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Fragrance transfer between fabrics for forensic reconstruction applications

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ABSTRACT

Sexual assault is a serious crime that often has low conviction rates. Recent literature has demonstrated that there is potential for fragrances to be valuable in forensic reconstructions where there has been contact between individuals. However, developing appropriate evidence bases for understanding the nature of fragrance transfer in these contexts is needed. This article presents three experiments that address the transfer process of fragrances that have been transferred from a primary piece of fabric onto a secondary piece of fabric, in a manner that could occur during an assault. The three variables studied were the ageing time of the fragrances on the first fabric prior to transfer, the contact time between the two fabrics, and lastly the fabric type (of the primary material and the recipient material). The transfer was evaluated using a validated solid phase micro-extraction gas chromatography–mass spectrometry (SPME GC–MS) method. The findings demonstrated that all three variables had an impact on the transfer of fragrances between clothing fabrics. Generally, lower volatility compounds were transferred and recovered in larger amounts than higher volatility compounds. All fragrance compounds were successfully recovered from a secondary piece of fabric even when the contact time was as short as 10 s, and even when the perfume was aged on the primary fabric for as long as 48 h. The nature of the fragrance transfer also depended on the fabric type, so that a clear discrimination was observed between the fragrance transfer that occurred onto a natural fabric (cotton) and onto a synthetic fabric (polyester).

1. Introduction

In the last decade, the number of sexual offences reported to police in England and Wales has increased [1]. For the year ending March 2017, the Crime Survey for England and Wales [2] estimated that 2% of adults aged 16 to 59 had experienced sexual assault, or attempted assault, corresponding to approximately 646,000 victims, and that 0.5% experienced rape or attempted rape, corresponding to approximately 151,000 victims. Many of the sexual assaults are not reported to the police, so that for the same period 121,187 sexual offences (approximately 1 in 6 of the total) and 41,186 rapes (approximately 1 in 4 of the total) were recorded by the police [2]. These incidents are at the highest level recorded since record tracking started in 2002. However, many of these cases do not go to court. For example, in 2016, 12,572 defendants were prosecuted for sexual offences, and 7511 were sentenced [1]. The c. 60% conviction rate was the lowest among all offence types. The disparity between cases recorded by the police and those leading to a prosecution has been explained by reference to various factors, including the vulnerability of victims, the relationship between victim and suspect, and the lack of the requisite evidence for a crime to have occurred [3]. The purpose of this current study is to address this latter issue of a lack of physical evidence.

Clothing is often collected in the course of an investigation into sexual assault and it is generally tested for various trace materials [4]. Transferred trace materials can be used to reconstruct activities and can help to identify contacts between objects, people, or locations. Perfumes are traces that are invisible to the eye, and are widely used by both men and women. It is therefore possible that during a contact

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Abbreviations: FM, Fragrance mix; HCA, Hierarchical cluster analysis; PAT, Perfume ageing time; PCA, Principal component analysis; PLS, Partial least square; RSD, Relative standard deviation; SEM, Scanning electron microscope; SPME GC–MS, Solid phase micro-extraction gas chromatography–mass spectrometry; VOCs, Volatile organic compounds.

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between individuals, components of those fragrances can transfer. The recovery of relevant fragrance components from clothing has the potential to be a form of trace evidence that can be used to assess the likelihood of a contact between individuals.

Gherghel et al. [5] developed, optimised, and validated a method able to identify volatile organic compounds (VOCs) from fabrics that had been spiked with perfumes diluted as much as 1500 times in the first study to demonstrate the potential of fragrances for forensic reconstructions. However, a correct identification of VOCs from fabrics is only the first step towards the ability to offer a reliable interpretation of fragrance evidence from clothing [6]. A second important step is undertaking studies to establish how the transfer of fragrance between clothing occurs, and what the limitations to that transfer occurring can be [7].

The first experimental studies undertaken to understand the evidence dynamics of forensic traces evidence were carried out by Pounds and Smalldon [8–10], who investigated the transfer, persistence, and the mechanisms involved during the transfer of fibres between items of clothing. In their initial study involving the transfer of textile fibres to wool and acrylic clothing [8], they determined that both the fabric type of the recipient garment and the force of contact affect the amount of fibres transferred, so that high pressures and coarse recipient garments lead to the transfer of shorter fibres. In a further study exploring the persistence of transferred fibres [9], the authors determined that the loss of transferred fibres from the surface follows an exponential decay, with a rapid loss initially followed by a subsequent slower loss. An initial loss of approximately 80% was observed after 4 h, which increased to around 95% after 24 h.

Pounds and Smalldon were the first to show empirically that the transfer of trace evidence is a dynamic process. They highlighted the importance of considering any potential changes to the trace evidence since its formation and transfer when interpreting the presence of a specific form of trace. Following their work, numerous studies have been carried out to investigate the evidence dynamics of a number of different forms of trace materials, such as glass [11–13], paint [14–16], hair [17–19] and pollen [4,20,21]. Similar patterns of loss to the two-stage model outlined by Pounds and Smalldon [9] have been shown in these studies; for example Bull et al. [4] determined a significant loss followed by a slower decay for pollen grains. Their study also showed that the decay was more influenced by the recipient material than the particle type when conducting experiments using pollen grains, powder and metal particulates. Looking at airborne particulates, rather than solid phase particles, Prada et al. [22] have shown that the highest number of volatile organic molecules and the highest scent mass amounts were transferred from the hands of individuals to fabrics when cotton was used as a collection material. However, there are currently no studies evaluating how the primary (donor) and the recipient material type impact the transfer of volatile organic compounds between clothing.

VOCs differentiate in their physical state from most forms of trace material, such as fibres, pollen, hair, because of their high vapour pressure at ordinary room temperature. For example, Hudson et al. [23] investigated the persistence of human scent VOCs collected on cotton under various environmental conditions over a 7-week period and identified a change in the human scent profile over time. Thus, it is paramount when designing experimental studies to test the ability of VOCs to be a form of trace evidence, to investigate the effect of time on the amount (number and abundance) of VOCs present at different stages in the transfer and persistence process. Therefore, in addition to fabric type, this study addressed the period of time that passed from the application of perfume onto the primary fabric until transfer, referred to as the “perfume ageing time” [24], and the period of the time two fabrics are in contact for, the “contact time” [24].

A full understanding of how trace materials transfer and persist is important for forensic reconstruction purposes. Establishing an empirical evidence base upon which to draw conclusions about the activities of a particular form of trace material is critical for a transparent and robust interpretation of what the evidence means in a specific case [6]. Availability of empirical data on the dynamics of trace materials can aid the forensic scientist at a crime scene, in the laboratory, and during the interpretation process.

Given the importance of understanding the changes that happen to trace materials throughout the forensic process, and how that information can offer insights to inform the effective collection, analysis, and interpretation of that evidence, this current study presents the findings from a series of experimental studies investigating the transfer of fragrances between clothing materials. The three variables studied were perfume ageing time, contact time, and fabric type. Empirical studies of this nature can enable a robust interpretation of what a particular form of trace evidence means in a specific case scenario and can offer valuable intelligence and evidence [4].

2. Material and methods

2.1. Chemical and materials

This study followed the method outlined by Gherghel et al. [5] and utilised reference standards ((+)-α-pinene (98.5% purity), (*R*)-(+) limonene (97%), linalool (97%), geraniol (98%), eugenol (99%), and ethylene brassylate (97%)) and internal standards (1,4-dibromobenzene and methyl nonanoate), as well as methanol (HPLC grade, 99.9% purity). The stock solutions were prepared in methanol on a monthly basis at concentrations between 10 and 25 mM.

