coatings extract analytes via absorbtion, so that the compounds are dissolved and diffused into the phase, basically migrating in and out of the coating without any competition effects taking place. On the other hand, the mixed coatings such as PDMS/DVB, CAR/PDMS, and DVB/CAR/PDMS extract analytes via adsorption, and thus they physically interact with the analytes. Divinylbenzene particles are considerably larger than the carboxen particles, ideal for C6–C15 analytes, while carboxen particles are ideal for C2–C12 range [37].

It is important that the properties of the coating materials, such as porosity and size of the particles, film thickness, and phase polarity are matched to those of the analytes. With a focus on forensic applications, Weyermann et al. [43] obtained better results for the extraction of organic volatiles from spent cartridges with PA fibre compared to 75 μm CAR/PDMS and 100 μm PDMS, and in a later study by Dalby and Birkett [44] involving seven fibres it was shown that 65 μm DVB/CAR had the highest extraction rates. Curran [45] determined that the 50/30 μm DVB/CAR/PDMS was the optimal fibre for the collection of human odour samples, and so this fibre has become in the last couple of years the main SPME fibre used for analysis of human scent for forensic applications [11,46,47]. For cosmetics formulations, Ortiz and Tena [48] determined 75 μm CAR/PDMS fibre to extract more VOCs, being more effective than 100 μm PDMS.

To overcome a general lack of literature and lack of agreement between those studies that exist, this study aimed to compare five different SPME fibres for the analysis of five VOCs specific to cosmetic industry, but also for the analysis of a commercial perfume. In terms of both recovery and repeatability, the DVB/CAR/PDMS, which covers both polarity ranges, performed the best overall for the fragrance mixture and for the commercial perfume. The repeatability of the DVB/CAR/PDMS was the highest amongst all fibres tested for the extraction of the seven VOCs of interest with a CV of 4.6%, followed by the PDMS/DVB fibre with a CV of 12.2%. The PDMS/DVB was also the second-best fibre for amount of the five VOCs extracted. Thus, the second-best results were obtained with a similar fibre coating containing two of three coating phases of best fibre, the DVB/CAR/PDMS. This confirms that the three phase fibre is the most suitable for extracting the selected VOCs in this study. It is important to note that the DVB/CAR/PDMS fibre is also the most commonly used fibre in forensic literature for analysis of human scent [11,46,47].

4.2. Optimisation of the HS-SPME extraction of fragrance mixtures

Besides coating material, the amount of analytes extracted by a SPME fibre can also be influenced by extraction temperature and time, incubation time, desorption time, etc. Incubation time, extraction time and temperature were chosen as the factors to be tested in a central composite design. The values for the three parameters were based on literature reviews for the VOCs from various matrices, such as alcoholic drinks and food samples [39,40].

When the HS-SPME methodology was applied to the analysis of fragrance mixtures, the only significant variable determined by the first CCD was extraction temperature. With an increase in extraction temperature to the maximum value studied of 56 °C, more of the VOCs from fabrics were extracted. The incubation time was determined not be significant, and therefore a short incubation time of 5 min was selected for further analyses. As incubation time resulted not to be a significant factor, there is an indication that headspace equilibrium happens in a very short period of time promoted by the high volatility of the studied compounds.

4.3. Optimisation of the HS-SPME extraction of fragrance mixtures from garments

A preliminary study showed that when the fragrance mixture VOCs were extracted from cotton rather than from the solution

Table 3
Determined concentration of target VOCs in the headspace of fabric samples spiked with four diluted commercially available perfumes after appropriate dilution.

Compound	Matrix	Found concentration (mM) (n = 2)[a]			
		Men's perfume #1	Men's perfume #2	Men's perfume #3	Women's perfume
α-Pinene	Cotton	0.47 (18)	1.10 (2)	1.43 (16)	1.97 (7)
	Polyester	0.34 (8)	0.81 (3)	0.83 (12)	1.55 (11)
Limonene	Cotton	11.47 (20)	45.30 (1)	22.02 (10)	35.55 (8)
	Polyester	8.00 (13)	52.59 (6)	19.88 (7)	45.03 (9)
Linalool	Cotton	21.98 (6)	75.13 (7)	40.57 (2)	119.88 (3)
	Polyester	17.48 (5)	68.18 (2)	34.15 (2)	98.84 (1)
Geraniol	Cotton	0.71 (7)	7.52 (3)	5.44 (5)	16.43 (3)
	Polyester	0.59 (19)	5.10 (1)	2.36 (5)	19.24 (3)
Eugenol	Cotton	ND[b]	ND	ND	ND
	Polyester	ND	ND	ND	ND
Ethylene brassylate	Cotton	20.65 (6)	4.76 (9)	1.94 (20)	84.21 (22)
	Polyester	16.74 (1)	4.85 (10)	0.42 (9)	97.55 (20)

