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The Potential Interference of Body Products and Substrates to the Identification of Ignitable Liquid Residues on Worn Clothing

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ABSTRACT

The question of whether deposits on clothing as well as their chemical composition are being mistaken for ignitable fluids is a concern for forensic analysts. Body products and oil secretions can have similar chemical profiles to ignitable liquid residues (ILRs) as a result of comparable chemical compounds that may be found in both sources. This study investigated whether substrates of unworn and worn clothing, with endogenous body secretions and body products could interfere with ILR analysis. Sample extraction was completed by passive headspace concentration with activated charcoal strips (ACS) and desorption with carbon disulfide followed by analysis with gas chromatography-mass spectrometry (GC-MS). Results showed that some body products produce similar patterns to heavy petroleum distillates and most clothing contained components that are commonly found in ignitable liquids. It was concluded that the clothing, body products and compounds released by the body all contribute to the GC-MS profile of worn clothing. These components can mimic or mask the presence of ILRs, however educated and experienced analysts would likely be able to differentiate these substrate patterns from ILRs.

KEYWORDS: forensic science, fire debris analysis, ignitable liquid residue, gas chromatography-mass spectrometry,

1. Introduction

In suspected arson cases involving clothing items, criminalists may question whether an ignitable liquid residue (ILR) is present or rather, if chemicals inherent in the clothing substrate have contributed to the pattern seen in the gas chromatogram. This is an under-explored problem of high importance, however there is minimal research in the forensic literature addressing this issue [1]. Differentiation between an ILR and its clothing substrate materials is of significant value, and can be the deciding factor facilitating a determination as to whether arson had actually been committed.

A useful case example is that of "State of Georgia v. John Metcalf and Kimberly Post" which involved a suspected arson fire. A man was wrongly accused of the arson when the suspect's shoes were found to contain an ignitable liquid residue, toluene. It was later discovered by a consulting criminalist that the compound was not from an added ignitable liquid but was simply a component of the substrate [2].

The aim of this research was to determine if the chemical composition of worn and unworn clothing can be mistaken for an ignitable liquid when recovered from a possible arson scene or suspect. Crude oil is the starting material for many common materials, including beauty products and ignitable liquids, which are separated during the petroleum refining process [3]. The chemical composition of the substrate, in this study worn and unworn clothing, was analyzed for various endogenous body secretions and exogenous body products as a result of transfer from skin to clothing. These results were then compared to chemical profiles of common ignitable liquids, and classifications were based on ASTM E1618 [4].

There is little research that has been done to investigate whether moisturizers, medical creams, perfumes and other items applied to the body can interfere with the process of identifying ignitable liquid residues on substrate materials such as clothing. This deserves attention because many of the same chemicals found in clothing can also be found in ignitable liquids such as kerosene [1]. A study done on clothing and fibers for the misidentification of an ILR, observed "a strong pattern typical of kerosene" for a pair of unworn spandex pants heated to 90°C in a polyester-lined paint can [1]. Other clothing materials such as cotton have displayed a noticeably similar C_3-alkyl benzene pattern found in gasoline, but not so close of a chemical profile that an experienced fire debris analyst would mistake cotton for an ILR [1]. The varied composition of clothing can create a complex matrix for the identification of ILRs. When analyzing worn clothing for ILRs, chemicals the person may have applied to their skin or may have been excreted from body glands should be taken into consideration. Numerous compounds can be detected from a fire debris sample aside from any ILR that may be present. The source of such compounds cannot always be determined, and it is therefore an analyst's job to differentiate between what could be an ILR and what could be a substrate contribution with a GC-MS profile that closely mimics an ILR.

2. Materials and Methods

2.1. Materials

Four different clothing materials were obtained from various vendors: sports bras, mesh shorts, short sleeve t-shirts, and ladies socks. The sports bras were made of 10% spandex and 90% nylon (Forever 21, Los Angeles, CA), the mesh shorts (DANSKIN, New York, NY) were made of 100% polyester, the womens short sleeve t-shirts (Hanes Brands, Winston Salem, NC) were of 100% cotton content, and the ladies socks (Hanes Brands, Winston Salem, NC)) were composed of 44% cotton, 52% polyester, 1% nylon, 2% rubber and 1% spandex.

The six body products analyzed in this research were Vaseline® Petrolatum Jelly (Unilever, Englewood Cliffs, NJ), Secret® Shower Fresh women's deodorant (Proctor & Gamble, Cincinnati, OH), Aspercreme® (Chattem, Inc., Chattanooga, TN), Johnson's® Baby Oil (Johnson & Johnson, New Brunswick, NJ), Coconut Pineapple Fragrance Mist perfume (Bath and Body Works, Trumbull, CT), Nivea® Essentially Enriched lotion (Beiersdorf, Hamburg, Germany). The three body products that most closely resembled ILRs (Vaseline®, baby oil, and perfume) based on classifications detailed in ASTM E1618-14 [4], in addition to the deodorant, were used in the worn clothing experiment.

2.2. Sample Collection

Three women between the ages of 22 and 30 were chosen for this study because the body products and clothing items selected are more commonly worn across the young adult female population. The other criteria for the three women was that they weigh within the range of 100 to 150 pounds to decrease variability and enable the same size clothing to be purchased.

The subjects were requested to apply one of the body products used in the study to a specific location on their skin one time after they showered. The subjects were instructed to apply amounts of the products consistent with their usual application methods. With perfume, it was added via multiple sprays after clothing had been put on, while the Vaseline® and baby oil were rubbed into the skin directly. Clothing was then put on within 15 minutes of applying the body product received from the researcher.

Subjects wore the clothes over a period of 12 hours. Subjects recorded all of their daily activities including, where they went, what they ate, what shampoo/conditioner or soap was used in the shower and use of any external medications. Subjects were asked not to wear any other body products aside from what was given to them by the researcher, but were allowed to wear provided deodorant. Additionally, subjects were asked to avoid gas stations and other locations that may have the presence of an ignitable fluid. After 12 hours, the clothing items were placed into a provided arson evidence can (quart - bra/socks; gallon – shorts/shirt) and the lid secured with a hammer.

Each of the three subjects wore the four clothing items separately with the three body products, resulting in thirty-six different combinations of substrate, body product and human secretions. Three replicates were collected for each combination, except duplicates rather than triplicates were performed for nine of the pairings for subject 3 (shirt with baby oil, shirt with perfume, shirt with Vaseline®, bra with perfume, bra with Vaseline®, shorts with baby oil, shorts with perfume, socks with perfume and socks with Vaseline®) and one pairing for subject 1 (the bra and Vaseline®). One extra sample of each clothing item was collected from each person where no body product within the study had been applied, excluding the deodorant, to serve as controls.

2.3. Extraction

Passive headspace concentration with extraction by 8 mm x 20 mm activated charcoal strips (ACS) (Albrayco Technologies, Inc., Cromwell, CT) and desorption by carbon disulfide was used in this experiment [5]. All evidence cans were preheated at 135°C for 24 hours before use. All samples (neat body products, unworn clothing, and the worn clothing) were extracted in new cans, with the ACS, which were placed in an oven and heated to 80°C for 16 hours. After extraction, the ACS was removed and eluted with 500 µL of carbon disulfide. The extract was then analyzed by GC-MS.

2.4. GC-MS Analysis

All analyses were performed on an Agilent Technologies 6890N Network Gas Chromatograph with a 7683B Series Injector interfaced to a 5975 Mass Selective Detector with a quadrupole mass filter (Agilent Technologies, Santa Clara, CA). The GC

was equipped with an Agilent DB-5ms capillary column (30 m x 0.25 mm x 0.25 mm) The carrier gas used was Helium. The inlet port temperature was set at 250°C and a volume of 1 μL from the extract was injected by an Agilent Technologies 7683B series automated liquid sampler. The method included a split injection ratio of 5:1 for collected samples and a split injection ratio of 50:1 for the neat ignitable liquid dilutions and body product preliminary study samples. The GC oven temperature was programmed for an initial hold at 40°C for 1 minute, followed by a temperature ramp to 80°C at 6°C/min, then 80°C to 250°C at 15°C/min, and last held at 250°C for 8 minutes. The MSD transfer line temperature was set at 280°C. The mass spectrometer electron energy was 70 eV and the mass scanning range of the quadrupole mass analyzer was m/z 29-450 at a scan rate of 15.96 scan/sec with a solvent delay of 2.50 minutes. No solvent delay was employed for the initial body product study so that early eluting compounds could be detected and identified. Clothing samples, both worn and unworn, were analyzed with a 2.5 min solvent delay due to the absence of significant peaks prior to that time. The products continued for the worn clothing experiments were also re-analyzed with the solvent delay.

Compounds were identified by doing a similarity search of the mass spectrum against the NIST Mass Spectral Database (NIST14), followed by manual mass spectral interpretation of the library results to verify results. All identified compounds had a library search quality match in excess of 80, either in the initial analysis or after spectral subtraction of the baseline, except where noted. For the straight chain alkanes, identification was based on the presence of the molecular ion peak, mass spectral pattern, and established retention time when compared with a known standard. Alpha-numeric identification for each compound from the products (P), substrates (S), and human excretions (H) are provided to associate their identification with the peaks in the figures and tables.

3. Results and Discussion

3.1. Neat Body Products

Six neat body products were analyzed to determine which three to use in the worn clothing experiments. Deciding criteria were based upon the chromatographic pattern and what particular compounds were present that may be common with those in ignitable liquids. Table 1 lists the GC-MS identified chemicals in the extracts of deodorant, baby oil, perfume and Vaseline®.