The headspace solid phase micro-extraction (HS-SPME) method used divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS) fibres that were purchased from Supelco (Bellefonte, PA, USA). Prior to first use and daily when used, the fibre was conditioned according to the manufacturer's recommendations. 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 beige jumper made of 100% acrylic, a white long sleeve T-shirt made of 100% cotton, a blue jacket made of 100% nylon, a long sleeve denim jacket made of 100% cotton, a blue tank top made of 100% polyester, a black jumper made of 100% wool, and a purple T-shirt made of polyester:viscose 50:50 (Fig. 1). 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

A Jeol JSM-6700F field emission scanning electron microscope (SEM) was used for the characterisation of the fabrics. Samples were coated with gold and placed on carbon tape to minimise electrical charging.

A previously validated chromatography-mass spectrometry (GC–MS) method was used for the VOCs extraction and instrumental analysis of the samples [5]. A Scion GC system coupled to a Scion QqQ-MS/MS instrument (Bruker Corporation, Freemont, CA, USA) and equipped with a Combi Pal autosampler (CTC Analytics, Switzerland) was used for all samples. The separation of the analytes was achieved on a VF-5 ms capillary column (30 m × 0.25 mm, 0.25 μm film thickness) from Varian (Palo Alto, CA, USA). Helium carrier gas (99.9999% purity) was maintained at a flow rate of 1 mL·min-1 using an electronic flow controller. 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 transfer line and the ion source temperatures of the mass spectrometer were set to 280 °C. As outlined in Gherghel et al. [5], the values for the SPME extraction of the VOCs from fabrics was an incubation time of 5 min, an extraction time of 60 min, and an extraction temperature of 58 °C. The thermal

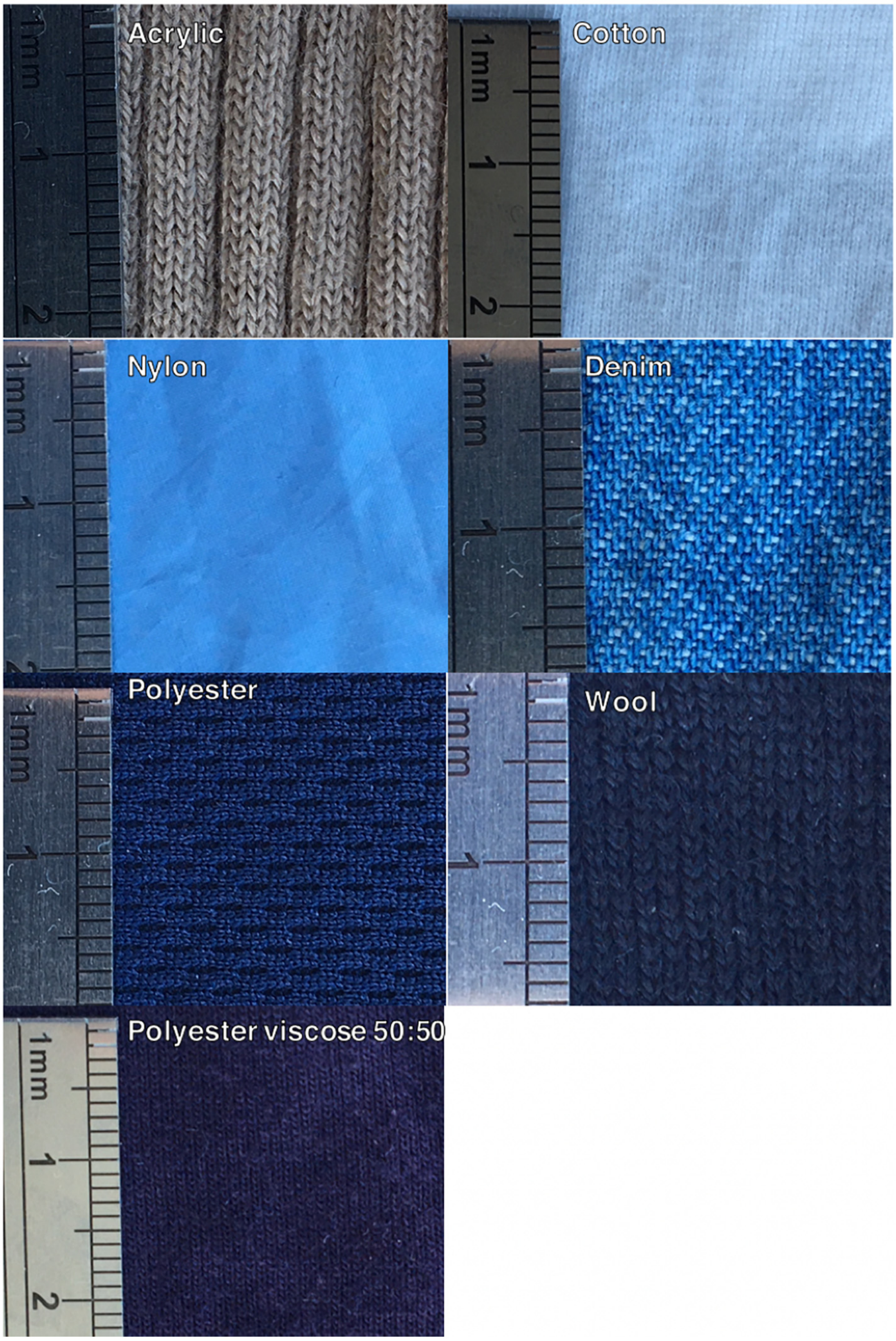

Fig. 1. Close-up photographs of the seven fabrics employed. Each individual mark on the ruler represents 1 mm.

desorption of the SPME fibre was carried out using an injector temperature of 250 °C in splitless mode for 3 min. 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.

A portable thermometer-hygrometer (model 82,021, VWR Scientific) was employed for measuring the laboratory temperature and humidity. Throughout this study, the laboratory ambient temperature ranged between 19 and 23 °C, and the humidity ranged between 25 and 48%.

Work carried out by Gherghel et al. [24] looked at the transfer of fragrances between fabrics using two different transfer methods, one that involved hand rubbing, and one that involved the two fabrics being left in contact under the pressure of a heavy weight. The authors identified that the two procedures led to similar number of perfume ingredients being transferred, however lower reproducibility was observed for the hand rubbing method. To overcome this issue, and to simulate closer to reality a sexual assault case where friction between fabrics occurs, a motorised crockmeter (Fig. 2) was used to simulate the transfer between fabrics. The crockmeter, also called a fabric abrasion tester, is generally used in the textile industry to determine the amount of colour transferred from fabrics to other surfaces by rubbing, however it has also been used in the published forensic science literature to simulate fabric contact in a reproducible way [25,26].The crockmeter finger covered with a piece of the primary fabric spiked with the VOCs was rubbed against a blank recipient sample fabric under a fixed load of 9 Newtons.

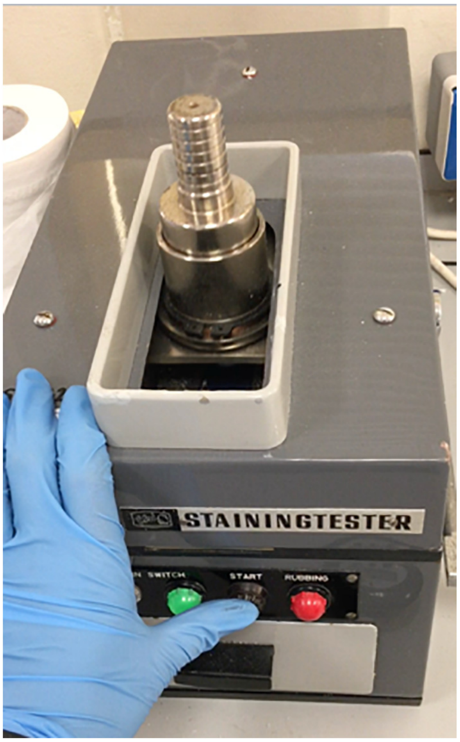

Fig. 2. Crockmeter employed to carry out the fragrance transfer between fabrics.

