

Flammable liquids in non-flammable products as potential interferences in the determination of ignitable liquid residues in fire debris

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ABSTRACT

The clothing of suspected arsonists is often analyzed for the presence of ignitable liquids. Personal care products (PCPs) are ubiquitous in our society and can contaminate clothing, so their potential interference is an important consideration in the interpretation of casework samples. Thirty-two samples of various hygiene products and hand cleaners were analyzed using headspace concentration-gas chromatography/mass spectrometry (GC/MS). Despite occasionally containing one or two hydrocarbon compounds found in ignitable liquids, all the antiperspirants and deodorants were readily distinguished from ignitable liquids because they lacked any of the key diagnostic features of ignitable liquids in their extracted ion profiles (EIPs). Two samples labeled as hand cleaners displayed characteristic patterns of heavy petroleum distillates, which, if found on a suspect's clothing, could cause the misleading assumption that the source of the liquid was flammable. However, the petroleum distillates in these two hand-cleaning products were not flammable, according to both their packaging and safety data sheets, because they were formulated as emulsions with water. This study also includes a casework example of a heavy petroleum distillate in a fire debris sample. However, the co-presence of abundant fatty acid methyl esters increased the probability that the original source was either a biodiesel blend or a non-flammable formulation product and therefore raises reasonable doubt about the flammability of the original product. The results of this work are limited by the GC/MS method, which could not detect volatiles like acetone, propanol, and ethanol eluting before a retention index of 700 nor non-volatile emulsifiers/surfactants.

Introduction

Over the past thirty years, the methods and standards of fire debris analysis and its interpretation have constantly evolved [1,2]. Fire debris analysts in the US tend to use ASTM-E3245 and ASTM-E1618 to identify the presence of ignitable liquid residues (ILRs) in fire debris, and these standards generally result in the use of headspace concentration followed by gas chromatography-mass spectrometry to determine if ILRs are present [3,4]. Ignitable liquids are often used to initiate and accelerate incendiary fires, so their presence is often informative in determining whether or not a fire was purposefully set [5].

Ignitable liquids are ubiquitous in our man-made environment [6–8], so their presence in fire debris cannot be dispositively linked to arson [8–11]. Interferences frequently observed during the identification of ILRs are those linked to background chemicals and pyrolysis products, including solvents in new footwear, nylon flooring, and printed logos on clothing [8]. Interferences, especially from pyrolysis,

can impede the identification of ILRs [6,8,9,12–16], so analysts must be aware of potential sources of interference, including domestic liquid products and personal care products (PCPs). PCPs may contain petroleum-based products in their formulations [17], but if they are formulated as a microemulsion, they may be non-flammable.

Emulsions are stable dispersions, or macroscopically homogeneous mixtures, of two immiscible liquids. They are normally formed with water and an oil/organic liquid through the addition of an amphiphilic surfactant to create micelles greater than 500 μm in diameter [18]. Microemulsions have smaller diameter droplets, among other differences, and they are used in a variety of products ranging from pharmaceutical products to insecticides and PCPs [19]. Common emulsifying agents in PCPs include cationic, anionic, zwitterionic, and neutral surfactants such as quaternary alkyl ammonium salts [20], alkyl phosphocholines, esters [21], ethers [22], and sulfate esters like sodium dodecyl sulfate (SDS) [12,23]. Neutral surfactants also include polyglycols [22] and cyclo-siloxanes [24]. None of these oxygenated

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emulsifiers are naturally present in petroleum distillates. However, some gel barbecue/fireplace/bonfire starters contain glycols and ethers co-formulated with oxygenated flammable liquids like ethanol, propan-2-ol, and 2-butanone [25]. The low interfacial tension of surfactants provides thermodynamic stability to an emulsion, and their presence as a co-formulation product with a petroleum-based liquid can be indicative of the non-flammable nature of a resulting product [19].

Oftentimes, when individuals are suspected of arson using an ignitable liquid, investigators will confiscate the individual's clothing and analyze the clothing for evidence of spillage during the crime [26–29]. The potential to find gasoline residues in the clothing of persons with different occupations and activities has been partially established in some relatively small-scale studies [30,31]. The presence of residues of petroleum containing PCPs in clothing of suspects or in fire debris could therefore complicate interpretations about the incendiary nature of any identified ignitable liquids. The purpose of this study is to identify the types of domestic products and of PCPs that are most likely to cause interferences during the analysis of ILRs in clothing or fire debris. A secondary purpose is to identify any emulsifying agents that might also appear in the resulting chromatograms that might indicate a non-flammable source of the ILR, as has been demonstrated before for foaming agents [12]. This project focused on men's hygiene products because arsonists are approximately six times more likely to be male than female [32,33]. The clothing and belongings of suspects who are male are therefore more likely to contain transfer residues from men's products.

