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Research Article

SPME–GC–MS analysis of solid alcohol fuel residues in forensic fire debris

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Abstract
Detection of ignitable liquid residues in burned materials is critical for forensic investigations, particularly for highly volatile alcohol-based solid fuels that rapidly dissipate after fire suppression. However, the persistence of solid alcohol fuel (SAF) residues under different suppression conditions remains poorly understood. This study investigated the effects of fire suppressants on the persistence of SAF residues using solid-phase microextraction gas chromatography–mass spectrometry (SPME–GC–MS). Cotton fabric piles (20 × 20 × 15 cm^3) were treated with SAF, ignited, burned for 30 min, and subsequently suppressed using either water or dry chemical powder. Burned debris samples (1 × 1 cm^2) were analyzed for ethanol and isopropanol, which were identified as the principal SAF constituents with retention times of 1.198 and 1.259 min, respectively. The analytical method achieved a limit of detection of 12 mmol for ethanol. Following water suppression, ethanol residues decreased to 46% (1,509 mmol) within 2 h and were undetectable after 3 h. Meanwhile, dry chemical suppression extended residue detectability up to 7 h, although only 4% (282 mmol) of the initial ethanol amount remained, with no residues detected after 8 h. These findings provide practical guidance for collecting post-fire evidence in investigations involving alcohol-based solid fuels.

Keywords: solid alcohol fuel, burned materials, residue analysis, SPME GC–MS, forensic accelerants

Introduction

Arson is a criminal offense that poses severe risks to human life and property. Although the act can be executed with relative ease, its consequences are often catastrophic. Fire development is driven by the interaction of fuel, oxygen, and an ignition source, collectively described as the fire triangle, which forms the fundamental basis of fire dynamics and forensic fire investigation [1]. Traditionally, gasoline has been the most frequently used accelerant because of its widespread use as a transportation fuel. However, recent reviews have highlighted a gradual shift toward nontraditional and alternative fuels in fire incidents, particularly alcohol-based fuels that are easily accessible in consumer products [2-3]. Solid alcohol blocks, widely used for domestic cooking and food warming, have emerged as potential accelerants, creating new challenges for forensic fire investigations.

Solid alcohol fuels (SAFs) are commercially available in solid, semi-solid, or gel-like forms. Their principal constituents typically include ethanol (C_2H_5OH), a colorless and highly volatile substance characterized by high flammability, and, in some formulations, isopropanol [4]. Although ethanol is extensively used in the food, beverage, and chemical industries, its combustibility when misused as a fire accelerant renders it a substance of forensic concern. Recent studies have emphasized that alcohol-based fuels behave differently from hydrocarbon fuels because of their lower molecular weight, higher volatility, and strong affinity for water [5-6]. Unlike liquid hydrocarbon fuels, SAFs often require highly flammable substrates, such as cloth or paper piles, to sustain ignition. Moreover, analytical challenges arise because ethanol and isopropanol evaporate rapidly at high temperatures and may be readily removed or diluted by fire suppression agents, making rapid and appropriate evidence collection essential for residue analysis.

The forensic examination of ignitable liquid residues (ILRs) in fire debris is a critical component of arson investigations because accelerants are frequently used to initiate or accelerate fire spread [7-8]. Gas chromatography–mass spectrometry (GC–MS) remains the gold standard for separating and identifying volatile compounds in complex fire debris matrices because of its high sensitivity and selectivity [9]. However, recent forensic chemistry studies have reported that highly volatile fuels, including short-chain alcohols, are susceptible to post-fire loss and suppression-related degradation, which can compromise conventional analytical workflows [3, 10]. Consequently, inconclusive results may occur when residues are extensively weathered, increasing both investigative cost and interpretative uncertainty.

To address the limitations associated with highly volatile fuels, solvent-free extraction methods have been increasingly explored in forensic fire debris analysis. In particular, headspace solid-phase microextraction (HS-SPME) has emerged as a robust solvent-free alternative, offering enhanced sensitivity for volatile compounds through optimized fiber coatings and controllable extraction parameters, such as temperature and equilibration time [10-12]. Recent comparative studies have also demonstrated that coupling HS-SPME with rapid or optimized GC–MS can improve throughput while maintaining adequate sensitivity for early-eluting alcohols [13]. Temperature and equilibration time are particularly critical for highly volatile fuels, such as ethanol, where their minor variations can substantially affect residue recovery. Rapid screening methods, such as ion mobility spectrometry (IMS) and GC–IMS, enable fast pattern recognition and sample triage but generally lack compound-level specificity and hence require confirmatory GC–MS analysis [14-15]. Ambient ionization methods, such as direct analysis in real-time mass spectrometry and rapid GC–MS, further reduce analysis time and solvent consumption; however, reduced chromatographic resolution and susceptibility to matrix interference may limit their effectiveness for highly volatile alcohol residues [10, 16].

Although a substantial body of literature has addressed traditional accelerants, such as gasoline and diesel, investigations specifically focusing on alternative accelerants—particularly SAFs—are inadequate. Existing studies have mainly examined liquid alcohols, mixed ignitable liquids, or alcohol-containing beverages, with relatively few addressing the persistence of SAF residues under realistic fire and post-fire conditions [2, 17]. This limitation has become pronounced given recent reports of severe fire incidents associated with alcohol-fueled consumer products and safety alerts that highlight the misuse of ethanol-based fuels [18]. These observations underscore the need for systematic studies that not only identify alcohol-based fuels but also characterize their detectability over time following fire suppression.