2.3. Preparation of solutions and experiments

A quality control process was applied by the analysis of blank samples after every three replicate samples in order to verify that no contamination of the fabrics, lab materials or instrument was observed. The series of three experiments were carried out as presented in Fig. 3. A swatch of primary material was spiked with VOCs, left to dry for a period of time called perfume ageing time (PAT), followed by transfer of fragrances onto a secondary piece of fabric for a period of time (referred to as contact time) using a crockmeter. The time from the transfer until analysis (the persistence time), was kept at 0 s for the purpose of this study.

2.3.1. Perfume ageing time and contact time experiments

For the perfume ageing time and fabric contact time experiments, a fragrance mix (FM1) containing 500 μM of each of the six VOCs, as well as 200 μM of the two internal standards was prepared in methanol. The fragrance levels in a typical personal-care perfume are in the range 0.5–2 wt% [27]. The fragrance levels for FM1 were between 0.008 and 0.009 wt%, 50 times lower than the regular lower limit of 0.5 wt%.

A cotton swatch of approximately 3 × 3 cm (primary material) placed in a clean Petri dish was spiked in the centre with 10 μL of the FM1 using a Hamilton syringe, following the method of Gherghel et al. [5]. For the ageing time experiments, the fabrics, in triplicates, were left on the Petri dish from 10 min up to 24 h, with a leftover sample being used for 48 h. For the contact time experiments, the fabrics, in triplicates, were left on the dish for a constant ageing time of 10 min. After the appropriate ageing time, the spiked primary fabric was placed onto the finger of the crockmeter for the fragrance transfer onto a secondary piece of cotton swatch (the recipient material). For the perfume ageing time experiment, the contact time was kept constant at 1 min, while for the contact time experiment the time varied from 10 s to 10 min. After the appropriate contact time, the recipient fabric was removed from the crockmeter, weighed, then added to a 20 mL vial, to which 10 mL of water were added, prior to agitating the vial using a vortex for 30 s.

2.3.2. Fabric type experiment

The fabric type experiment was carried out in a similar manner to the first two experiments with a few modifications. The spiking fragrance mixture (FM2) contained 2 mM of each of the six VOCs in methanol. The internal standard mixture was prepared separately at a concentration of 20 μM of the two IS in methanol. The FM2 was spiked onto the primary piece of fabric as above, however the internal standard mix was added to the secondary piece of fabric (the recipient) prior to adding it to the vial and adding the 10 mL water. In this way, the internal standards were not submitted to the transfer process and they were only used for the GC calibration step. Quantitative curves were verified when standards were submitted to the SPME GC–MS analysis checking the consistency of the extraction efficiency and instrumental response along the calibration range.

The ageing time was kept at 0 min, and the contact time at 1 min. Whilst the two time-related experiments above, used cotton for both the donor and the recipient material, for the fabric type experiment, all seven fabrics available were used as primary materials, and cotton and polyester were used as recipient materials. However, when the nylon fabric was used as a donor material it kept slipping off the crockmeter finger, even for contact times as short as 1 min, and therefore it could not be used.

The inclusion of an internal standard just prior to extraction allowed for quantification using calibration curves. Six different calibrant concentrations of the six studied VOCs were prepared in methanol, ranging from 0.2 to 200 μM. The same internal standard mixture of 20 μM in methanol used for the samples was used for the calibration. The calibrants were spiked directly onto cotton or polyester swatches, followed by spiking with the internal standards mixture. The fabrics were then added to a 20 mL vial, to which 10 mL of water were added, prior to agitating the vial using a vortex for 30 s.

2.4. Data analysis

The quantitative composition of the VOCs recovered from the primary fabrics was evaluated by hierarchical cluster analysis (HCA), principal component analysis (PCA), and partial least square (PLS) analysis using the software programme SIMCA-P 12.0.1. (Umetrics AB, Umeå, Sweden).

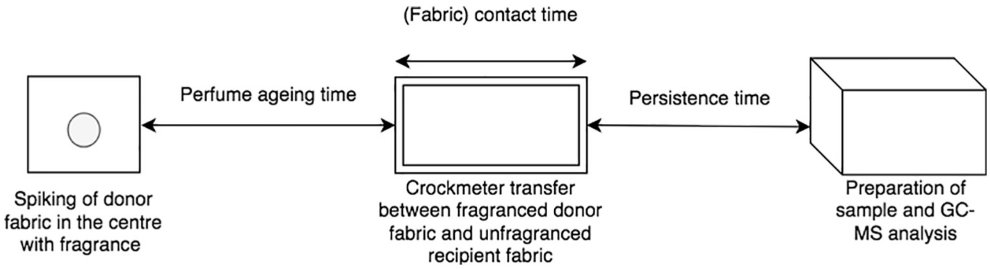

Fig. 3. Schematic of the fragrance transfer experimental process.

3. Results

3.1. Perfume ageing time

For this experiment, the internal standards were added to the FM1 used to spike the primary piece of fabric. It was observed that by varying the perfume ageing time (PAT), besides the expected change in the amounts of VOCs recovered, there was also a considerable change in the amounts of internal standards recovered. Fig. SI-1 presents scatter plots with error bars for the internal standards, with each point representing the mean peak area, whilst the error bars represent the relative standard deviation (RSD) of the three replicates. This figure shows how for both dibromobenzene and methyl nonanoate, very large chromatographic peak areas were obtained using an ageing time of 1 h, compared to all perfume ageing times investigated. This behaviour might be due to time needed to reach equilibrium and therefore, it was deemed that the internal standards as used here are not appropriate for quantitation.

Instead, the recoveries of the VOCs were calculated using as control two reference samples. These reference samples were fabric swatches spiked with the FM1 and analysed at the beginning and at the end of the batch of the sampling sequence. Average peak area values were considered for comparison with those obtained experimentally. Additionally, the fabric weight was taken into consideration for a more accurate calculation. And so, the amounts of analytes recovered from the recipient fabrics are reported in % as sample analyte peak area per fabric weight divided by the reference analyte peak area per fabric weight.

By varying the period of time that a fragrance mix has been on a primary piece of fabric, prior to transfer, considerable differences in the amount of VOCs recovered from the secondary piece of fabric were observed (Fig. 4). Generally, and especially for lower volatility molecules, it was noted that a short PAT lead to higher amounts recovered from the secondary fabric. Linalool, geraniol, and eugenol follow a typical decay curve, where high amounts were recovered for short times followed by a steady decrease until a plateau was reached. For example, for linalool approximately 3% of the total 100% reference peak area was recovered from the secondary fabric using a 10 min PAT, and then the recovery slowly decreased with the time increasing, so that at 1 h PAT around 1% was recovered, at 3 h around 0.4%, after which it levelled off until 48 h PAT. Limonene and ethylene brassylate display an initial spike prior to the decay curve, at 3 and 1 h PAT, respectively. For pinene the trendline is not very clear.

Moreover, it was noted that different VOCs were recovered at different rates as it can be noted on the y scale in Fig. 4. For example, for pinene, very small amounts were recovered from the recipient fabric for all ageing times, between 0.005 and 0.05% of the original spiked amount. In comparison, the lower volatility compounds were recovered in higher levels (2–5% of the amount spiked on the original fabric), especially for shorter PAT.