Methods and materials

All products used in this experiment were purchased through online providers. Thirty-two unique product types from fourteen brand names were analyzed (Table 1). Samples of gasoline, kerosene, and diesel were purchased from local retailers. All samples were analyzed using passive headspace concentration followed by GC–MS, in general accordance with ASTM E1412-19 [34] and ASTM E1618-19 [4]. For each analysis, 50–100 mg of each sample was spiked onto a folded 14.7"x16.6" Kim-wipe® (Kimberly Clark, Roswell, GA) and placed into a paint can that had been pre-baked at 210 °C for at least 6 h to remove organic contaminants. An activated charcoal strip (Albrayco Technologies, Cromwell, CT) was then placed on a suspended paper clip in the headspace of each paint can. Each paint can was then spiked with 50 µL of 4-phenyl toluene (Sigma Aldrich, St. Louis, MO) as an internal standard. The

Table 1
List of all 32 personal care products (PCPs) used in the study.

Hand/body cleansers	Antiperspirants/deodorants	
Axe Apollo shower gel	Adidas body fragrance	Dove Men's Care antiperspirant dry spray
Gojo hand cleaner	Arrid XX stick deodorant	Gillette Endurance clear gel antiperspirant
Goop hand cleaner	Arrid XX aerosol deodorant	Old Spice After-Hours deodorant
Lava hand cleaner (with pumice)	Axe Anarchy stick deodorant	Old Spice Swagger antiperspirant
Rough Touch hand wipes	Axe Apollo fragrance spray	Old Spice amber body spray
Simple Green hand cleaner	Axe Phoenix antiperspirant	Old Spice Stronger Swagger deodorant
Working Hands hand balm	Brut Classic deodorant	Playboy All-Over body spray
	Degree antiperspirant spray	Right Guard aerosol
	Degree Cool Rush antiperspirant	Right Guard X-treme Defense deodorant
	Degree Extreme dry spray	Speed Stick deodorant
	Degree antiperspirant	Static Guard spray
	Dove Men Care stick deodorant	Ultra Max antiperspirant
	Dove Men's Care non-irritant deodorant	

cans were sealed before heating to 60 °C for 16–20 h. After baking and cooling, the activated carbon strips were removed, and the analytes were extracted by vortexing for 30 s in 1 mL of pentane (Acros Organics, Pittsburgh, PA). A method blank, consisting of only the internal standard in a paint can is provided in Fig. S0.

All samples were analyzed using an Agilent Technologies 7890B GC/5977A with a 10 m × 150 µm × 0.15 µm DB-5-MS Agilent capillary column (Santa Clara, CA). Two GC methods were used during this study. Method A had a total run time of 11.5 min and used a starting temperature of 50 °C for 1 min followed by a ramp of 25 °C/min before holding at 280 °C for 1 min. The solvent delay employed in Method A prevented the detection of analytes with retention indices smaller than 850. Therefore, method A was not able to detect certain light distillates or light oxygenated liquids. Method B had a total run time of 22 min and used a starting temperature of 100 °C for 2 min followed by a ramp of 15 °C/min before holding at 280 °C for 6 min. Method B was able to detect compounds with retention indices as small as 700, which, although superior to Method A, still would not detect certain oxygenated liquids like acetone, propanol, or ethanol, which may be common in personal care products. In both methods, the mass spectrometer was scanned from *m/z* 40–500 after a solvent delay of 0.6 mins and 2 mins for the fast and slow methods, respectively. The MS quad and source temperatures were 200 °C and 250 °C, respectively, and the transfer line was held at 280 °C.

All samples were run in duplicate with a solvent blank between each sample and *n*-alkane ladder (*n*C₇ to *n*C₃₀) with each set of samples for retention index (RI) calibration. A TIC of the *n*-alkane ladder is provided in Fig. S1. The total ion chromatogram (TIC) of each sample was initially viewed using Mass-Hunter Qualitative Analysis Version B.06.00 (Santa Clara, CA) and confirmed using the automated mass spectral deconvolution and identification system (AMDIS), version 32 [35]. Chemical identifications are defined as peaks that provide spectral library database match factor of 800 or higher with measured retention index within twenty units of a previously recorded sample using a similar column type.

All samples examined followed the ignitable liquid classification scheme specified in ASTM E1618-19 [4]. Samples were examined for both the presence of individual compounds that regularly appear in ILRs (Table 2), but more importantly for characteristic patterns in the relative abundances of extract ion chromatograms (EICs). Such patterns in EICs are described as key diagnostic features (KDFs) in a new standard under development by the NIST Organization of Scientific Area Committees (OSAC) to replace ASTM-E1618-19 [36].