Deodorant was provided to subjects to allow for good personal hygiene practices while keeping the applied body products controlled. The extract of deodorant had multiple peaks of high intensity (Fig. 1A). The range of response was 11.00 to 23.00 minutes. An intense peak at 11.45 minutes was identified as 2,2,4,4,6,6,8,8,10,10-decamethyl-1,3,5,7,9,2,4,6,8,10-pentaoxapentasilecane (P1), a common component of antiperspirants and cosmetics. The peaks between 16.00 and 23.00 minutes had a Gaussian pattern centered at 19.17 min, appearing similar to a heavy petroleum distillate but not as broad. However, these peaks were not identified as straight-chain alkanes, which they are in heavy petroleum distillates, with the exception of heptadecane (P6) at 16.39 minutes. Additionally, several oxygenated compounds, such as esters, were identified that could possibly be found in the oxygenated class of the ASTM Ignitable Liquid Classification scheme, although their high retention times are not typical of those that elute prior to C8 as contemplated in the ASTM standard [4]. Therefore, further research would be required.

The lotion was analyzed and its extraction product was found to not contain many peaks (Fig.1B). The elution time range of the peaks was from 11.50 to 22.00 minutes. No particular pattern was observed nor were there any compounds of interest in relation to ignitable liquids identified except for a few low-level peaks with alkane mass spectral fragmentation patterns at 18.33 and 20.20 minutes. Aspercreme® was similar to the lotion where not many compounds were observed in its extract; mainly heavy compounds eluted (Fig. 1C). No particular pattern was observed and no compounds of interest characteristic of ignitable liquids were identified.

The baby oil extract displayed few chromatographic peaks (Figure 1D), with only two intense peaks at 11.45 and 18.21 minutes. These two peaks were identified as 2,2,4,4,6,6,8,8,10,10-decamethyl-1,3,5,7,9,2,4,6,8,10-pentaoxapentasilecane (P1) and

hexyl dodecanoate (P15), respectively. The baby oil chromatogram did not contain a pattern nor compounds characteristic of an ignitable liquid.

Perfume was analyzed and the chromatogram of its extraction product possessed numerous peaks of varying intensity (Figure 1E), in a non-Gaussian distribution, with a large number of oxygenated compounds identified in the sample. Despite perfume being a volatile substance, no early eluting peaks before 10.00 minutes were observed. The highly volatile components common to perfume (e.g. methanol, ethanol, isopropyl alcohol, or acetone) were not detected in the extract prior to the peak of the carbon disulfide (1.70-2.1 min) in the initial investigation, and thus were not cut off by the solvent delay. Either these compounds were not in this perfume, they evaporated prior to analysis, they co-eluted with the carbon disulfide solvent, or they were displaced by other components on the carbon strip during passive headspace concentration. The compounds isopropyl myristate (propan-2-yl tetradecanoate) (P24) and ethylene brassylate (1,4-dioxacycloheptadecane-5,17-dione) (P25) were identified in the perfume sample. Isopropyl myristate is commonly found as an emollient in cosmetic and medicinal products while ethylene brassylate is used as a flavor and fragrance agent. Ester components were identified in the perfume sample and are possible components of ignitable fluids found in the oxygenated class within the ASTM Ignitable Liquid Classification scheme.

The chromatographic pattern of the Vaseline® extract (Fig. 1F) was Gaussian in shape with four peaks of maximum intensity 14.92, 15.67, 16.39 and 17.07 minutes. These peaks were identified as the homologous straight-chain alkanes of pentadecane (P30), hexadecane (P31), heptadecane (P32) and octadecane (P33), respectively. This chromatogram is indicative of a heavy petroleum distillate, such as diesel, and has the potential to be misidentified as an ignitable liquid.

3.2. Unworn Clothing

Four pieces of unworn clothing used in the study were analyzed as controls: a t-shirt, sports bra, shorts and socks. Table 2 lists the GC-MS identified chemicals in the extracts of the unworn clothing.

The chromatogram of the extract of the t-shirt showed a number of peaks over the range of 4.00 and 20.00 minutes (Fig. 2A). There did not appear to be a discernible peak pattern, and based on a mass spectral analysis, they were identified as primarily an unresolved envelope of hydrocarbons composed of alkanes and compounds with alkyl groups. Several siloxanes, alcohols and esters were also detected and identified. The presence of siloxanes in the t-shirt were attributed to silicone textile treatments that are commonly applied by manufacturers to provide a more durable and long-lasting product because they provide water repellency, softness, durability, stretching ability, enhancement of deep coloring, weather and heat resistance, and lastly can serve as soil-release agents [6]. Some of the siloxanes identified are flammable and incompatible with strong oxidizing agents. One example found in the t-shirt, 2,2,4,4,6,6-hexamethyl-1,3,5,2,4,6-trioxatrisilinane (S1), is a flammable solid. These early eluting siloxanes can be classified as "miscellaneous" ignitable liquids within the ASTM Ignitable Liquid Classification scheme.

The chromatogram of the extract of the bra contained many peaks of varying intensity, with no distinct pattern (Fig. 2B). The peak retention time range was from 3.00 to 20.00 minutes, with peaks primarily attributed to the unresolved envelope of hydrocarbons. Several compounds common to ILRs were identified, including toluene (S12), ketones (S16), xylene (S13) and the following straight chain alkanes: dodecane (S17), tetradecane (S18), pentadecane (S19), and hexadecane (S21). The arrangement of the alkanes on top of the unresolved envelope in the sample is similar to the pattern of a heavy petroleum distillate but only a few straight-chain alkanes could be identified. In addition, the homologous series is incomplete due to the absence of tridecane.

The chromatogram of the extract of the shorts also showed the unresolved envelope of hydrocarbons, without a specific pattern (Fig. 2C). Several compounds common to ILRs were identified, such as toluene, esters, and the following straight-chain alkanes: tetradecane (S18), pentadecane (S19), hexadecane (S21), and heptadecane (S31). The compound caprolactam (azepan-2-one) (S29) was also identified in the shorts and is commonly used in the manufacturing of synthetic fibers.

The chromatogram of the extract of the socks did not contain an explicit pattern, and contained the largest unresolved envelope of hydrocarbons (Fig. 2D). There were two

alcohols and two straight-chain alkanes identified: 2-ethyl-1-hexanol (S14), dodecane (S17), tetradecane (S18), and 1-dodecanol (S30). A few branched pentadecane compounds (isoparaffins; S33) were tentatively identified but were difficult to confirm due to the unresolved hydrocarbon envelope.

3.3. Worn Clothing

The clothing controls were analyzed after each subject had worn their own set without any body products except the provided deodorant. These samples served as background when identifying what compounds from the body products were being transferred. All chromatograms of the extractions of the worn samples contained compounds from the unworn clothing and many showed a transfer of deodorant compounds, such as esters of benzoic acid (branched benzoates, P8-P11) and 2,2,4,4,6,6,8,8,10,10-decamethyl-1,3,5,7,9,2,4,6,8,10-pentaoxapentasilecane (P1). Additional compounds were also observed, but were not attributed to the deodorant nor the items of clothing. Several of these components were identified as those observed in studies examining compounds released from the human body. Specifically, several aldehydes and ketones were identified, including 2-butoxyethan-1-ol (H1), benzaldehyde (H2), octanal (H3), nonanal (H4), decanal (H5), and 6,10-dimethyl-5,9-undecadien-2-one (H6). Additionally, there were compounds detected that could not be sourced from the clothing, body secretions, or deodorant, such as linalool. The worn clothing also showed a decrease in the unresolved envelope of hydrocarbons or most samples.

3.4. Worn Clothing with Body Products

The chromatograms of the extracts from the baby oil worn clothing contained compounds present from the baby oil for all three subjects but not for every item of clothing. Analysis of the chromatograms of the extracts from the worn t-shirt with baby oil (Fig. 3A) showed transfer for only two of the subjects, and only two identified compounds, linalool (P13) and hexyl dodecanoate (P15). Although a tall peak identified as 2,2,4,4,6,6,8,8,10,10-decamethyl-1,3,5,7,9,2,4,6,8,10-pentaoxapentasilecane was observed in extracts from all three subjects, it could have come from the t-shirt, the deodorant, or the baby oil (S4 or P1). The chromatograms of the extracts from the sports

bra worn with baby oil showed the transfer of the baby oil compounds for all subjects (Fig. 3B). Additionally, subject 3 had a small concentration of xylene (S13). The chromatograms of the extracts from the shorts worn with baby oil showed transfer from both the baby oil and background subject control compounds. The two most commonly identified compounds from the baby oil were present; 2,2,4,4,6,6,8,8,10,10-decamethyl-1,3,5,7,9,2,4,6,8,10-pentaoxapentasilecane (P1) and hexyl dodecanoate (P15). Moreover, the unresolved envelope of hydrocarbons showed a significant decrease from the unworn and worn controls. The chromatograms of the extracts from the socks worn with baby oil, showed transfer from the baby oil and background subject control compounds. However, identification of compounds was complicated by the intense unresolved envelope of hydrocarbons, previously described in the controls. These results indicate that although baby oil can be transferred to worn clothing, this transfer is not consistent across all subjects and clothing items.

Analysis of the chromatograms of the extracts from the perfume worn clothing demonstrated that perfume could be transferred and retained by the textile, but like the baby oil, this was not consistent for all subjects and clothing items. The shirt worn with the perfume exhibited a transfer of the perfume, the deodorant and background subject control compounds for all subjects (Fig. 4A). It was noted that there was variation within subjects on the transferred perfume, specifically a change in peak height ratios of the perfume compounds. Two of the three subjects showed transfer of perfume to the bra (Fig. 4B). Both the perfume worn shorts and socks showed a transfer of perfume and background subject control compounds (Fig. 4C and 4D). Of note, xylenes were observed in small concentrations at 5.74 minutes in one sample chromatogram of the perfume worn socks for subject 2.