Additionally, when looking at the error values for the triplicate samples, it can be observed that good RSD values ($n = 3$) were obtained for most samples. Pinene displays higher RSD, with values between 9.8 and 76% for PAT lower than 6 h. The pinene recoveries are generally around 100 times lower compared to low volatility compounds, which can explain the higher RSD. It should be noted that only one sample was available for the 48 h time, and so no RSD values are available for this time.

3.2. Contact time

For the contact time study, the donor and recipient fabrics were rubbed against each other using the crockmeter for a series of different lengths of time ranging from 10 s (0.17 min) to 10 min. It was noticed that with the longest contact time (10 min), there was a higher risk of the primary piece of fabric becoming detached from the crockmeter finger, in which case a new sample was prepared.

Similar to the PAT experiment, the internal standards added to the fragrance mix behaved differently depending on the contact time (Fig. SI-2), thus the quantification of VOCs from the samples was again carried out without the use of internal standards, but rather using reference samples spiked with FM1, and thus the amounts of VOCs recovered are expressed as percentages.

As can be seen in Fig. 5, for all six VOCs, with an increase in the contact time between the fragranced fabric and the fragrance-free fabric, a consistent amount of analyte was recovered for contact times of up to 3–5 min, after which the recovery slowly decreased. For example, for linalool the mean recoveries were between 18 and 25% for contact times of 10 s to 5 min, and around 10% for a contact time of 10 min. The lowest recoveries were at 10 min contact time for all six analytes.

As observed with the perfume ageing time experiment, there were big differences in the amounts of limonene and pinene recovered from the donor materials compared to lower volatility compounds. Generally, around 0.5% of pinene and 1% of limonene were recovered from the secondary piece of fabric, whilst for the other four VOCs the recoveries were generally between 15 and 35%.

3.3. Fabric type

For the last transfer experiment, seven different fabrics, shown in Fig. 1, were employed as donor materials and two of these (polyester and cotton) as recipient materials.

- SEM analysis

The fabrics were examined under SEM to establish the fabric weave characteristics and to provide insight into how these characteristics might play a role in the transfer of fragrances. The SEM results (Fig. 6) show the seven different fabrics using a 250× resolution. In terms of width, the wool fibres had the largest fibre width and nylon the smallest. Acrylic, nylon and polyester show smooth and regular surfaces, wool a scale-like structure, and cotton a ribbon like structure. Although denim is made of 100% cotton, there is a clear difference in the weave of these two materials, with denim showing tightly woven fibres. Also noticeable is the dissimilarity between the 100% polyester material and the 50/50 blend of polyester and viscose. Whilst the former presents more order and it has depth, the latter presents many loose fibres. Nylon, a waterproof material, shows a very ordered structure, with no gaps between the fibres.

- VOCs analysis

For the quantification of the six VOCs from the fabric type samples, calibration curves were carried out in both cotton and polyester. As the calibrants span a large range of concentrations from 0.2 to 200 μM, weighted curves were fitted which apply more emphasis to some concentration points than others, specifically to the lower concentration points. The weighting factors are generally between 0 and 1, and most commonly are $1/x$ or $1/x^2$, where x is the concentration [28]. The results of fitting weighted curves are shown in Table 1. With the exception of α-pinene in polyester which was fitted to a linear curve, all other calibrations were fitted to quadratic curves. Excellent R^2 were obtained for all curves with values above 0.996, with the exception of ethylene brassylate in cotton for which the R^2 was 0.988.

For the fabric type experiment, a natural (cotton) and a synthetic (polyester) fabric were used as recipient fabrics, whilst six of the seven fabrics available were used as donor materials. The name of the samples starts with the name of the donor material, followed by the name of the recipient material, so that for the sample "acrylic_polyester" the fragrance mix was pipetted onto acrylic, and then transferred onto a polyester material using the crockmeter for a contact time of 1 min.

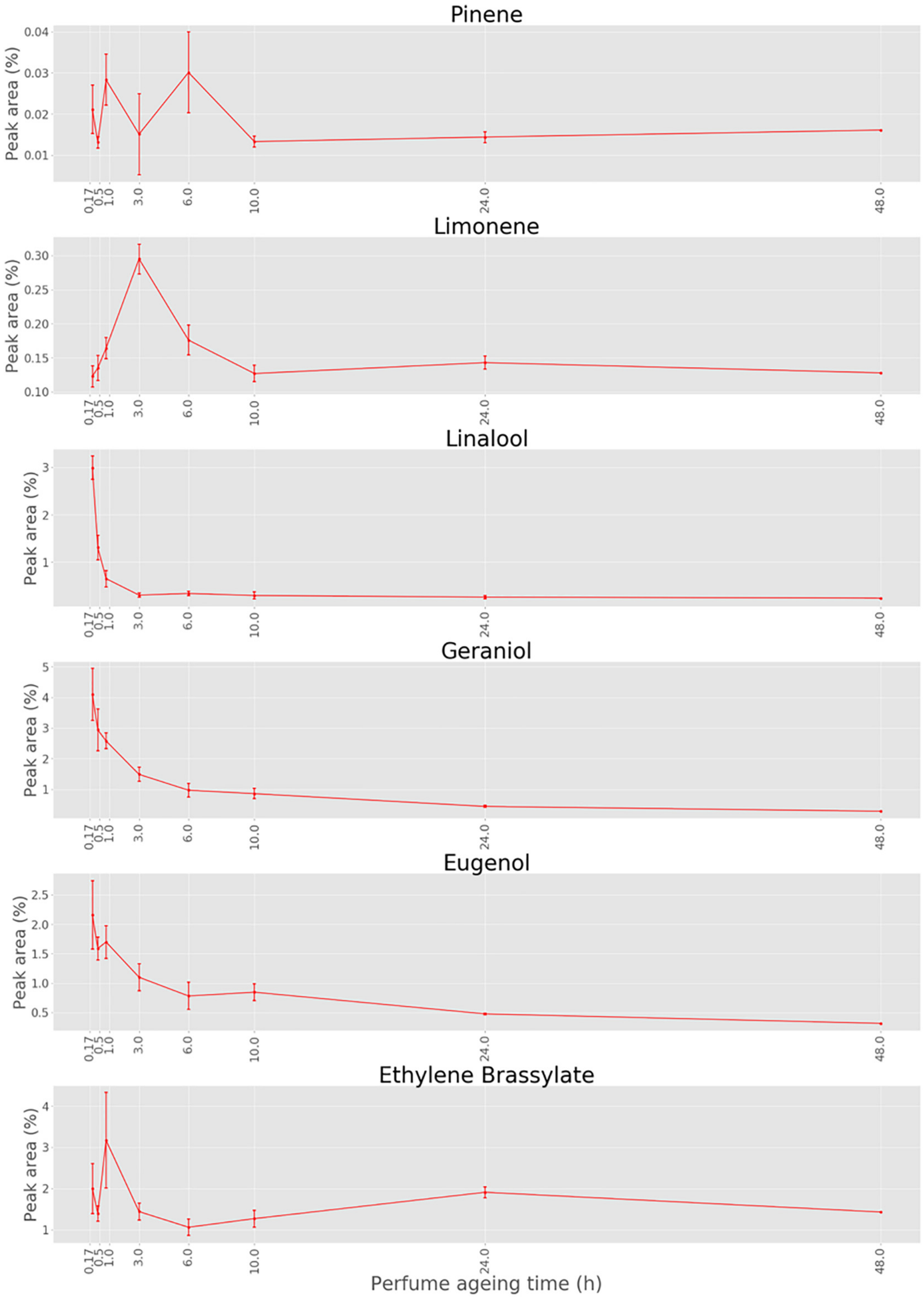

Fig. 4. Recovery of the six analytes from the secondary piece of fabric when the perfume on the primary piece of fabric was aged for different periods (10 min to 48 h) prior to contact. The error bars are standard deviations (n = 3). The difference in scaling between analytes should also be noted.