The terms 'present', 'most abundant', and 'trace amounts' are used in the discussion to describe the approximate relative abundance of peaks found in the TICs. Obviously, the most abundant peak in a chromatogram is the peak with the largest total ion current at the peak apex. The term 'trace amounts' refers to compounds that have signal-to-noise ratios less than ~20 in the TIC. Such compounds are still readily identified using automated spectral deconvolution and database searching algorithms such as AMDIS. Peaks defined as 'present' have *S/N* ratios greater than ~20 and are readily observed in the TIC.

Table 2
List of compounds that regularly appear in many petroleum distillates.

Toluene	Decane
Ethylbenzene	Undecane
Naphthalene	Dodecane
1-methylnaphthalene	Tridecane
2-methylnaphthalene	Tetradecane
o-xylene	Pentadecane
m/p-xylene	Hexadecane

Results and discussion

The SDSs for some of the gel and spray deodorants list volatiles like ethanol, isopropanol, propane, butane and isobutane in their formulations. Some of these substances, like propane and butane, are so volatile that they would not be detectable in any condensed-phase residues at room temperature. Other substances, like ethanol and isopropanol, should be detectable in liquid formulations. However, our GC/MS method was limited to substances with retention indices greater than 700, so light oxygenated substances/liquids are beyond the scope of this study.

Ignitable liquids in antiperspirants and deodorants

Of the 32 PCP samples, 25 were classified as antiperspirants and deodorants. Of these 25 hygiene products, 23 did not contain any compounds commonly found in ignitable liquids nor any key diagnostic features of ILRs. The labeled TICs of all of the tested samples are provided in the supplementary material Figs. S1-S34. These samples would therefore not cause any interference in the analysis of ignitable liquids. The remaining two samples contained certain compounds common to ignitable liquids, but at trace or present amounts and with no key diagnostic features. For example, Right Guard antiperspirant (Fig. 1) contained hexadecane and Dove men's stick deodorant contained trace levels of both tridecane and tetradecane. However, neither product contained any key diagnostic features of ignitable liquids. For these reasons, none of the antiperspirants and deodorant samples contain ignitable liquids. The most commonly occurring compounds found in the headspace-concentration chromatograms were fragrances, emollients, and antioxidants, as listed in Table 3.

Ignitable liquids in hand and body cleaners

Seven of the 32 PCPs were body cleaners or industrial-strength hand cleaners. Four of the seven samples, including Rough Touch hand wipes, Simple Green hand cleaner, Axe Apollo Shower Gel and Lava hand cleaner with pumice, did not list any petroleum distillates in their safety data sheets (SDS's), but they did exhibit trace amounts of certain *n*-alkanes. Chromatograms of the first two products in this list are provided in Fig. 2. Despite the presence of trace *n*-alkanes, none of these hand cleaners would be classified as ignitable liquids because they lack any other identifying characteristics of ignitable liquids.

Working Man's hand balm also did not list any petroleum distillates in its SDS, and this sample did not contain any *n*-alkanes. An example chromatogram is provided in Fig. 2D for Working Man's hand balm, along with other hand cleanser products that displayed the trace

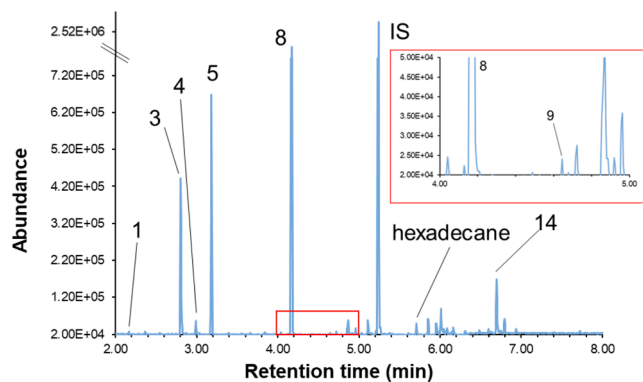


Fig. 1. Headspace concentration-GC/MS chromatogram of Right Guard antiperspirant using method A. Chromatogram shows trace amounts of hexadecane, which is commonly found in many ILRs. However, no key diagnostic features of ignitable liquids are present. The numbering scheme is detailed in Table 3.

Table 3

Peak identities and frequencies of occurrence for the most frequently observed compounds in personal care products (PCPs).