Transfer of Vaseline® to the clothing items was inconsistent, but was demonstrated in a significant number of the chromatograms of the extracts from worn clothing (Fig. 5). No identifying compounds from the Vaseline® were detected in the extracts from the shirts for any of the subjects, although components from the deodorant were still observed. The chromatogram of the extract of the worn sports bra with Vaseline® showed a transfer of Vaseline® compounds, specifically the series of straight-chain alkanes, in all three subjects. Additionally, a small concentration of xylene (S13)

and small amounts of heavy straight-chain alkanes were present in all replicate chromatograms for subject 3. The chromatograms of the extracts of the Vaseline® worn shorts and socks both showed the presence of compounds from the Vaseline®, specifically the series of straight-chain alkanes in a Gaussian pattern (Fig. 5C and 5D) that are found in ignitable liquids within the heavy petroleum distillate class.

3.5. Discussion

Of the body products tested, only the Vaseline® resulted in a chromatogram similar to an ignitable liquid. The perfume and baby oil contained individual components of ignitable liquids, however no identifiable ignitable liquid patterns were present in either body product. Vaseline® was of particular interest due to its chromatographic similarity to ignitable liquids within the heavy petroleum distillate class, as evident by a similar Gaussian shape and identified straight-chain alkanes.

All four clothing items showed the unresolved envelope of hydrocarbons. The unresolved envelope of hydrocarbons contained fragmentation in the individual mass spectra indicative of alkanes and compounds containing alkyl groups. The source of these components could be the clothing items themselves or the plastic packaging. The decrease in the unresolved envelope of hydrocarbons for some items after being worn lends support for the latter hypothesis, however additional research would need to be done to make a definitive conclusion. This unresolved envelope of hydrocarbons does present a problem for identification of ILRs, as it has the ability to mask components present at low concentrations. Additionally, the identification capabilities of the mass spectral library are diminished for compounds eluting within this retention time range because multiple compounds are present within one area. Larger compounds with longer retentions times also have lower hit qualities due to similarities in their retention times and mass spectra to those with similar structures. Additionally, many of these compounds cannot be found in the mass spectral library.

Although the unworn clothing samples did not have identifiable patterns of ignitable liquids, they contained chemicals that could be found in oxygenated solvents and other classes of ignitable liquids. Of particular interest was the presence of xylene in the sports bra. Alkylbenzene compounds (e.g., xylenes) have been detected in carpet

samples exposed to fire conditions [4], but its detection in other textiles, specifically clothing, has not yet been reported in the literature. Xylenes are also present in gasoline, but their detection alone would not warrant identification of gasoline because additional compounds must be present within the sample to make a positive identification [4].

Control samples obtained from subjects with only the supplied deodorant showed a number of compounds related to those released by the human body. Those components observed were compared to references that studied human hand odors on textiles [7] and volatile organic compounds (VOCs) from the upper back and forearms [8]. Most of the compounds found correlated with those in both studies. Common groups of compounds observed were aldehydes and ketones.

Compounds identified in the worn controls that could not be sourced to the clothing, deodorant or bodies were thought to have come from other personal care products consistently worn by the subjects. Although the use of body products was controlled, all personal care products were not and thus could be a source of variation. One example is the presence of linalool in subject 2's shirt and shorts control. Linalool is commonly found in perfumes or fragrant products. Another example was in the perfume worn bra sample for subject 3, which contained a very intense peak identified as [2,2,4-trimethyl-3-(2-methylpropanoyloxy)pentyl] 2-methylpropanoate. Although its source could not be definitively identified, it is commonly used as a plasticizer, thus there can be many possible reasons for its presence [9]. Residues of hair gels, shampoos and conditioners used by the subjects could also have been transferred to the clothing items. Additionally, one must also consider hand washes, face medicines, and shower soap, as well as unknown external sources of transferred material, all which could contribute to detected compounds.

Although there was some variance between the subjects who wore clothing with body products, there were meaningful similarities. All samples demonstrated that transfer does occur from a person to their clothing, whether it was from an applied body product or the human body's volatile organic compounds, specifically, the presence of aldehydes. There were several components detected consistent with those in ILRs, such as straight-chain alkanes and ketones.

A straight-chain alkane series was seen in several of the chromatograms, however these could be distinguished from those found in ILRs due to their abundance, lack of a homologous series, or failure to form a Gaussian-shaped pattern. In some instances, other compounds filled gaps in the homologous series if a Gaussian formation was observed. In another subject, such as in subject 2 and 3's Vaseline® worn shorts and socks (Figures 5C and 5D), several heavy straight-chain alkanes eluted giving either half a Gaussian shape or provided the front and tail of one. Heavy alkanes within an ignitable liquid are classified in ASTM E1618 as n-hydrocarbons that fall within the boiling range of C_9-C_{20} and greater [4]. Medium range is classified as C_8-C_{13} and light as C_4-C_9 [4]. It can be seen in the chromatograms that the unresolved envelope of hydrocarbons masks much of the heavy petroleum distillate pattern, which may prohibit identification of an ignitable liquid. As per ASTM E1618, the identification of an ignitable liquid would not be possible due to the pattern being "overwhelmed by extraneous components" [4]. Thus, no identification could be made and another method for identification would be required.

The presence of ketones and aldehydes absorbed in the clothing materials to various extents could also be due to the location of the piece of clothing on the body. Different parts of the body excrete compounds at varying concentrations [8] as a result of the presence of sweat glands such as the apocrine, eccrine and sebaceous human glands [10]. For example, the chromatograms of the extracts from the polyester and cotton fibers of the shorts and shirt, respectively, contained ketones, however they were absent from the chromatograms of the extracts of the cotton/polyester socks. The explanation for this is not known, but it is conceivable that ketones may not be released from the glands on the feet or not in detectable concentrations. Another possible explanation is that the unresolved envelope of hydrocarbons in the chromatogram of the extract of the socks masked the presence of ketones and aldehydes.

The results from this research had notable intra- and inter-sample variation; specifically, deviations in compound ratios within replicate samples from the same individual and differences in components between different individuals. Some components were quite abundant in one subject or replicate, and much lower or nonexistent in another. This is a result of the fact that all subjects will have unique chromatographic profiles due to the particular products they use everyday, the quantity of

product applied, as well as their human body VOCs. These chromatograms will also vary based on the activities performed on a given day, as well as what a subject ate or drank. All of these factors should be considered because they can affect the kind and the amount of compounds that will arise in a given chromatographic sample. For example, it was noted that there were patterns in the chromatograms when the subjects logged exercise activity. On the days when exercise was performed, the chromatograms of the extract of the socks for one subject contained more early eluting compounds in addition to a greater prevalence of benzoate esters. The amount of intra-sample variance emphasizes the complex and unpredictable evidence that can be submitted to a forensic laboratory for ILR analysis.

The process of weathering may also be significant when analyzing ILR samples. Weathering can leave partial profiles of ignitable liquids behind. As described before, Vaseline®, when hidden substantially by the unresolved envelope of hydrocarbons, could be mistaken at first glance for a weathered ILR. In a weathered sample, the less volatile or heavier compounds are more likely to be left behind, which is similar to the heavy straight-chain alkane profile of Vaseline®.

Further research into the transfer of body products to worn clothing could include analysis of the early eluting compounds, such as acetone and the small alcohols. Although these were not detected in the products tested in this research, they are known human volatile organic compounds and are present in other products. These early eluting chemicals are analytes of interest in ILR investigations, and thus warrant additional study. The experiment could also be repeated with washed clothing, using unfragranced detergent or water. This could have removed fabric treatments and residues present on clothing due to manufacturing, shipping, handling, and the off-gassing of packaging. Lastly, solvent extractions of the clothing items could also be an area for further research, as it may provide added information that could help distinguish body products from ignitable liquid residues. However this procedure is rarely performed in forensic laboratories on clothing because of the absorbent nature of fabric and the large amount of solvent required for the extraction making this analysis impractical.

4. Conclusion

This research demonstrated that components from worn clothing, specifically the textile substrate, a transferred body product, or the transferred natural body excretions, have the potential to interfere with the identification of an ILR. The chromatograms of the extracts of unworn clothing items contain components, such as those making up the unresolved envelope of hydrocarbons, which could potentially mask the presence of ILRs. Body products were indeed transferred to the clothing during normal wear and subsequently detected by GC-MS. It was found that some compounds and patterns are similar to those in ignitable liquids, specifically the Vaseline® body product. The baby oil and deodorant products did not contain many components commonly found in ignitable liquids but the perfume consisted of numerous oxygenated compounds that could possibly be identified within the oxygenated solvent class of the ASTM Ignitable Liquid Classification scheme. However, an experienced analyst should be able to differentiate between components from body products as identified in this study and those from an ignitable liquid. In the event that both a body product, such as Vaseline®, is present in addition to an ignitable liquid, the body product could mask a low abundance pattern and make identification of an ILR difficult.

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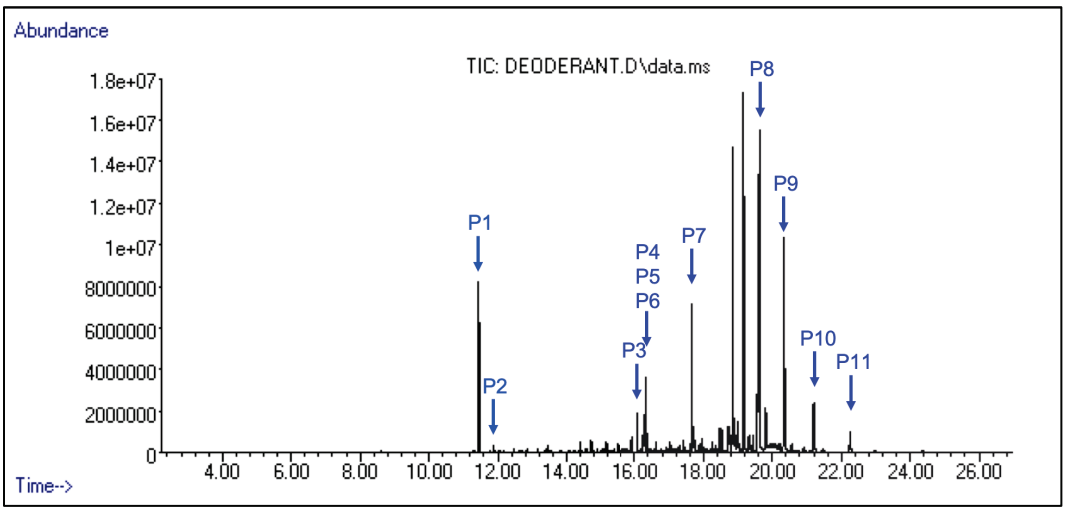
References

[1] J.J. Lentini, J.A. Dolan, J.A., C. Cherry, C, The petroleum-laced background, *J Forensic Sci*. *45* (2000) 68-989. https://doi.org/10.1520/JFS14819J.