[a] RSD is given in brackets.
[b] Not detected.

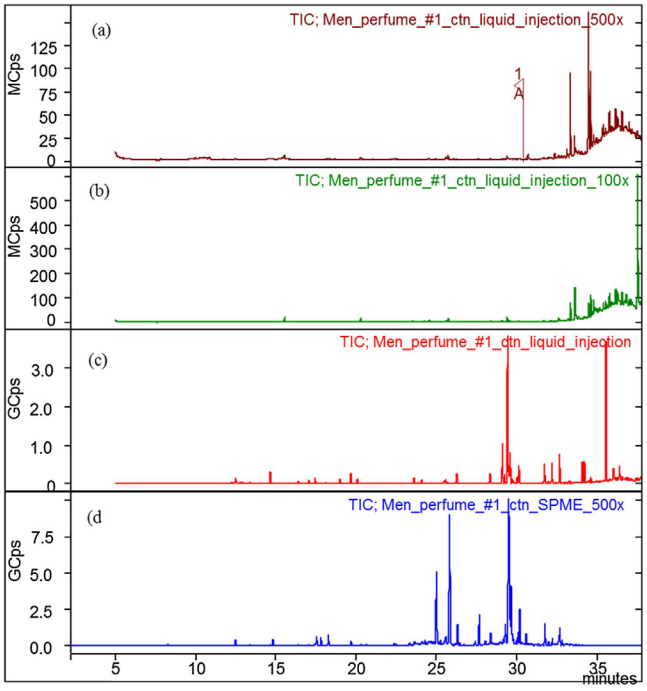

Fig. 5. Gas chromatograms of a men's perfume recovered from cotton using liquid extraction and a dilution factor of 500 (a), 100 (b), 1 (c)), and using SPME and a dilution factor of 500 (d). MCps (Mega Counts per sec); GCps (Giga Counts per sec).

itself, the recovery of compounds with alcoholic groups was lower. This could be explained by the formation of strong hydrogen bonds with the cellulose backbone of cotton. As a result, a second CCD was designed for the VOCs extraction from a cotton swatch.

The results from the CCD using cotton determined the extraction time to be the only significant factor that influenced the extraction of the VOCs of interest, so that the maximum recoveries were obtained when an extraction time of 60 min was used. Despite the method being automated, with a chromatographic run of 38 min, an incubation time of 5 min, and a maximum tested extraction time of 60 min, each sample was taking just under 2 h. Therefore, a further increase in the extraction time was considered not a viable option in terms of time and analytical output given the constraints of forensic analysis in casework.

Whilst the CCD results for the extraction of VOCs from fragrance mixtures showed that extraction temperature was a significant factor, the CCD results for the extraction of VOCs from fragrance mixtures from cotton swatches showed that the extraction time was the only significant factor.

With the optimal values determined for the extraction of VOCs from cotton, two further studies were carried out to optimise the extraction solvent and the desorption conditions. No improvements were observed when two different organic modifiers, acetone and methanol, were added to the water solvent or when the injector temperature was increased from 250 to 270 °C. A longer splitless time from 0.5 to 3 min in the injector allowed higher recoveries of the VOCs of interest.

4.4. Validation of the HS-SPME extraction of fragrance mixtures from garments

The validation was carried out with cotton and polyester fabrics. These natural and synthetic fibres are popular in the fashion industry, and therefore, in forensic science research [23,49,50]. For example, cotton is one of the most popular fabric materials available commercially; so that in the US in 2010, 64% of male clothing was made of 100% cotton, while 68% of female clothing contained cotton [51]. Polyester is by far the most popular synthetic fibre with a reported 82% share of the synthetic fibre market in 2014 [52]. Moreover, whilst the global cotton consumption went from 38% of the global fibre mill consumption in 2000 to 27% in 2015, the polyester consumption grew from 37 to 55% in the same period [53].