Peak #	RT	Compound identity	Property	Frequency
1	2.161	Octamethyl-cyclotetrasiloxane (CAS 556-67-2)	emollient	10
2	2.508	Limonene (CAS 138-86-3)	fragrance	4
3	2.807	α -Citronellol (CAS 6812-78-8)	fragrance	19
4	2.989	Linalool (CAS 78-70-6)	fragrance	10
5	3.184	Decamethyl-cyclopentasiloxane (CAS 541-02-6)	emollient	24
6	3.777	l-Citronellol (CAS 7540-51-4)	fragrance	5
7	3.900	Linalyl acetate (CAS 115-95-7)	fragrance	4
8	4.168	Dodecamethyl cyclohexasiloxane (CAS 4098-30-0)	emollient	11
9	4.645	Biphenyl (CAS 95-52-4)	fragrance	17
10	5.113	α -isomethyl ionone (CAS 127-51-5)	fragrance	4
11	5.271	Butylated hydroxytoluene (BHT) (CAS 128-37-0)	antioxidant	8
12	5.383	Lilial (CAS 80-54-6)	fragrance	10
13	6.086	Patchoulol (CAS 5986-55-0)	fragrance	5

amounts of *n*-alkanes. The two remaining samples—Goop hand cleaner and Gojo hand cleaner—either specifically listed petroleum distillates as ingredients in their SDS's and/or exhibited TICs and extracted ion chromatograms (EICs) consistent with those of ignitable liquids. For example, Goop hand cleaner, in Fig. 3C, showed a dominant series of *n*-alkanes between nC_{12} - nC_{14} , which is consistent with a narrow-range heavy petroleum distillate. The TIC even displays the 'hash and trash' peaks of specific branched alkanes between the abundant linear alkanes [37] and a raised baseline that is indicative of less-abundant and unresolved branched and cyclic alkanes.

The two samples containing ignitable liquids were re-analyzed using method B, with traditional ignitable liquid standards for comparison. This longer method allowed for better resolution and identification of compounds with smaller retention indices. Other indicative characteristics of heavy petroleum distillates can be found in key diagnostic features of EICs of the two samples. Medium and heavy petroleum distillates with narrow ranges of three to four consecutive *n*-alkanes are quite common in the ignitable liquid reference collection of the National Center for Forensic Science (NCFS). The two non-flammable hand cleaners in Fig. 3 have TICs that resemble some weathered medium petroleum distillates (E.g., SRNs 1120 and 1250) and several unweathered heavy petroleum distillates (e.g. SRNs 269 and 519) [38] in the NCFS database. The key diagnostic features of *n*-alkanes, branched alkanes, and cyclic alkanes imply that these two hand cleaners could be classified as containing ignitable liquids in the class of heavy petroleum distillates (HPD). Therefore, spillage, or residues, of these two hand cleaners on the clothing of suspects could lead to the correct identification of an ignitable liquid residue in the HPD class, but the misleading impression that the ignitable liquid was from a flammable source.

There are no readily observable compounds within these hand-cleaning products that could be used to distinguish them from pure heavy petroleum distillates. For example, Tire-Wet, a reference ignitable liquid (Fig. 3B), and Goop® hand cleaner (Fig. 3D) contain an ingredient labeled as "hydrotreated light petroleum distillates," and both show chromatograms consistent with heavy petroleum distillates, as described by ASTM E1618-19 [4]. However, Tire-Wet is flammable and Goop® hand cleaner has a flammability of "0" on its SDS. The SDS only accounts for 40–60 % by mass of the product, so presumably the remaining non-hazardous portion is 40–60 % water by mass, thus rendering the product non-flammable.

In Goop® hand cleaner, the SDS lists oleic acid as present at 3–7 % by weight, ethoxylated alcohols at 3–7 % by weight, and triethanolamine at 1–5 % by weight, but these ingredients were not detected in the headspace concentration sampling method. The SDS for Gojo® hand cleaner (Fig. 3C) lists C11-15 alkane/cycloalkane and mineral oil among