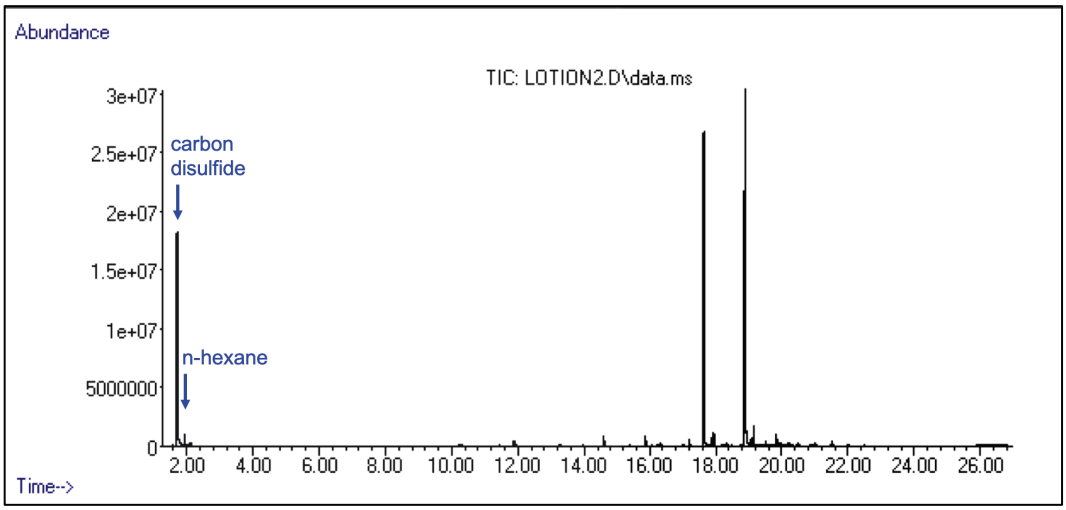
[2] J.J. Lentini, Sources of error in fires investigation, in: Scientific protocols for fire investigation, Taylor and Francis Group, LLC, Boca Raton, 2013, pp. 507-590.
[3] E. Stauffer, J.A. Dolan, R. Newman, Fire debris analysis. Elsevier, Burlington, 2008.
[4] ASTM E1618-14, Standard Test Method for Ignitable Liquid Residues in Extracts from Fire Debris Samples by Gas Chromatography-Mass Spectrometry, ASTM International, West Conshohocken, PA, 2014, www.astm.org.
[5] ASTM E1412-16, Standard Practice for Separation of Ignitable Liquid Residues from Fire Debris Samples by Passive Headspace Concentration With Activated Charcoal, ASTM International, West Conshohocken, PA, 2016, www.astm.org.
[6] Shin-Etsu Chemical Co., Ltd, Textile treatments, Shin-Etsu Silicone, Akron, 2011 .
[7] P.A. Prada, A.M. Curran, K.G. Furton, The evaluation of human hand odor volatiles on various textiles: A comparison between contact and non-contact sampling methods. *J Forensic Sci*. 56 (2011) 886-881. https://doi.org/10.1111/j.1556-4029.2011.01762.x.
[8] M. Gallagher, C.J. Wysocki, J.J. Leyden, A.I. Spielman, X. Sun, Analyses of volatile organic compounds from human skin, *Br J Dermatol*. 159 (2008) 780-791. https://doi.org/10.1111/j.1365-2133.2008.08748.x.
[9] Santa Cruz Biotechnology. 2,2,4-Trimethyl-1,3-pentanediol diisobutyrate (CAS 6846-50-0). https://www.scbt.com/scbt/product/2-2-4-trimethyl-1-3-pentanediol-diisobutyrate-6846-50-0/, 2007-2015 (accessed 22 October 2015).
[10] R.C. Smallegange, N.O. Verhulst, W. Takken, Sweaty skin: an invitation to bite? *Trends in Parasitology*. 27 (2011) 143-148. https://doi.org/10.1016/j.pt.2010.12.009.

Fig. 1: Chromatograms of the extracts of the body products: (A) deodorant, (B) lotion, (C) Aspercreme®, (D) baby oil, (E) perfume, and the (F) Vaseline®. Alpha-numeric codes are provided for each identified compound from these products (P).

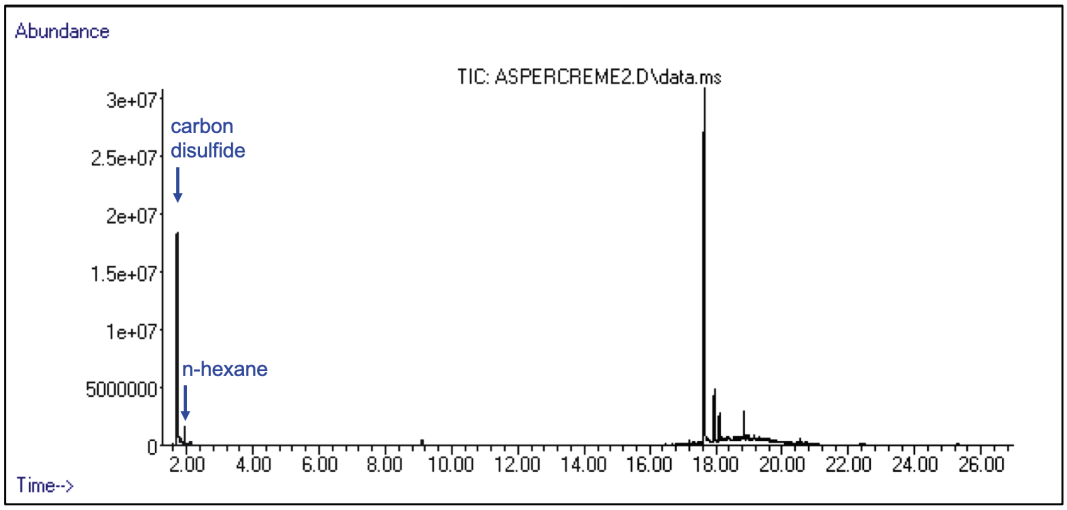
(A)



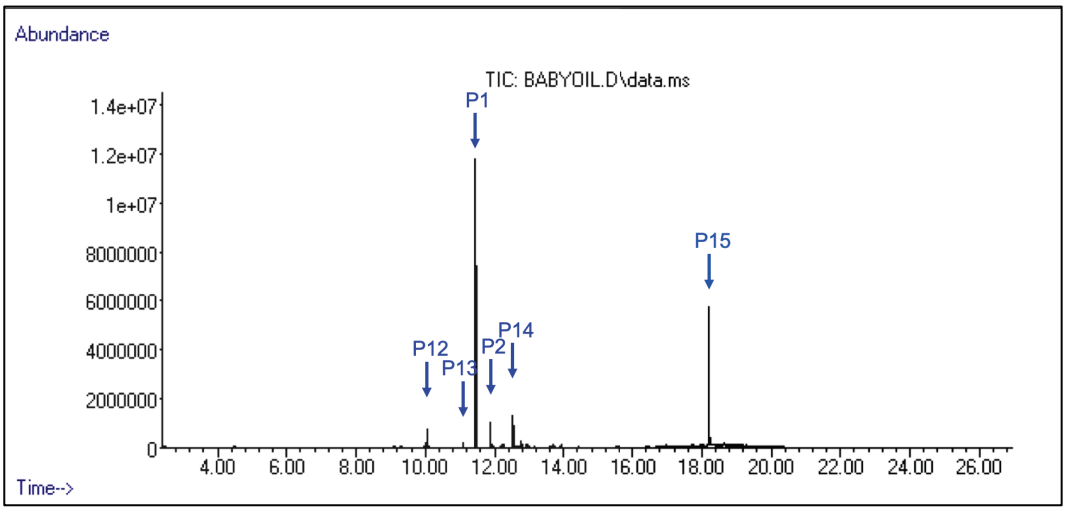
(B)



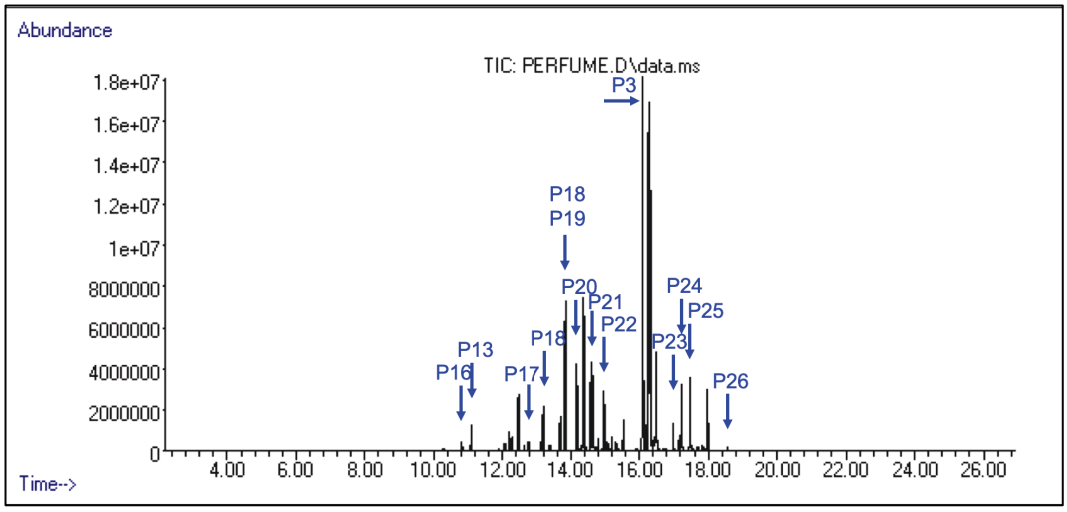
(C)