As noted for the two time-related experiments, very low amounts of α-pinene are transferred and recovered from recipient fabrics. This was also observed in the fabric type experiment, even though FM2 contained a higher concentration of VOCs compared to the FM1 used for the other two experiments. Many samples led to the recovery of this compound below the lower limit of the working range (0.5 µM in cotton and 0.2 µM in polyester), and so only the other five VOCs (limonene, linalool, geraniol, eugenol, and ethylene brassylate) were employed for data analysis.

To obtain an overview and a visual representation of the samples (6 blanks + 6 donor fabrics * 2 recipient fabrics * 3 replicates) principal component analysis (PCA) was employed. PCA is an unsupervised method (no labels are given) that reduces the dimension of the data with the aim of retaining as much information as possible. It creates an artificial set of variables, called principal components, that account for the most variance in the data set. PCA showed a clear separation of the

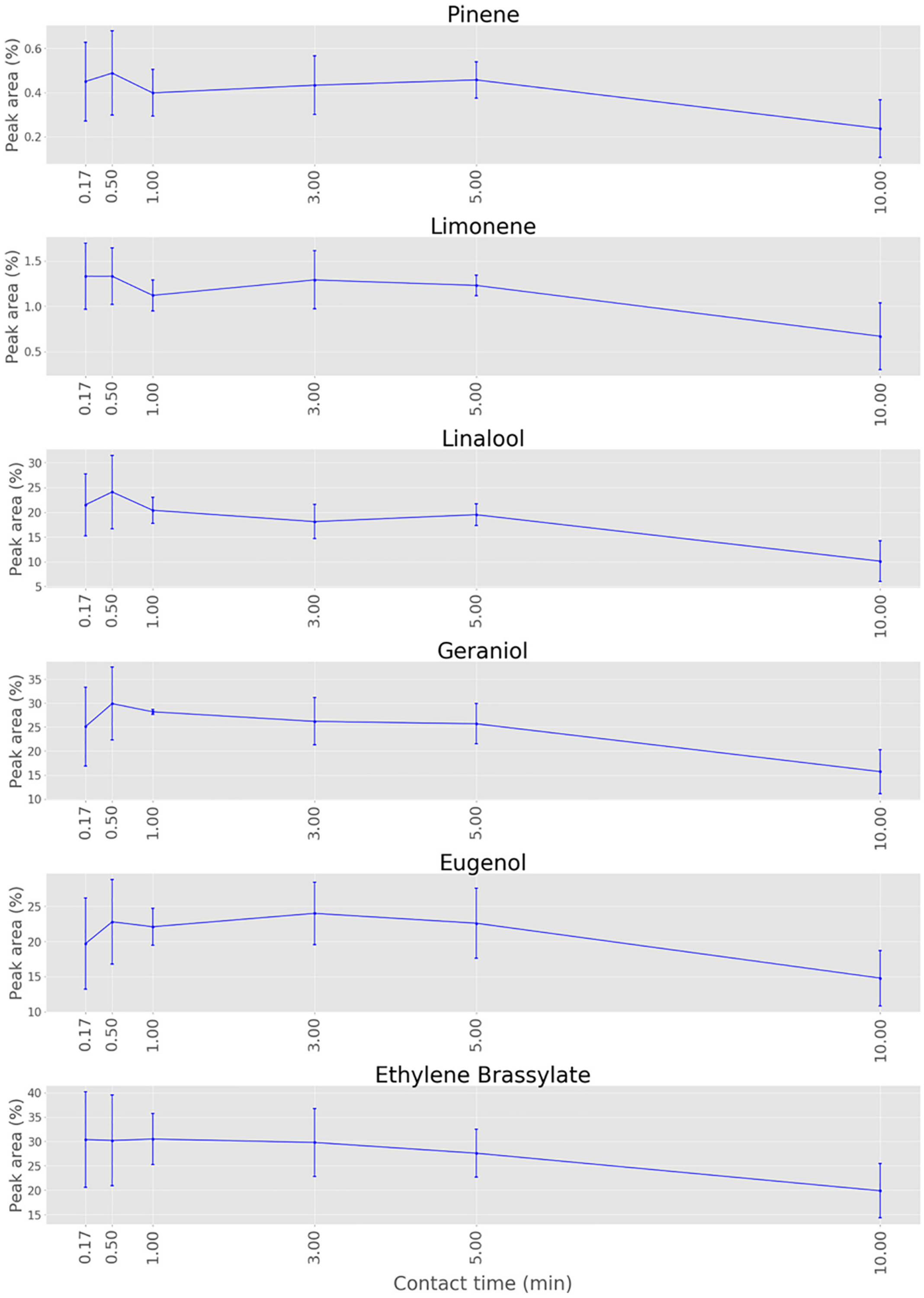

Fig. 5. Recovery of the six analytes from the secondary piece of fabric when the contact between the fabrics varied from 10 s to 10 min. The error bars are standard deviations ($n = 3$). The difference in scaling between analytes should also be noted.

blank samples in the set of 42 samples (Fig. SI-3). The sum of three principal components accounted for 89.1% of the total variability.

Further statistical analysis was carried out without the blanks. It was noticed that when the 36 fabric type samples were used to create a new PCA model, the Distance to model (DModX) analysis identified the viscose_cotton_R3 sample as being an outlier (Fig. SI-4). This sample displays the largest portion of unexplained variation as it is the farthest away from the model plane and above the critical distance.

The new PCA permitted a reduction of the 35 samples to three principal components. These three PCs were extracted explaining 98.1% of the total variance of fabric type samples. The obtained three-dimensional PCA representation is colour coded in Fig. 7a-b according to the recipient material (polyester or cotton), the donor material (the six fabrics), or as a combination of recipient and donor material (12 different groups). In Fig. 7a it can be observed that the transfer of perfume from all different materials onto cotton is very different from