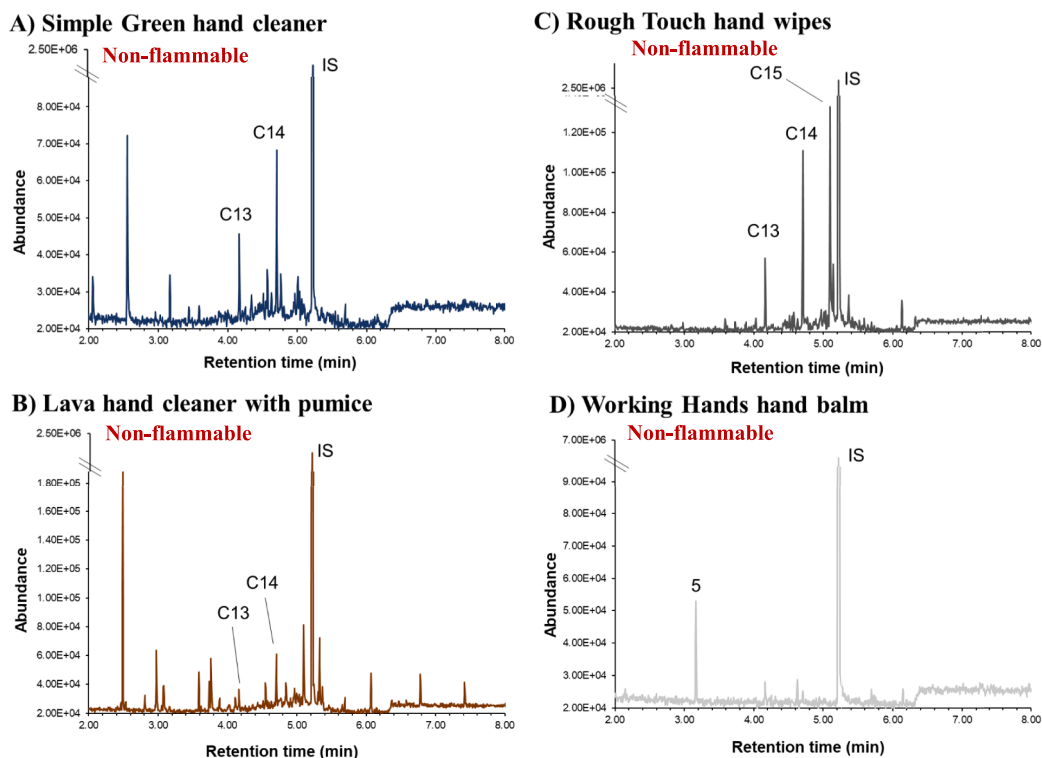


Fig. 2. Headspace concentration-GC/MS chromatograms of selected samples containing *n*-alkanes: (A) Simple Green hand cleaner; (B) Lava hand cleaner with pumice, (C) Rough Touch hand wipes, and (D) Working Hands hand balm. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

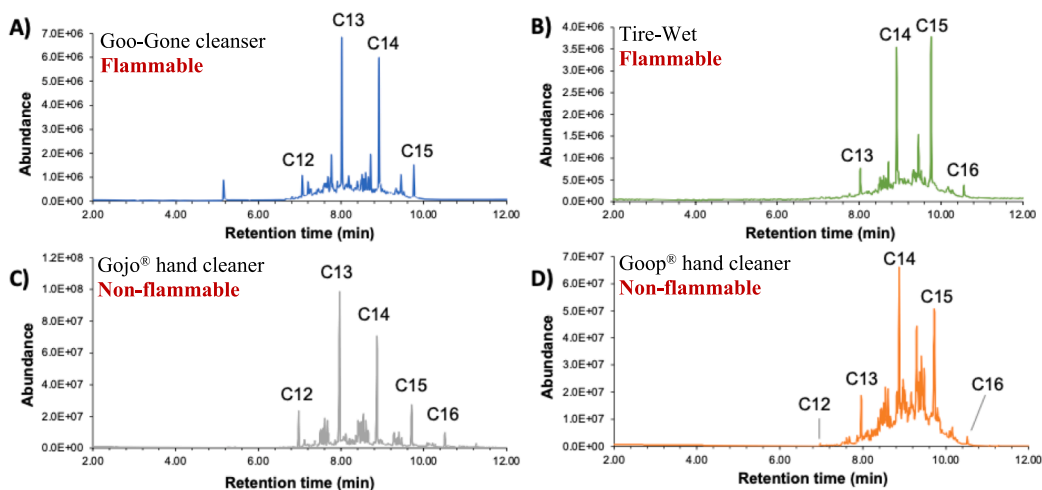


Fig. 3. Headspace concentration-GC/MS analysis using method B of: (A) Goo-Gone® liquid/surface cleanser, an ignitable liquid reference; (B) Tire-Wet® automobile product, an ignitable liquid reference; (C) Gojo® hand cleaner, a non-flammable personal care product; and (D) Goop® hand cleaner, a non-flammable personal care product. Normal alkanes are labeled.

oxygenated ingredients like glycol ethers comprising the organic ingredients totaling ~60 % of the ingredients by mass. We presume that the remaining ~40 % by mass is water. The ether/glycol emulsifiers in Gojo® were also not detected in the headspace concentration sampling mode. We presume that liquid extraction, as described in ASTM-E1386, followed by GC/MS or LC/MS analysis, would reveal the presence of these relatively non-volatile emulsifying agents in both products [39].

Emulsifiers in antiperspirants and deodorants

When examining personal hygiene product samples for characteristic compounds of microemulsions, the most frequently identified compounds were cyclopentasiloxanes, such as decamethyl cyclopentasiloxane. Decamethyl cyclopentasiloxane was present in 23 (92 %) of the 25 samples analyzed. This siloxane-based compound is commonly used in PCPs because it is a skin conditioning agent, emollient, slip-agent and surfactant [12]. However, decamethyl cyclopentasiloxane shares similar synthetic origins and chemical/physical properties with other

cyclic siloxanes, so hexamethyl cyclotrisiloxane, octamethyl cyclotetrasiloxane, dodecamethyl cyclohexasiloxane, and hexadecamethyl heptasiloxane were also commonly observed in the hygiene products. Some samples, like Dove Men's anti-irritant deodorant, displayed decamethyl cyclopentasiloxane as the most abundant compound (Fig. 4). Other samples, such as Old Spice Refresh Amber body spray, contained decamethyl cyclopentasiloxane in quantities marginally above the column bleed (Fig. 4). Given that siloxanes are not present in ignitable liquids, their presence in fire debris is unremarkable and can presumably be ignored.