Abundance
TIC: ASPERCREME2.D\data.ms
carbon
disulfide
n-hexane
Time-->

(D)


Abundance
TIC: BABYOIL.D\data.ms
P1
P2
P12
P13
P14
P15
Time-->

(E)


Abundance
TIC: PERFUME.D\data.ms
P3
P13
P16
P17
P18
P18
P19
P20
P21
P22
P23
P24
P25
P26
Time-->

(F)

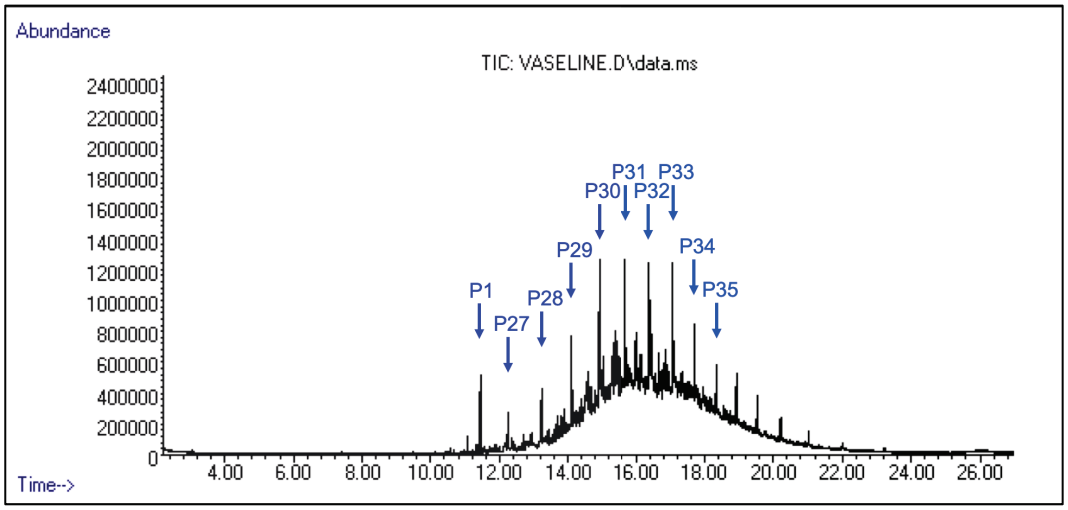
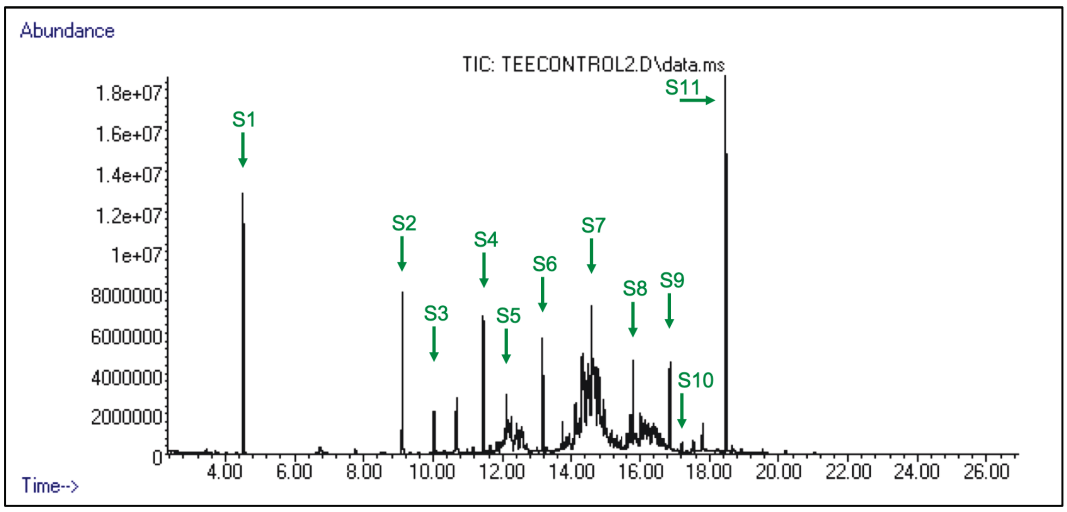
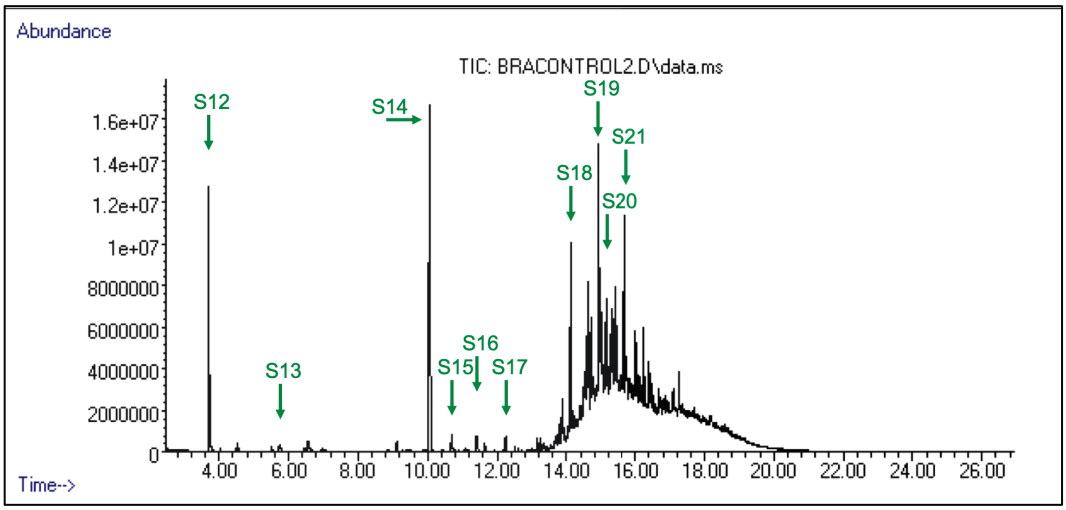

Abundance
TIC: VASELINE.D\data.ms
2400000
2200000
2000000
1800000
1600000
1400000
1200000
1000000
800000
600000
400000
200000
0
P1
P27
P28
P29
P30
P31
P32
P33
P34
P35
4.00
6.00
8.00
10.00
12.00
14.00
16.00
18.00
20.00
22.00
24.00
26.00
Time-->

Fig. 2: Chromatogram of the extracts from the unworn clothing: (A) the t-shirt, (B) the bra, (C) the shorts, and (D) the socks. Alpha-numeric codes are provided for each identified compound from these substrates (S).

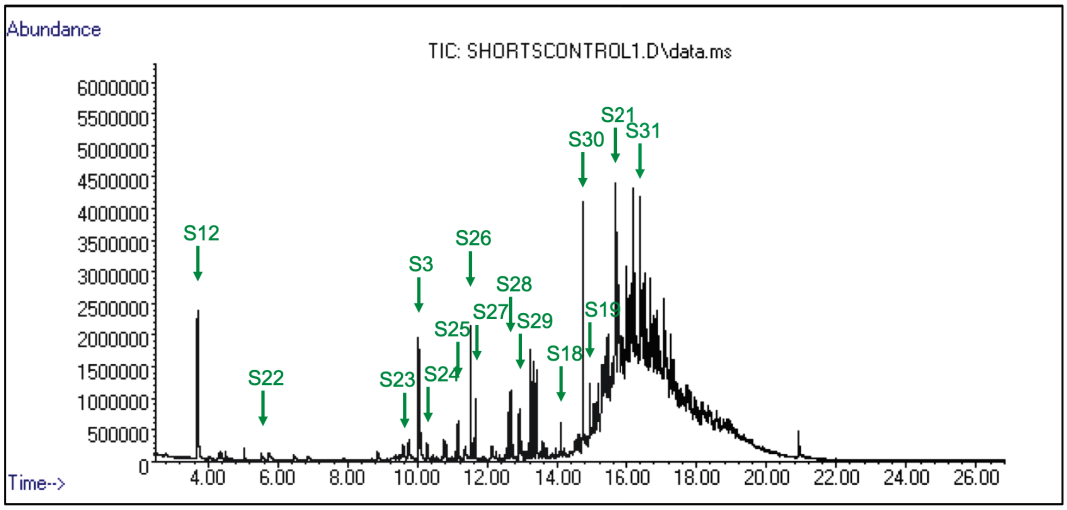
(A)



(B)



(C)


Abundance
TIC: SHORTSCONTROL1.D\data.ms
6000000
5500000
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
S12
S22
S23
S24
S3
S25
S26
S27
S28
S29
S18
S19
S30
S21
S31
Time-->
4.00
6.00
8.00
10.00
12.00
14.00
16.00
18.00
20.00
22.00
24.00
26.00

(D)