For successful analyte quantification, proper calibration needs to be carried out. As the analytes studied varied in their chemical structure, two internal standards with different chemical structures were used. Methyl nonanoate was employed for the quantification of the two linear compounds, linalool and geraniol, whilst 1,4-dibromobenzene was employed for all cyclic compounds, including α-pinene, limonene, eugenol, and ethylene brassylate.

Given that this analytical method is intended for the extraction of traces of VOCs from fabrics originating from sexual assault cases, a focus on the extraction of lower concentration was given. As a result, for most analytes it was necessary to split the working range in two ranges rather than fitting a polynomial equation in order to determine more accurately the concentration of lower concentration analytes. Good linearity, with a R^2 value above 0.98 was observed for most analytes in both fabrics. Generally, polyester produced lower LOD and LOQ than cotton, especially for ethylene brassylate where the LOD and LOQ were approximately 6 and 11 times, respectively, lower. Additionally, the sensitivity of ethylene brassylate in polyester (slope for lower range = 0.0021) was more than two times higher than in cotton (slope for lower range =

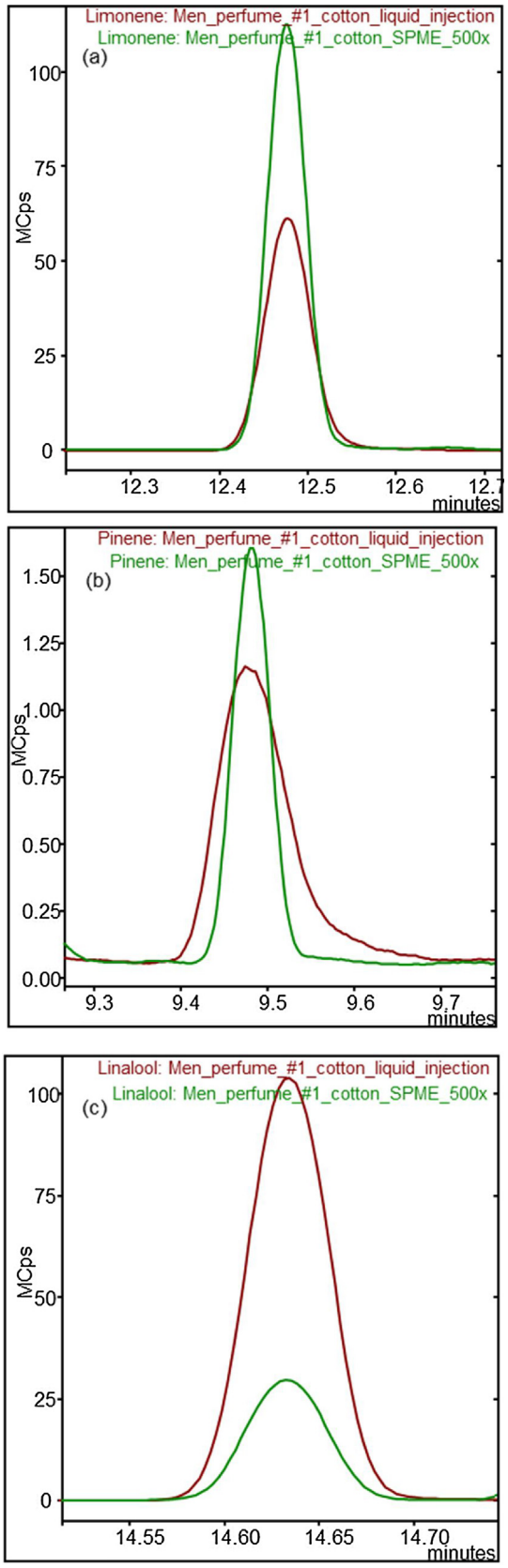

Fig. 6. Gas chromatograms showing the recovery of: (a) limonene, (b) α-pinene, and (c) linalool from an undiluted men's perfume recovered from cotton using liquid extraction (red), and of the same men's perfume diluted 500 times and recovered from cotton using SPME (green). MCps (Mega Counts per second). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

0.0009). This could be caused by an absorption of this compound onto cotton, in turn leading to lower method sensitivity.