Emulsifiers in hand and body cleaners

Five of the seven hand and body cleaners contained neutral emulsifying agents/co-solvents that were observable in the headspace concentration-GC/MS chromatograms. These emulsifiers/co-solvents included phenylethyl alcohol (CAS 60-12-8) and 4-*tert*-butylcyclohexyl acetate (CAS 1900-69-2), which is also an odorant. Three of these samples contained decamethyl cyclopentasiloxane (CAS 541-02-6), which was also abundant in the previously discussed hygiene product samples. The neutral surfactants used in these products have boiling points that are significantly greater than the components of ignitable liquids that precede them in the chromatograms. The difference in boiling points makes the surfactants considerably less volatile than the components of the ignitable liquids, so the headspace concentration and analysis method is biased against them. Their involatile nature implies that the condensed (liquid) phase of the hand cleaners would contain a relatively larger proportion of emulsifying agents than is indicated by the headspace concentration-GC/MS results. For example, in related work, Goodman et al. and Stauffer and Byron examined the presence of fatty acid methyl ethers (FAMES) in biodiesel under different analysis conditions [40,41]. The FAMES in biodiesels are significantly less

volatile than most of the petroleum compounds in the biodiesel. So, whereas liquid injections of the biodiesels displayed obvious peaks for the FAMES relative to the less-volatile *n*-alkanes that were present, headspace concentration analyses of the same samples introduced significant bias against the non-volatile FAMES. The FAMES were considerably less abundant and easy to miss when analyzed via their headspace concentration methods [40,41].

The results on FAMES in biodiesels aligns with our analyses, where many of the non-volatile components listed in the safety data sheets are absent from the samples analyzed via headspace concentration-GC/MS. For this reason, liquid/liquid separation or dissolution of the hygiene products and hand cleaners in an organic solvent would likely result in more abundant peaks for the non-volatile compounds and provide a more representative profile of the relative proportions of compounds in the original formulations. However, given that the goal of the current work is to identify whether or not hygiene products and hand cleaners are likely to interfere with casework samples, and given that most casework samples are analyzed using headspace concentration-GC/MS, the chromatograms shown here are considered most relevant to the current goals. For these reasons, headspace concentration-GC/MS will struggle to identify emulsifying agents that could indicate a non-flammable source of medium/heavy petroleum distillates in casework samples. However, emulsifiers should be detectable using different approved standards, like solvent extraction—as described in ASTM E1386—or solvent extraction and derivatization, as described in ASTM E2881 [39,42]. The identification of surfactants with petroleum distillates could provide a way to identify non-flammable, and therefore non-incendiary, formulations of petroleum distillates in clothing of suspected arsonists and other relevant matrices.