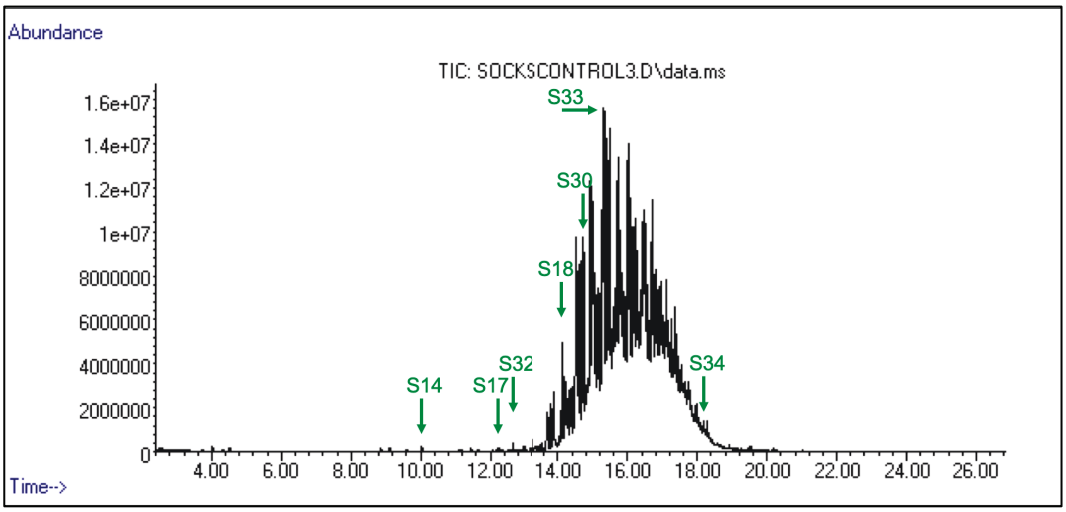
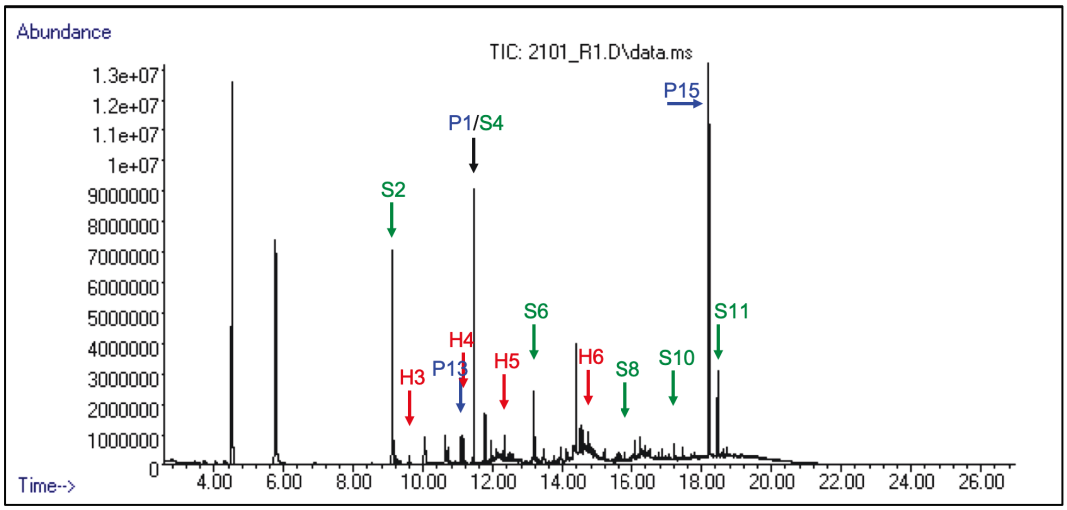

Abundance
TIC: SOCKSCONTROL3.D\data.ms
1.6e+07
1.4e+07
1.2e+07
1e+07
8000000
6000000
4000000
2000000
0
S14
S17
S32
S18
S30
S33
S34
Time-->
4.00
6.00
8.00
10.00
12.00
14.00
16.00
18.00
20.00
22.00
24.00
26.00

Fig. 3: Chromatograms of the extract of the t-shirt worn by Subject 2 after applying baby oil, and (B) the extract of the bra worn by subject 3 after applying baby oil. Both show peaks from the baby oil, the deodorant, the clothing item, and body secretions. Alpha-numeric codes are provided for each identified compound from a product (P, in blue), substrate (S, in green), or human secretion (H, in red).

(A)



(B)

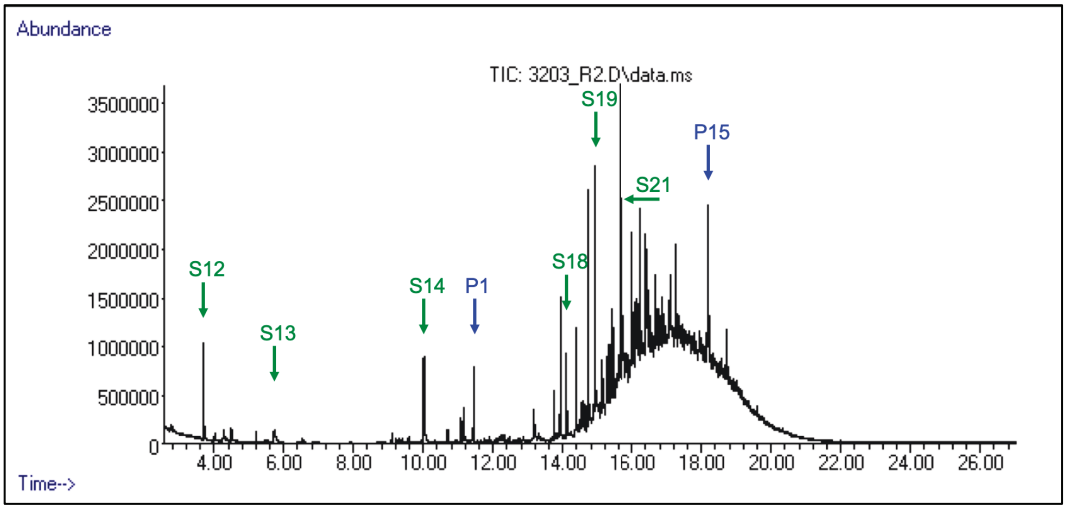
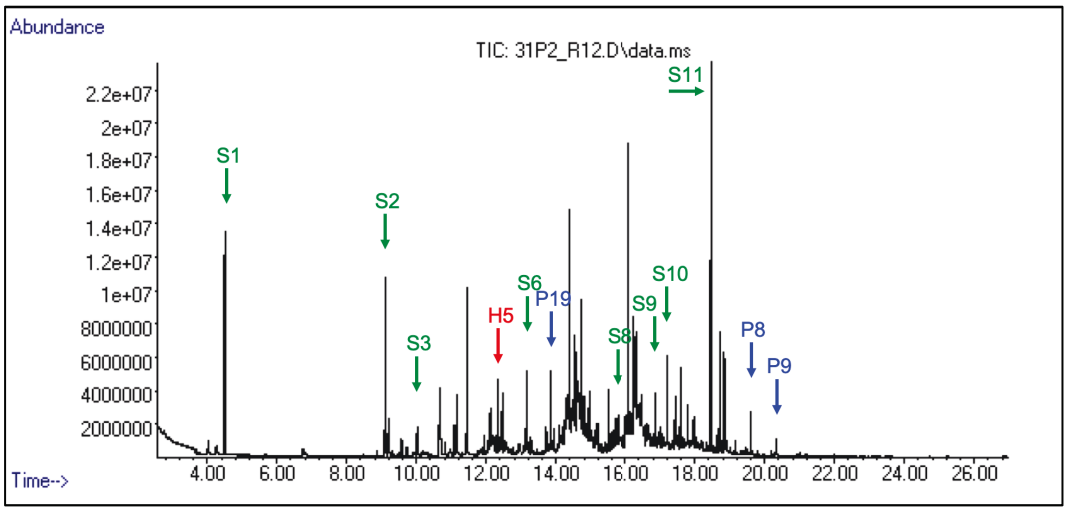
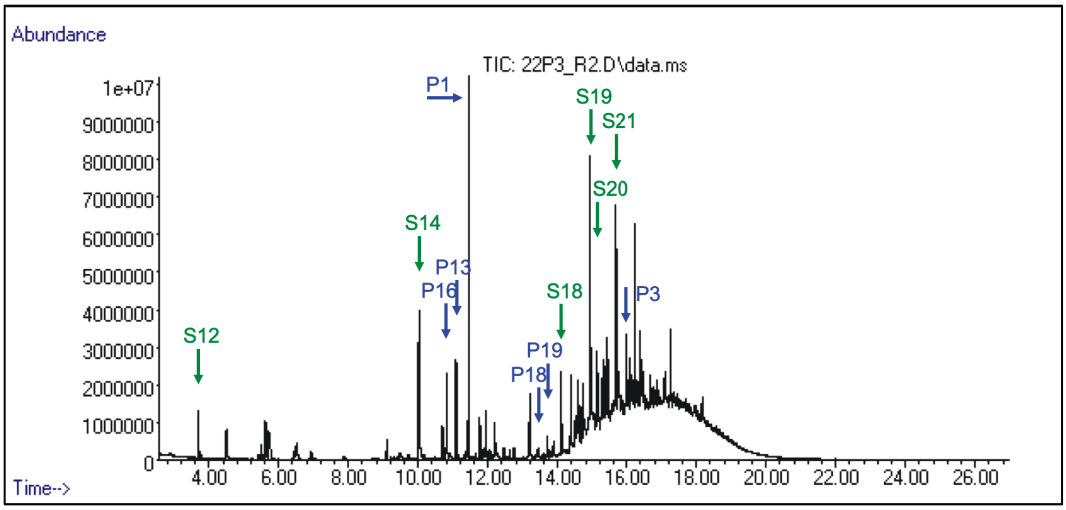


Fig. 4: Chromatograms of the extract of (A) the t-shirt worn by subject 3 after applying perfume, (B) the bra worn by subject 2 after applying perfume, (C) the shorts worn by subject 2 after applying perfume, and (D) the socks worn by subject 2 after applying perfume. Alpha-numeric codes are provided for each identified compound from a product (P, in blue), substrate (S, in green), or human secretion (H, in red).