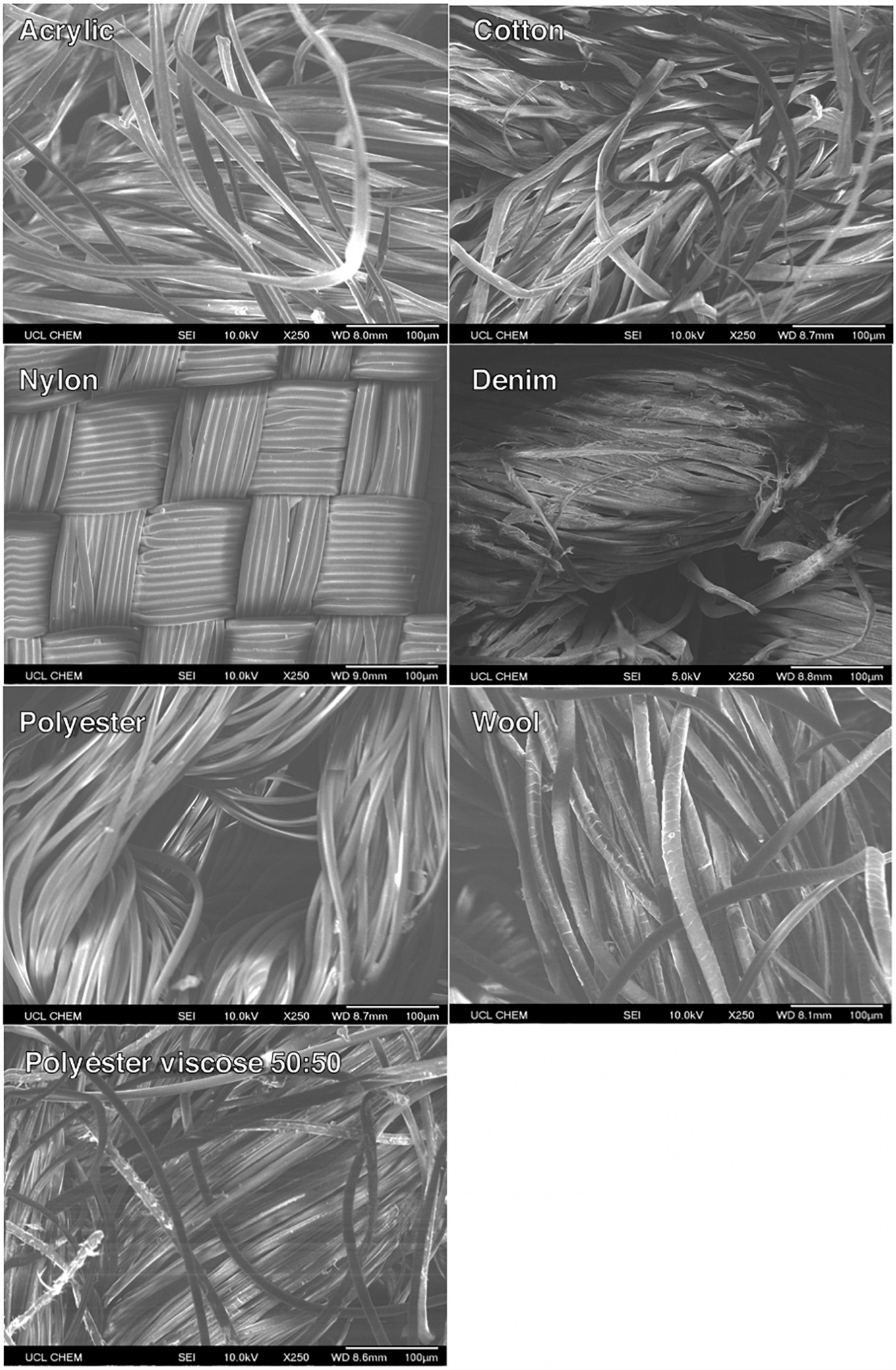

Fig. 6. SEM images showing the seven fabrics using a 250× resolution with the man-made blends on the left side and the natural blends on the right side.

the one onto polyester. The two groups are clearly distinguishable between each other, as emphasised by the dashed circles. In Fig. 7b, it can be observed that the acrylic fabric as a donor it is clearly different from the rest of the fabrics studied, when transferred to polyester. Moreover, Fig. 7b shows how the three natural fibres tested, cotton, denim, and wool exhibited a similar transfer behaviour when transferred onto polyester (highlighted by the ellipse), with the exception of one wool replicate. However, when the VOCs were transferred to cotton, the natural fibres were also close or overlapping on the PCA with some man-made fibres.

Table 1
Calibration results for the fabric type experiment.

Compound	Matrix	R^2	Calibration curve	Working range (μM)
α-Pinene	Cotton	0.998	$Y = -0.00042{*}X^2 + 0.62552{*}X + 0.15118$	0.5–200
	Polyester	0.996	$Y = 0.42279{*}X + 0.00019$	0.2–200
Limonene	Cotton	0.999	$Y = -0.00225{*}X^2 + 2.04015{*}X + 0.48393$	0.2–200
	Polyester	0.999	$Y = -0.00107{*}X^2 + 1.41214{*}X + 7.15824$	0.5–200
Linalool	Cotton	0.999	$Y = -0.00041{*}X^2 + 0.25149{*}X-0.00799$	0.5–200
	Polyester	0.999	$Y = -0.00019{*}X^2 + 0.14212{*}X-0.03347$	0.5–200
Geraniol	Cotton	0.999	$Y = 0.00019{*}X^2 + 0.12994{*}X-0.03017$	0.5–200
	Polyester	0.998	$Y = 0.00003{*}X^2 + 0.11365{*}X-0.00327$	0.5–200
Eugenol	Cotton	0.998	$Y = 0.00012{*}X^2 + 0.03240{*}X + 0.00682$	0.5–200
	Polyester	0.999	$Y = 0.00005{*}X^2 + 0.06418{*}X-0.00637$	2.5–200
Ethylene brassylate	Cotton	0.988	$Y = 0.00002{*}X^2 + 0.00317{*}X + 0.03172$	0.5–200
	Polyester	0.999	$Y = 0.00008{*}X^2 + 0.03283{*}X + 0.00476$	0.2–200

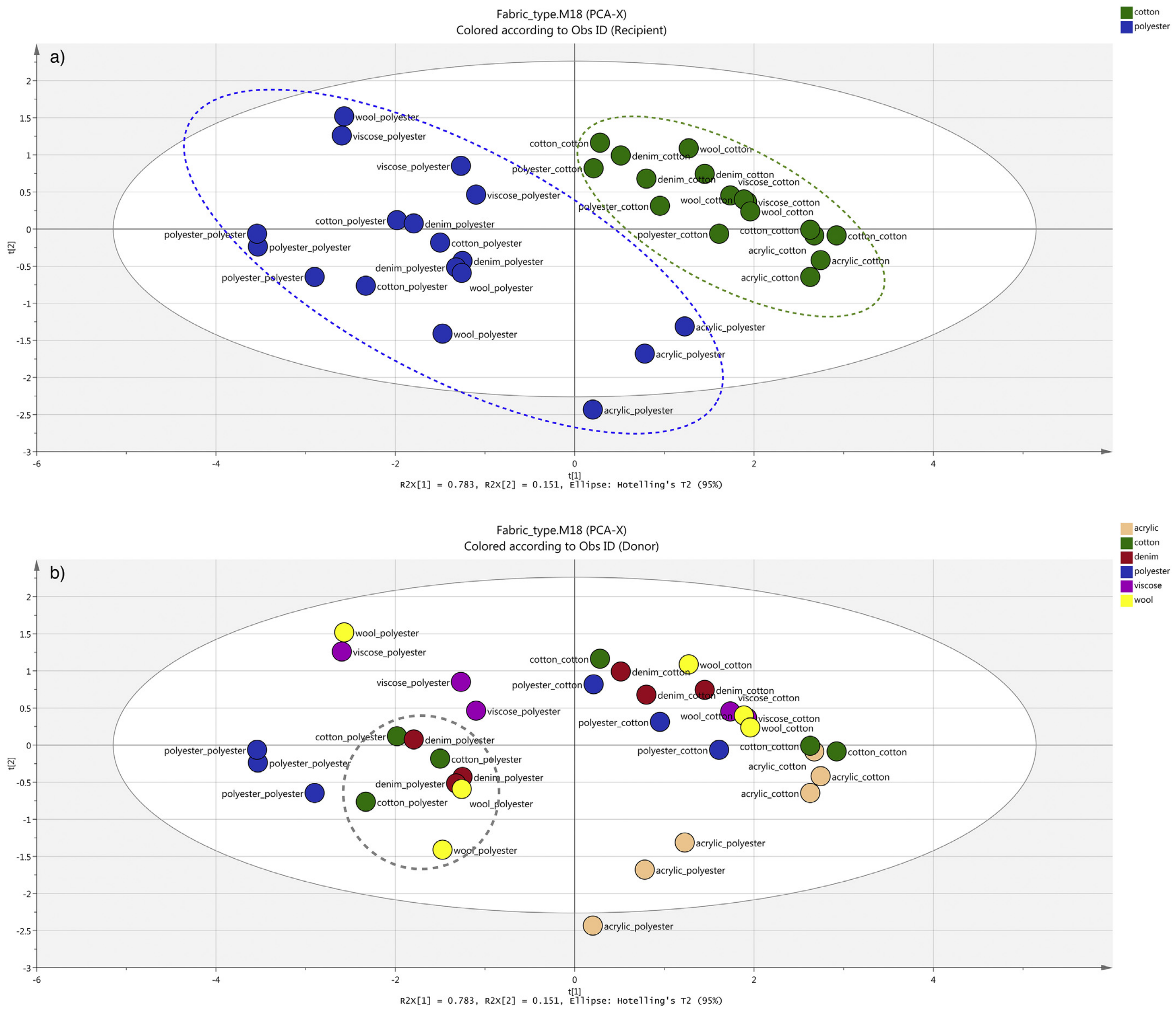

Fig. 7. PCA representations using peak areas of 5 VOCs (limonene, linalool, geraniol, eugenol, ethylene brassylate) from the fabric type transfer data, and coloured by: a) the recipient fabric, b) the donor fabric. The ellipses were drawn on to facilitate identification.