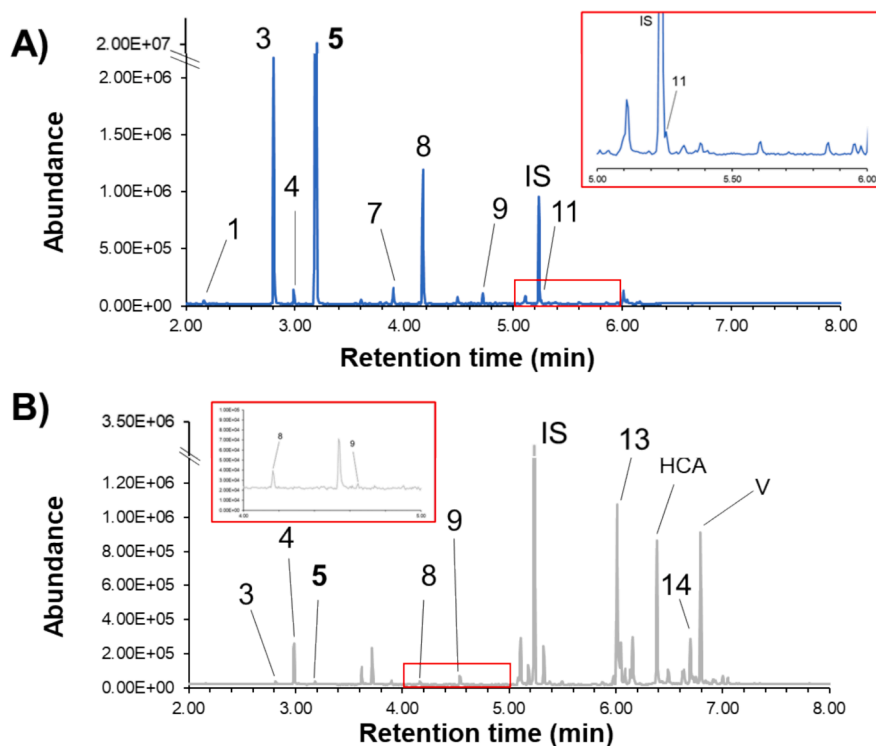


Fig. 4. Headspace concentration-GC/MS chromatograms. (A) is Dove Men's anti-irritant antiperspirant with decamethyl cyclopentasiloxane (5) as the most abundant compound present. This sample also contained six more commonly identified compounds along with abundant peaks of hexyl cinnamic aldehyde (HCA) and versalide (V). (B) is Old Spice Refresh Amber body spray with trace amounts of decamethyl cyclopentasiloxane. Both samples used Method A. The most abundant compounds are labelled according to Table 3.

Application to casework

In 2008, a man managed to escape a house fire, but his wife and two children did not and they died in the fire. Various state and private investigators determined the origin to be a vehicle that was parked in the car port that was attached to the house. Various hypotheses were promulgated regarding the cause of the fire. One hypothesis was a faulty cruise control switch, which had caused fires in other vehicles of the same make and model and was the cause of a recall on the vehicle in question. Another hypothesis was intentional arson using an ignitable liquid. Various samples of charred remains from the car were analyzed by investigators working for both the state and an insurance agency, and the insurance agency found that a charred rag from the footwell on the passenger side contained a heavy petroleum distillate (Fig. 5), thereby indicating arson. In 2016, the man filed a lawsuit against the manufacturer, alleging that the faulty switch was the cause of the fire, so the manufacturer used the arson postulate as a basis for defending the claim. In 2019, eleven years after the fire, the man was arrested and accused of arson and aggravated murder for his wife and two children. In 2020, he was acquitted of all charges by a panel of three judges. In 2021, a federal jury cleared the manufacturer of any fault. The case has now been resolved in criminal and civil court, and the exact cause of the fire remains unknown.

A total ion chromatogram (TIC) of the charred rag from the insurance agency's contractor lab is provided in Fig. 5. Post-hoc extracted ion chromatograms (EICs) and comparisons of this chromatogram to reference samples from the same laboratory confirmed the presence of a medium/heavy petroleum distillate (MPD/HPD). The original lab report did not identify any chemicals outside those found in MPD/HPDs, nor did they provide any context for potential sources or interferences. However, at least two fatty acid methyl esters (FAMES) are also present in this sample: tetradecanoic acid methyl ester (14:0 FAME) and hexadecanoic acid methyl ester (16:0 FAME). These FAMES were identified post-hoc by retention index comparisons and mass spectral fragmentation patterns relative to standards in the NIST database. Unfortunately, the chromatogram ends before 16 min, so the method does not provide information on low-volatility pesticides or other formulation products that may have eluted later in the chromatogram.

Given that the abundance of the FAMES are similar to the *n*-alkanes in this headspace concentration chromatogram, and given that FAMES have considerably lower vapor pressures than the *n*-alkanes, this chromatogram indicates that the concentration of FAMES relative to the *n*-alkanes in the debris sample is considerably greater than indicated in

the chromatogram [40,41,43]. FAMES are not common pyrolysis products, but they are co-formulated with MPDs/HPDs in certain biodiesel blends and consumer products and, for example, as adjuvants or emulsifiers in non-flammable pesticides [8,9,40,41,43–45]. The substrate database at the National Center for Forensic Science/University of Central Florida provides example chromatograms of consumer products (e.g., biodiesels in SRNs 0468 and 0470) that contain FAMES with MPDs/HPDs [38]. The same database includes insecticide formulations (e.g., SRN 0054) containing an obvious distribution of C2- and C3-alkyl benzenes, but with a flammability of "0" (non-flammable) on the SDS because the formulation is an emulsion. Non-flammable emulsions of aerosolized/pressurized insecticides—like ant, roach and wasp killers—are ubiquitous in the public domain.

According to ASTM D6751-20a [46], the minimum flash point for biodiesel (B100) is 93 °C (200F), so biodiesel falls under the non-hazardous category under National Fire Protection Association codes. Biodiesel blends with MPDs/HPDs, such as B50 or B20, may have lower flash points than B100 biodiesels, but obviously they are not as easy to ignite as gasoline or a pure MPD/HPD. If the casework sample had been analyzed using liquid extraction-GC/MS, or if the conditions would have enabled low-volatility pesticides to be detected, the chromatogram may have identified more components that would have pointed to a non-flammable emulsion as the source of the MPD/HPD [10].