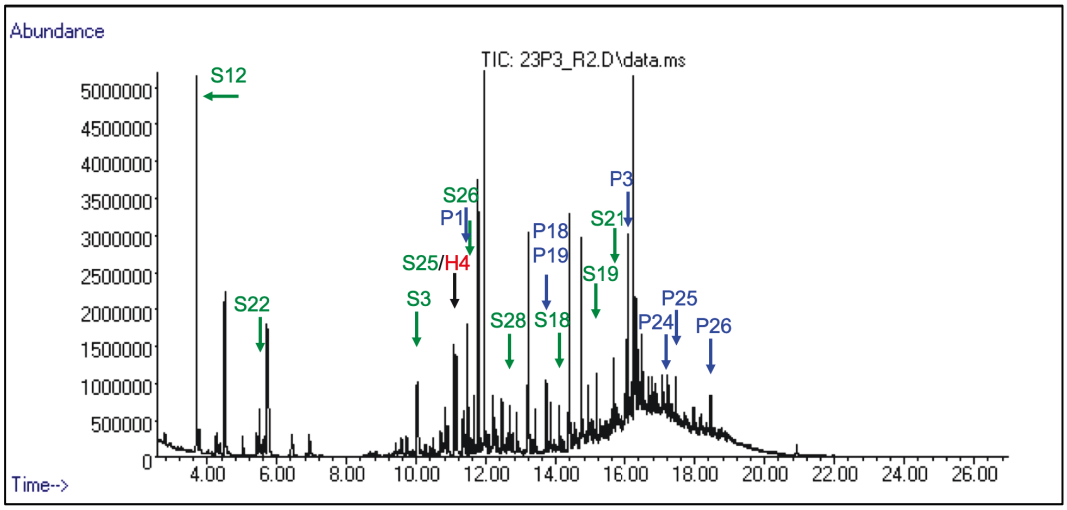
(A)



(B)



(C)


Abundance
TIC: 23P3_R2.D\data.ms
S12
S22
S3
S25/H4
P1
S26
S28
P18
P19
S18
S19
S21
P3
P24
P25
P26
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
4.00
6.00
8.00
10.00
12.00
14.00
16.00
18.00
20.00
22.00
24.00
26.00
Time-->

(D)

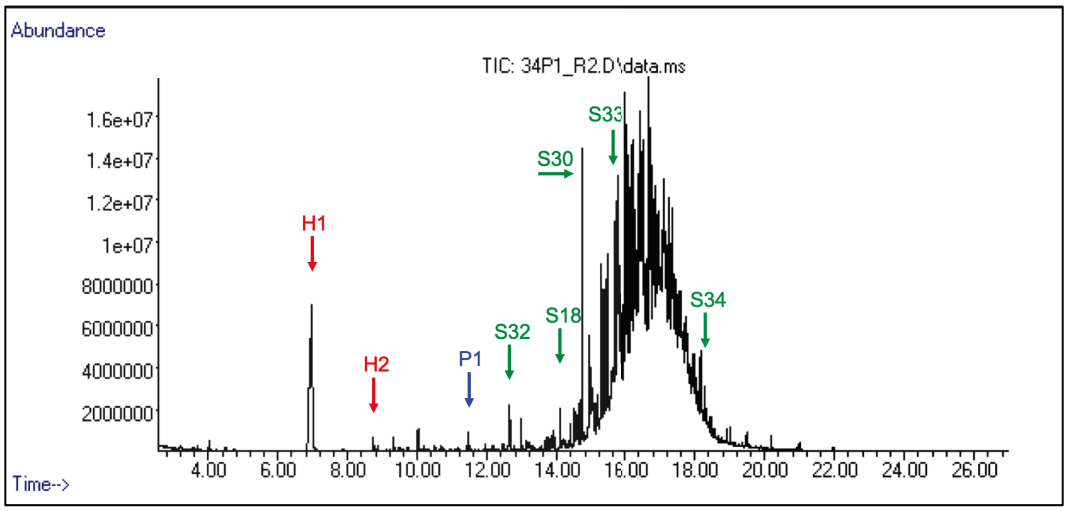
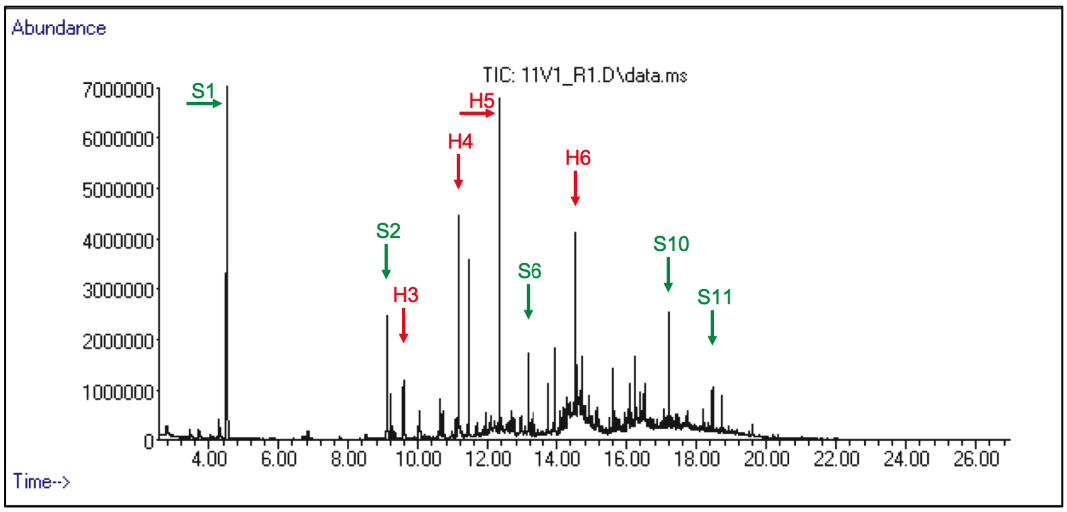
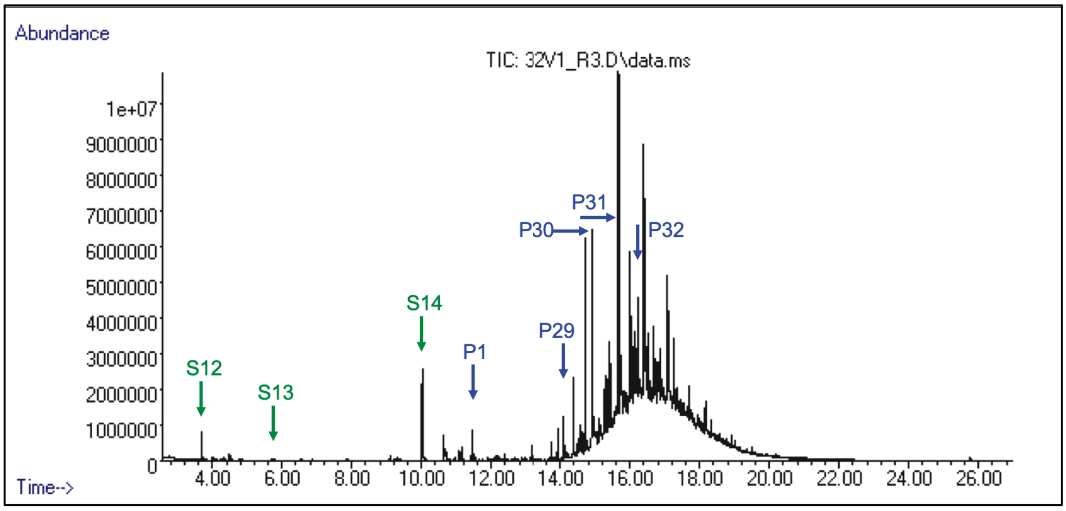

Abundance
TIC: 34P1_R2.D\data.ms
H1
H2
P1
S32
S18
S30
S33
S34
1.6e+07
1.4e+07
1.2e+07
1e+07
8000000
6000000
4000000
2000000
4.00
6.00
8.00
10.00
12.00
14.00
16.00
18.00
20.00
22.00
24.00
26.00
Time-->

Fig. 5: Chromatograms of the extract of (A) the t-shirt worn by subject 1 after applying Vaseline®, (B) the bra worn by subject 3 after applying Vaseline®, (C) the shorts worn by subject 2 after applying Vaseline®, and (D) the socks worn by subject 2 after applying Vaseline®. Alpha-numeric codes are provided for each identified compound from a product (P, in blue), substrate (S, in green), or human secretion (H, in red).

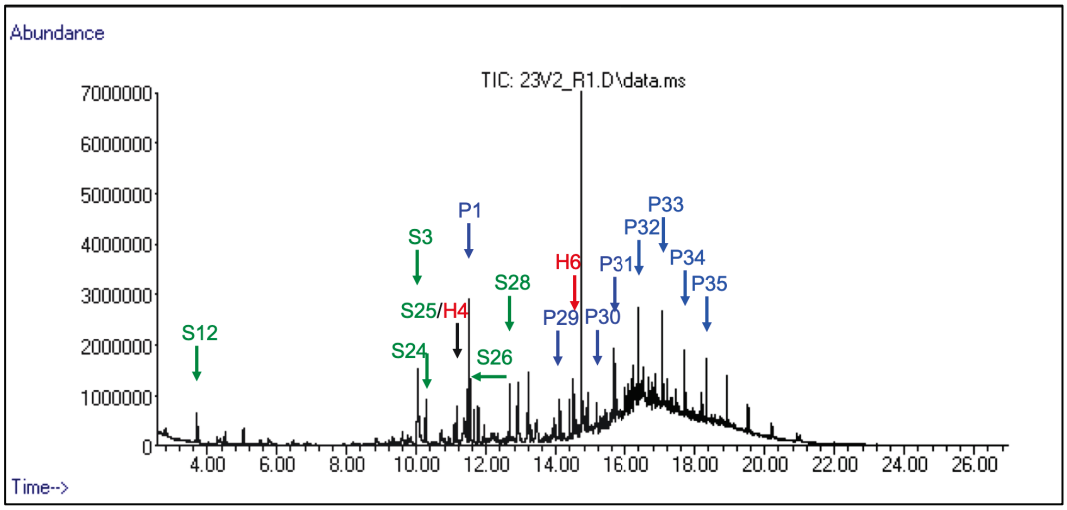
(A)