To explore and identify structures within the data gathered, hierarchical cluster analysis (HCA) was employed. HCA is an exploratory data analysis algorithm for the organisation of samples in groups and among groups depicting a hierarchy. The result of HCA is generally presented in a dendrogram (Fig. 8). With one exception, the dendrogram shows that the samples separate clearly into two major groups according to the recipient fabric, cotton and polyester. The three acrylic to polyester samples were misassigned by the HCA as belonging to the

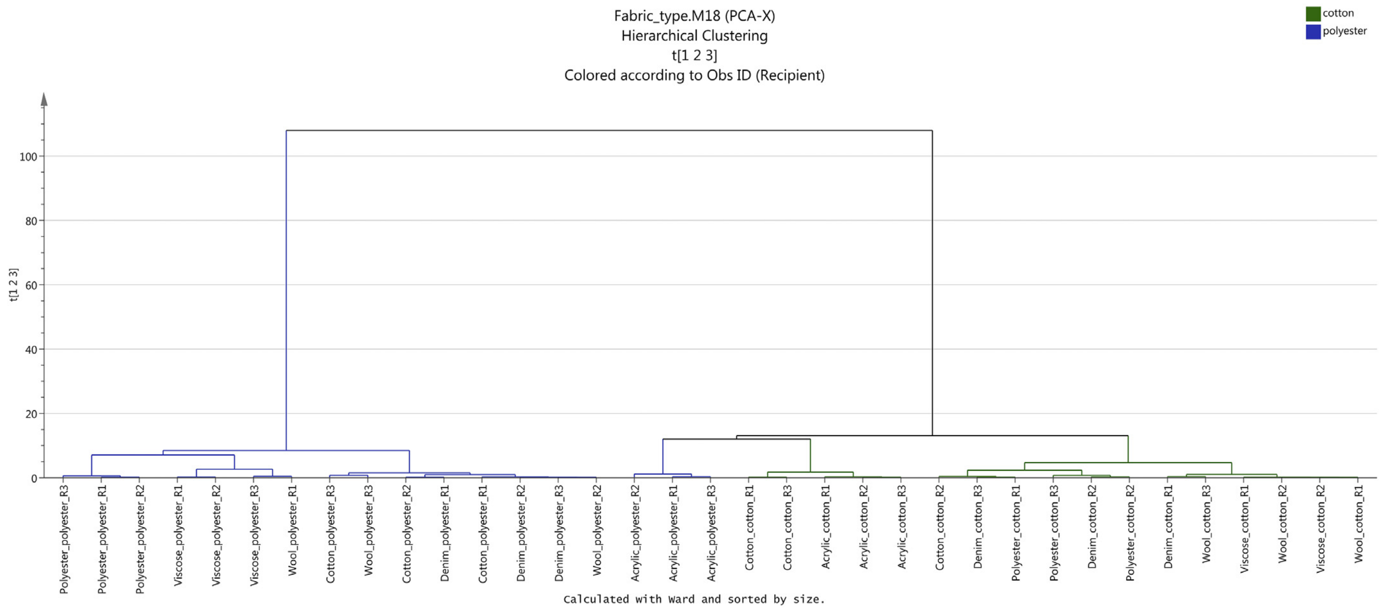

Fig. 8. Dendrogram obtained by hierarchical cluster analysis using the samples from the fabric type experiment.

cotton recipient samples. These samples were close to the cotton recipient samples in the PCA, as it can be observed in Fig. 7b. Within these two major HCA groups, various subgroups are formed. It can be observed how all three polyester to polyester replicates are grouped together, showing minimal dissimilarity. However, it can be observed that not all triplicates are grouped together, and there is an overlap for some samples, for example the replicate 3 of wool to polyester samples is grouped with viscose to polyester samples. Such overlap in the triplicates can also be observed in the PCA in Fig. 7b.

Finally, a PLS (partial least square) discriminant analysis was used to determine a model able to predict the nature of the recipient fabric depending on the transfer of the VOCs studied. The graphical result is shown in Fig. 9. The model was able to successfully distinguish the two groups, accounting for 96% (R^2 value of 0.96) of the variance in the observed samples for the training set. The Q^2 value obtained was 88.8%. The Q^2 value is an estimate of the predictive ability of the model and is a result of the cross-validation, where a 1/7th of the data is removed at a time, and the model's prediction ability is tested.

4. Discussion

To our knowledge, these are the first experimental studies carried out on the transfer process of fragrances between fabrics for forensic applications using an optimised and validated SPME-GC–MS method. Three variables (fabric type, perfume ageing time and fabric contact time) considered to have an important effect on the dynamics of the transfers were investigated, following the studies of Bull et al. [4] and Hudson et al. [23], which demonstrated the importance of material type and the dependence of perfume volatility with time. The experiments for this study were also designed to closely recreate the type of contact between fabrics relevant to a sexual assault case.

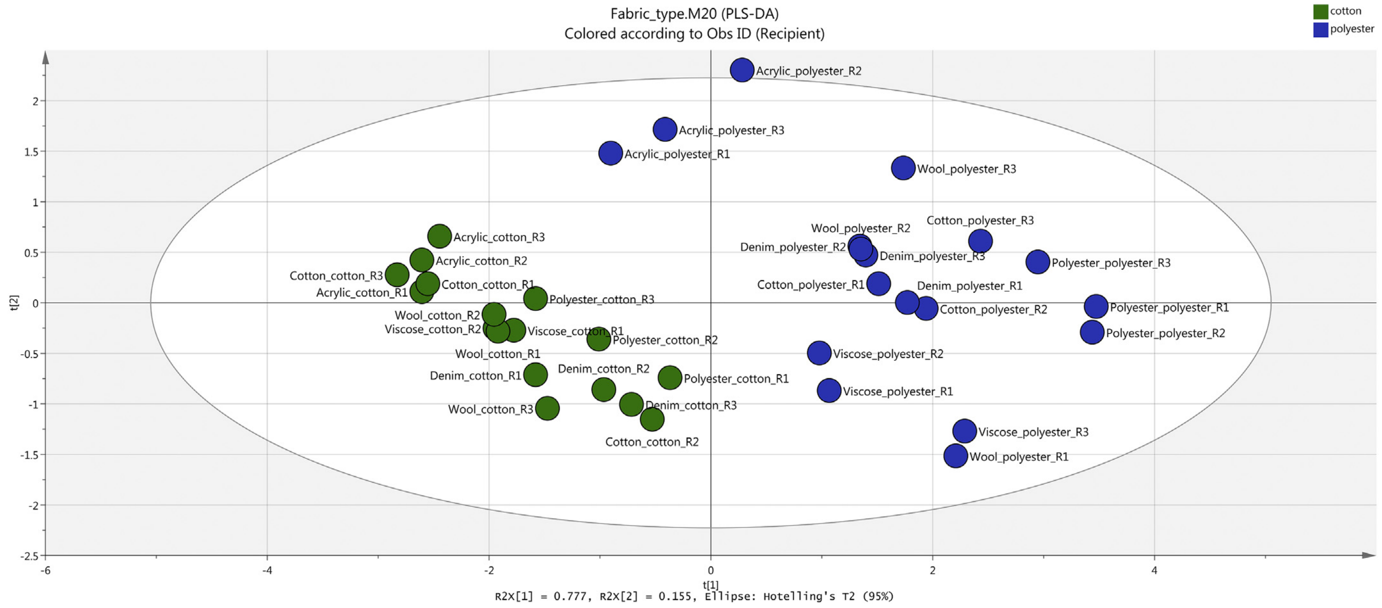

Fig. 9. Partial least square (PLS) discriminant analysis representation showing the classification of the transfer type samples based on the donor material.