Conclusion

The results of this work are somewhat limited by the selected GC/MS method, which could not detect volatiles like acetone, propanol, and ethanol eluting before a retention index of 700. For example, the method cannot detect light petroleum distillates or light oxygenated solvents. However, the main conclusions are not affected by this limitation in the method. Most of the samples (30/32 or ~94 %) identified as personal hygiene products did not contain any of the hydrocarbons commonly found in ignitable liquids. Extracted ion profiles (EIPs) using selected *m/z* values recommended in ASTM E1618-19 and OSAC 2022-S-000 did not provide the patterns or key diagnostic features that were indicative of ignitable liquid residues. Therefore, most of the samples are unlikely to cause interference with the identification of ignitable liquid residues fire debris or the clothing of suspects. Two of the 32 samples (6 %) were industrial-strength hand cleaners and contained heavy petroleum distillates, which, if detected on clothing of a suspect or victim, could correctly be categorized as ignitable liquids despite their non-flammable formulation. These industrial hand cleaners could therefore cause

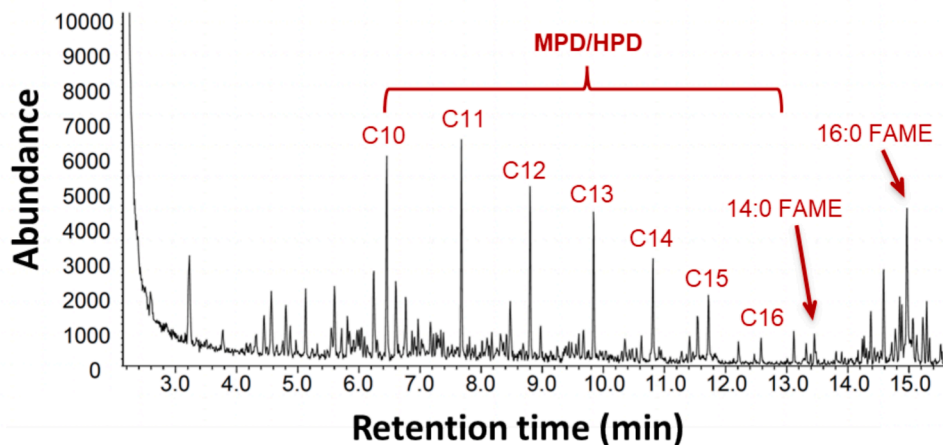


Fig. 5. Headspace concentration-GC/MS total ion chromatogram of a casework sample. The label MPD/HPD indicates the range containing dominant *n*-alkane peaks of a heavy petroleum distillate; the labels 14:0 FAME and 16:0 FAME refer to tetradecanoic acid methyl ester and hexadecanoic acid methyl ester, respectively. The conditions provided by the contractor lab did not afford the observation of less-volatile components.

misleading inferences about the flammable nature of the ignitable liquid. The occurrence of neutral emulsifying agents such as phenylethyl alcohol are sometimes observed at trace levels in the headspace of these hand cleaner product samples. In general, passive headspace concentration-GC/MS is not ideal for the detection of low-volatility emulsifiers/surfactants, and certainly not for polar or charged emulsifiers [40]. Therefore, the existence of neutral emulsifying agents with MPDs/HPDs should be verified with a different form of analysis, such as liquid/solid extraction followed by GC/MS or LC/MS [39,43]. These findings show that, whereas certain industrial strength hand cleaners may result in the correct identifications of ignitable liquids, the co-occurrence of emulsifiers like phenylethyl alcohol can help point to a non-flammable source of MPDs/HPDs.

Finally, a casework sample comprising a charred rag in the fire debris of a car fire was found to contain MPD/HPD. The sample also contains significant levels of C14 and C16 FAMES. These relatively non-volatile components indicate that the source of the MPD/HPD is likely to be a biodiesel blend or a non-flammable emulsion, possibly from an industrial-strength hand cleaner or a pesticide formulation. Additional testing at the time, to investigate the presence of low-volatility co-formulation products, might have pointed more confidently to a non-flammable source of the MPD/HPD. In the examples studied here, oxygenated formulation products in the matrix provided clues about the original sources of ignitable liquids and their lack of flammability.

CRedit authorship contribution statement

Chaney A. Ganninger: Writing – review & editing, Writing – original draft, Formal analysis. **Gabriel M. Walkup:** Writing – review & editing, Writing – original draft, Methodology, Formal analysis, Data curation, Conceptualization. **Sierra M. Fleegle:** Writing – review & editing, Formal analysis, Data curation, Conceptualization. **Glen P. Jackson:** Writing – review & editing, Supervision, Project administration, Methodology, Investigation, Formal analysis, Data curation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.forc.2025.100639>.

Data availability

Data will be made available on request.

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