4.5. Analysis of commercial perfumes from garments using the validated SPME method

Various perfumes marketed for both men and women were successfully recovered from cotton and polyester fabrics using the validated SPME method, even when they were spiked at concentrations 1500 times lower than in the original perfumes. This highlights the suitability of the method for the analysis of traces of fragrances for forensic applications.

It was observed that the blank cotton fabric contained various analytes, including aldehydes and alcohols, such as nonanal, decanal, and 1-undecanol (Fig. 3 top), although they did not interfere to the chromatographic peaks of the target analytes. Aldehydes have been previously shown to be extracted by SPME from various textile materials used in forensic sciences for the collection of human scent samples, including when these materials were sterilised [54]. It is therefore important to have an understanding of the compounds originating from the fabric itself.

4.6. Analysis of commercial perfumes from garments using liquid extraction

The sample procedure developed by Gherghel et al. [24] for the extraction of VOCs from fabrics using methanol was followed to analyse a perfume diluted 500 times as carried out with HS-SPME. However, for the methanol extracts of the perfume diluted 500 and 100-times, no perfume compounds were recovered. Only when the perfume was used undiluted were similar results obtained to those found for SPME analysis of perfume diluted 500 times.

The proposed HS-SPME extraction method is longer (approximately 2 h) than the liquid extraction option (approximately 1 h when it was carried out by a trained analyst), however the properties of HS-SPME such as high sensitivity, lack of use of organic solvents, simplicity, ability for full automation and coupling to GC–MS, and minimisation of analyte losses or external contaminations make the HS-SPME methodology clearly more suitable for the analysis of traces of VOCs in garments.

5. Conclusions

A method for the determination of VOCs specific to the cosmetic industry using HS-SPME coupled to GC–MS was developed, optimised, and validated. It was determined that a three phase SPME fibre, the DVB/CAR/PDMS fibre, was the most suitable for the extractions of VOCs from a commercial perfume and from an in-house perfume. High extraction rates were also obtained using a two phase fibre, such as the PDMD/DVB and CAR/PDMS fibres, although with poorer repeatability. This highlights the importance of selecting a multiple phase fibre that covers a wider range of molecular weights and volatilities.

For the optimisation of the SPME extraction, a multivariate approach was used, where three different variables were studied simultaneously using a CCD. This approach allowed the identification of the most significant variables and the determination of the optimal experimental conditions, whilst taking into account the interactions between the variables. Two optimisation designs, where incubation time, extraction time and temperature were studied at various levels, were carried out for the extraction of VOCs from an in-house perfume, and from cotton matrix impregnated with the same in-house perfume. For the former, the incubator extraction temperature and the quadratic term coefficient of extraction temperature were determined as the only significant variable, so that highest extraction rates were obtained

with an increase in the extraction temperature. This methodology can be a useful tool for establishing VOCs chromatographic profiles and obtaining quantitative results about commercial perfumes. For the SPME extraction of VOCs from fabric, the extraction time was the only significant variable, so that better results were obtained with a longer extraction time. This second methodology improves the ability to acquire indications of potential transfer of VOCs between the fabrics of individuals where the donor wears perfume.

The optimised SPME method was successfully validated for the extraction of six different VOCs from cotton and from polyester. This validated SPME method was applied for the analysis of cotton and polyester samples spiked with commercial perfumes diluted between 500 and 1500 times. The chromatographic results allowed the successful quantification of the analytes of interest when present. Using a liquid extraction method similar results to the SPME results were obtained only when the fabrics were spiked with undiluted perfumes. The results presented in this paper demonstrate that the developed SPME method represents a robust and sensitive method for the analysis of fragrance traces from fabrics that can be used to develop an understanding of the evidence dynamics of these traces for application to forensic reconstructions.

Declarations of interest

None.

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Contributors

SG, RMM, JAL, RRG and IPP collaborated on the experimental design. SG carried out the literature review, experimental work, and the data analysis. RMM contributed to the forensic implications. JAL closely supervised and oversaw the experimental work. RRG participated to the optimisation and validation studies. IPP contributed to the fabric-VOCs molecular interactions. All authors participated in the article preparation. All authors approve the final submission.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.forsciint.2018.07.015.

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