4.1. Perfume ageing time

As the samples were spiked with the VOCs and the internal standards at the same time, it was observed that the behaviour of the internal standards during the transfer process at various PAT was not constant. Therefore, the internal standards were deemed not suitable for the quantification of the VOCs. Instead, the amount of VOCs recovered from the recipient cotton swatches was calculated using the reference amounts of VOCs from a spiked cotton swatch, i.e. the amount of VOCs on a primary swatch.

Overall, longer perfume ageing times led to lower amounts of VOCs being recovered from the secondary piece of fabric. Lower volatility compounds, such as linalool, geraniol, and eugenol followed a typical decay curve, identified in many other forensic studies concerning the persistence of traces on clothing, such as by Dachs et al. [29] for hair scalp and Robertson et al. [25] for textile fibres. Additionally, it was observed that for all perfume ageing times very low amounts of high volatility compounds, such as pinene and limonene were recovered from the donor fabric, with values lower than 0.04% for pinene and 0.3% for limonene, when compared to a reference spiked fabric. For the other VOCs, the recovery was generally between 0.5 and 5%. This suggests that highly volatile compounds might not be suitable candidates for forensic VOCs analyses.

Moreover, when looking at the RSD values for the triplicate analytes at all ageing time, it can be observed that large RSD values were obtained for pinene, with values between 9.8 and 76%. This further consolidates the point of view that such high volatility compounds may have limited value in forensic studies, firstly because they transfer in very small amounts for all ageing time studies, and secondly because of the high variability. On the other hand, lower volatility compounds presented lower RSD values, higher recovery rates, and steady decay curves. Ethylene brassylate, the least volatile compound, showed an initial spike in recovery for an ageing time of 1 h prior to the decay curve.

4.2. Contact time

Once again, the quantification was carried out using reference samples that had been directly treated with the VOCs. Generally, for contact times between fabrics from 10 s up to 3–5 min, no discernible differences in the amount of VOCs recovered from the secondary piece of fabric were observed. The recovery did decrease for longer contact times, such as 10 min. This is in contrast with work carried out by Gherghel et al. [24], where an increase in the amount of VOC recovered from the donor fabric was observed for longer contact times between fabrics. This can be potentially explained by the difference in the transfer methods between the two studies. In Gherghel et al. [24], the two fabrics were kept in contact under the pressure of a weight. The weight could act as a hermetic seal, not allowing the evaporation of VOCs. In the current study, a crockmeter was employed to better simulate the reality of a sexual assault case. The fabrics were rubbed against each other under high pressure, and thus generating heat by the friction. The increase in temperature could lead to the evaporation of some compounds with a longer contact time, and thus explain the lower recovery rates observed for the longest studied contact time of 10 min.

Similar to section 4.1, small amounts of pinene and linalool were recovered from the recipient fabric, compared to the lower volatility compounds. So that, for shorter contact times, the recoveries for pinene and limonene were around 0.5 and 1.2%, respectively, whilst for the other VOCs the recoveries were around 20–35%.

4.3. Fabric type

Scanning electron microscopy was employed to obtain information about the structure of the fabric and the weaving patterns of the seven different fabrics, both natural and man-made. The nylon fabric, originating from a waterproof jacket, was a tightly woven fabric, which can explain its natural low permeability. All other fabrics presented gaps between threads or bundles of threads, allowing for air or liquid flow. The fibre structure varied between the fabrics studied, with synthetic fibres generally showing smoother surfaces (Fig. 6). However, studies such as DeGreeff et al. [30] and Prada et al. [22] have shown that both the fabric weave and the molecular structure play a role in the transfer of human scent to fabrics.

When looking at the transfer of VOCs onto cotton and polyester, clear differences were readily noticeable in the PCA plot (Fig. 7a) and in the HCA dendrogram (Fig. 8) with two distinctive groups formed based on the recipient material. Moreover, a PLS-DA model was able to discriminate between the two recipient fabric samples with a R^2 value of 96% (Fig. 9).

Within these two major groups, various donor samples were distinctive. For example, when acrylic was used as the donor material this appeared on the 3-D PCA well discriminated from the rest of the samples, especially when polyester was used as the recipient fabric (Fig. 7b). In spite of the weave differences observed by SEM analysis, the natural fabrics (cotton, denim, wool) showed overlap on the PCA, especially when the VOCs were transferred from these fabrics onto polyester.

5. Conclusions

The transfer behaviour of six VOCs between fabrics has been investigated in this study. All factors studied, the perfume ageing time, the contact time, and the fabric type, affected how volatile compounds are transferred onto a secondary piece of fabric.

The results from the perfume ageing time study showed that lower volatility compounds were recovered from recipient fabrics in higher amounts compared to higher volatility compounds. It was also observed that the longer the time period since fragrance VOCs have been applied to a piece of fabric, the lower the recovery of compounds from the secondary piece of fabric (Fig. 4). This decrease follows a typical decay curve, where the recovery drops considerably for the samples when the fragrance mixture was aged for 1 to 3 h, after which the recovery drops steadily. Perfume traces were recovered from the recipient fabric even when the perfume was aged on the donor fabric for as long as 48 h.

The data from the contact time experiment demonstrated that even for contacts as short as 10 s, VOCs were successfully transferred and recovered from recipient cotton swatches. Moreover, the amounts recovered for all six VOCs maintained rather constant for the first 5 min of contact, after which a decrease was noticed (Fig. 5). This can be explained by the evaporation of VOCs with increased rubbing time, and thus increase in the heat generated by rubbing the fabrics together.

When looking at the fabric type, clear differences were observed in the VOCs behaviour when they were transferred onto cotton and onto polyester. Two distinctive groups were determined by the PCA based on the recipient fabric (Fig. 7a). On the other hand, when looking at the influence of the primary fabric for each of these two groups, some samples were distinctive, whilst other samples displayed some overlap on the PCA plot (Fig. 7b).

Overall, this study has confirmed that VOCs have the potential to be a helpful form of trace evidence as detectable amounts were recovered from a recipient fabric for fabric contacts as short as 10 s and when the perfume on the donor fabric was applied as long as 48 h prior to transfer. However, factors that affect the transfer, such as the ones studied here, should be taken into consideration when seeking to interpret the presence of VOCs traces recovered from fabrics. Further studies will be beneficial to test the variability in the number and abundance of VOCs that transfer and persist under different environmental conditions. For forensic reconstructions where clothing from two individuals may have been in contact, such as a sexual assault, this study indicates that there may be value in testing the clothing items for VOCs. Depending on the type of fragrance originally applied, these findings indicate that it may be possible to identify specific fragrance compounds on clothing exhibits which may provide trace specimens that can contribute to a forensic reconstruction seeking to establish whether a contact may have taken place.

Declarations of interest

None.

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