(B)



(C)


Abundance
TIC: 23V2_R1.D\data.ms
7000000
6000000
5000000
4000000
3000000
2000000
1000000
0
S12
S3
P1
S24
S25/H4
S26
S28
H6
P29
P30
P31
P32
P33
P34
P35
4.00
6.00
8.00
10.00
12.00
14.00
16.00
18.00
20.00
22.00
24.00
26.00
Time-->

(D)

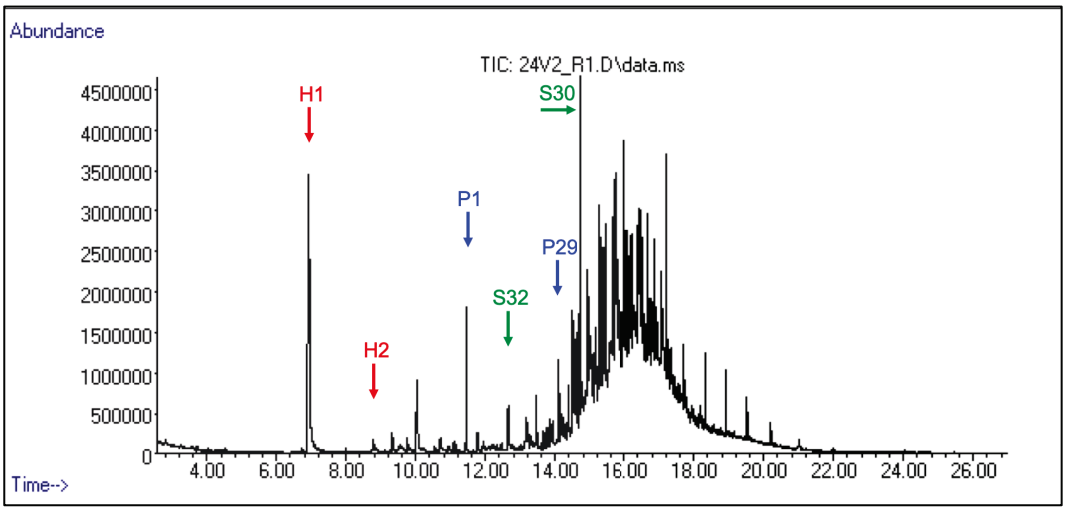

Abundance
TIC: 24V2_R1.D\data.ms
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
H1
H2
P1
S30
S32
P29
4.00
6.00
8.00
10.00
12.00
14.00
16.00
18.00
20.00
22.00
24.00
26.00
Time-->

Table 1: Identified components from the chromatograms of the extracts of deodorant, baby oil, perfume, and the Vaseline®, with their retention times. Hit qualities (HQ) are included for those compounds which had percentages less than 80. Alpha-numeric identification for each compound from these products (P) is provided to associate their identification with the peaks in Figures 1, 3, 4, and 5.

Deodorant Compounds	**Baby Oil Compounds**	**Perfume Compounds**	**Vaseline Compounds**
P1: 2,2,4,4,6,6,8,8,10,10-decamethyl-1,3,5,7,9,2,4,6,8,10-pentaoxapentasilecane (11.45)	P12: 1-methyl-4-prop-1-en-2-ylcyclohexene (10.05)	P16: Prop-2-enyl hexanoate (10.80)	P1: 2,2,4,4,6,6,8,8,10,10-decamethyl-1,3,5,7,9,2,4,6,8,10-pentaoxapentasilecane (11.45)
P2: Benzyl acetate (11.88)	P13: Linalool (3,7-dimethylocta-1,6-dien-3-ol) (11.09)	P13: Linalool ((3,7-dimethylocta-1,6-dien-3-ol) (11.09)	P27: Dodecane (12.25; HQ 62.3)
P3: Methyl 2-(3-oxo-2-pentylcyclopentyl) acetate (16.08)	P1: 2,4,4,6,6,8,8,10,10-decamethyl-1,3,5,7,9,2,4,6,8,10-pentaoxapentasilecane (11.45)	P17: 3,7-dimethylocta-1,6-dien-3-yl acetate (12.75)	P28: Tridecane (13.23; HQ 70.2)
P4: [(Z)-hex-3-enyl] 2-hydroxybenzoate (16.27)	P2: Benzyl acetate (11.88)	P18: (1-butoxy-1-oxopropan-2-yl) butanoate (13.70)	P29: Tetradecane (14.11; HQ 78.2)
P5: Hexyl 2-hydroxybenzoate (16.32)	P14: (R)-3,7-dimethyl-6-octen-1-ol (12.53)	P19: 5-pentyloxolan-2-one (13.84)	P30: Pentadecane (14.92)
P6: Heptadecane (16.39)	P15: Hexyl dodecanoate (18.21)	P20: Vanillin (4-hydroxy-3-methoxybenzaldehyde) (14.18)	P31: Hexadecane (15.67)
P7: Benzyl 2-hydroxybenzoate (17.67)		P21: Ethyl Vanillin (3-ethoxy-4-hydroxybenzaldehyde) (14.65)	P32: Heptadecane (16.39)
P8: Branched benzoate (19.62)		P22: 4-Methyl-2-pentadecyl-1,3-dioxolane (15.32)	P33: Octadecane (17.07; HQ 73.1)
P9: Branched benzoate (20.35)		P3: Methyl 2-(3-oxo-2-pentylcyclopentyl)acetate (16.10)	P34: Nonadecane (17.71; HQ 68.4)
P10: Branched benzoate (21.20)		P23: Benzyl benzoate (16.98)	P35: Eicosane (18.33; HQ 67.6)
P11: Branched benzoate (22.26)		P24: Isopropyl myristate (propan-2-yl tetradecanoate) (17.21)	

		P25: 4,6,6,7,8,8-hexamethyl-1,3,4,7-tetrahydrocyclopenta-[g]isochromene (17.47)	
		P26: 1,4-dioxacycloheptadecane-5, 17-dione (18.55)	

Table 2: Identified components from the chromatograms of the extracts of the clothing: the t-shirt, the bra, the shorts, and the socks, with their retention times. Alpha-numeric identification for each compound from these substrates (S) is provided to associate their identification with the peaks in Figures 2, 3, 4, and 5.

T-Shirt	**Bra Compounds**	**Shorts Compounds**	**Socks Compounds**
S1: 2,2,4,4,6,6-hexamethyl-1,3,5,2,4,6-trioxatrisilinane (4.51)	S12: Toluene (3.71)	S12: Toluene (3.70)	S14: 2-ethyl-1-hexanol (10.03)
S2: 2,2,4,4,6,6,8,8-octamethyl-1,3,5,7,2,4,6,8-tetraoxatetrasilocane (9.11)	S13: xylene (5.71)	S22: N-benzylaniline (5.52)	S17: Dodecane (12.23; HQ 67.1)
S3: 2-ethylhexan-1-ol (10.03; HQ 78.2)	S14: 2-ethyl-1-hexanol (10.07; HQ 73.2)	S23: Octanal (9.59)	S32: 1,3-benzothiazole (12.65)
S4: 2,2,4,4,6,6,8,8,10,10-decamethyl-1,3,5,7,9,2,4,6,8,10-pentaoxapentasilecane (11.45)	S15: 1-octanol (10.67)	S3: 2-ethylhexan-1-ol (10.03)	S18: Tetradecane (14.11; HQ 65.2)
S5: 2-(2-butoxyethoxy)-ethanol (12.13)	S16: 3,5,5-trimethylcyclohex-2-en-1-one (11.41)	S24: 3,3,5-trimethylcyclohexan-1-one (10.27)	S30: 1-dodecanol (14.73; HQ 70.6)
S6: 2,2,4,4,6,6,8,8,10,10,12,12-dodecamethyl-1,3,5,7,9,11-hexaoxa-2,4,6,8,10,12-hexasilacyclododecane	S17: Dodecane (12.25; HQ 70.2)	S25: Nonanal (11.15)	S33: Branched pentadecane compounds (15.29-15.50)

(13.17)			
S7: 2,2,4,4,6,6,8,8,10,10,12,12,14,14-tetradecamethyl-1,3,5,7,9,11,13-heptaoxa-2,4,6,8,10,12,14-heptasilacyclotetradecane (14.59)	S18: Tetradecane (14.12; HQ 72.7)	S26: Dimethyl pentanedioate (11.52)	S34: Ethyl hexadecanoate (18.28)
S8: 2,2,4,4,6,6,8,8,10,10,12,12,14,14,16,16-hexadecamethyl-1,3,5,7,9,11,13,15-octaoxa-2,4,6,8,10,12,14,16-octasilacyclohexadecane (15.81)	S19: Pentadecane (14.93)	S27: 2-ethylhexyl acetate (11.65)	
S9: 2,2,4,4,6,6,8,8,10,10,12,12,14,14,16,16,18,18-octadecamethyl-1,3,5,7,9,11,13,15,17-nonaoxa-2,4,6,8,10,12,14,16,18 nonasilacyclooctadecane (16.86)	S20: Bis[[[dimethyl(trimethylsilyloxy)silyl]oxy-dimethylsilyl]oxy]-dimethylsilane (15.14)	S28: Dimethyl hexanedioate (12.66)	
S10: Isopropyl myristate (propan-2-yl tetradecanoate) (17.20)	S21: Hexadecane (15.68; HQ 74.4)	S29: Caprolactam (azepan-2-one) (12.91)	
S11: Isopropyl palmitate (propan-2-yl hexadecanoate) (18.47)		S18: Tetradecane (14.11)	
		S30: 1-dodecanol (14.73)	
		S19: Pentadecane (14.91)	
		S21: Hexadecane (15.67)	
		S31: Heptadecane (16.39)	