Besides fuel composition, fire suppression agents play a pivotal role in determining residue persistence. Water-based suppression can accelerate ethanol loss through dilution, dissolution, and capillary absorption into porous substrates, followed by enhanced evaporation from wetted surfaces [5, 19]. Meanwhile, dry chemical powder suppressants may form particulate layers on charred materials that restrict mass transfer and partially shield residues from ambient airflow, thereby retarding volatilization [6, 20]. Despite their widespread use in real-world fire scenarios, recent reviews emphasize that the comparative influence of different suppressants on alcohol-based fuel persistence remains underexplored [3].

Accordingly, this study addresses these gaps by investigating the extraction and identification of SAF residues in simulated fire debris using SPME–GC–MS, with particular emphasis on the comparative effects of two commonly used fire suppressants, water and dry chemical powder. Because of their prevalence in commercial SAFs, ethanol and isopropanol were selected as target markers. By integrating optimized analytical conditions with time-resolved residue analysis, this study provides mechanistic and practical insights into alcohol-based fuel persistence and offers guidance for evidence collection in forensic fire investigations. To the best of our knowledge, this study represents one of the first systematic investigations that compared the persistence of SAF residues after water and dry chemical fire suppression using SPME–GC–MS.

Materials and Methods

Fuel samples

SAF samples were purchased from a local commercial supplier in Thailand (RIKO brand, Bangkok). The fuel samples were obtained as standardized pink cubic blocks (approximately 3 × 3 × 3 cm^3; Figure 1a). Each block was individually labeled, stored in airtight polyethylene bags at room temperature (25°C ± 2°C), and protected from direct sunlight before analysis. According to the manufacturer's specifications, the fuel samples primarily comprised ethanol (>95%) with minor amounts of isopropanol (<5%), solidified using polymeric stabilizers.

Chemicals and standards

Analytical-grade ethanol (≥99.9%) and isopropanol (≥99.5%) were obtained from Sigma-Aldrich

(Germany) and used for calibration and method validation. Chemicals were used as received; batch or lot numbers were recorded at the time of purchase and are available upon request. Ultrapure water (18.2 MΩ·cm) was produced using a Milli-Q purification system (Millipore, USA).

Substrates

Cotton fabrics (100% cotton, 200 g m^{-2}, locally sourced) were used as combustible substrates in fire simulation experiments. Fabric bundles measuring 20 × 20 × 15 cm^3 were loosely packed to reflect realistic household textile arrangements and conditioned for at least 24 h under ambient laboratory conditions (25°C ± 2°C; relative humidity 60%) before use.

Fire suppressants

Two fire suppressants were employed: distilled water and a commercial dry chemical fire extinguisher (Imperial brand, Model Dry 2.2 lbs). According to the manufacturer's specifications, the dry chemical formulation primarily comprised monoammonium phosphate with minor additives (e.g., silica and magnesium stearate) and nitrogen propellant gas. These agents were selected because they are the most commonly encountered suppressants in real-world fire investigations (**Figure 1b**).

Consumables and SPME materials

Headspace vials (20 mL; Agilent Technologies, USA) were precleaned with acetone, baked at 120°C for 2 h, and sealed with PTFE/silicone septa (Supelco, USA). SPME fibers (50/30 µm DVB/CAR/PDMS; Supelco) were conditioned at 270°C for 1 h before first use, according to the manufacturer's instructions. Quality assurance procedures included daily blank analyses of empty headspace vials, solvent blanks, and SPME fiber blanks to ensure the absence of carryover and background contamination.

Duplicate measurements (n = 2) were performed for each experimental condition to assess analytical repeatability under controlled laboratory conditions. Instrument calibration and performance verification were performed in accordance with ASTM E1618 [21]. Given the exploratory nature of this study, emphasis was placed on qualitative identification and temporal detection trends rather than extensive statistical evaluation. Future studies will incorporate triplicate measurements and appropriate statistical analysis to better account for volatilization variability and residue persistence.

Optimization of analytical conditions for SAF identification using SPME-GC-MS

SAF samples were obtained as pink cubic blocks (RIKO brand; **Figure 1a**) and used as the primary test materials. Approximately 1-g SAF was sampled by cutting a portion from the interior of the block using a clean stainless steel blade to minimize surface weathering and volatilization effects. Approximately 1 g of each fuel block was accurately weighed and transferred into a 20-mL headspace glass vial, which was immediately sealed with a PTFE/silicone septum to minimize analyte volatilization before analysis. Headspace extraction was performed using SPME, a solvent-free technique widely applied for analyzing volatile and semi-volatile compounds in forensic fire debris because of its high sensitivity and minimal sample handling. A 50/30-µm DVB/CAR/PDMS fiber (Supelco, 23-Ga autosampler) was selected based on its proven high sorptive capacity for low-molecular-weight alcohols, including ethanol and isopropanol [10]. Given the high volatility of ethanol and isopropanol at ambient temperatures (approximately 20°C–40°C), extraction parameters were carefully optimized to enhance recovery while minimizing analyte loss.

Figure 1. Experimental materials: (a) SAF samples obtained in pink cubic blocks (Brand: RIKO) and (b) dry chemical fire extinguisher employed for suppression experiments (Brand: Imperial, Model: Dry 2.2 lbs)

The extraction procedure involved equilibrating the vial headspace at 40°C for 20 min, followed by adsorption onto the SPME fiber for an additional 20 min under the same temperature conditions, selected as a compromise between analyte recovery and volatilization loss for highly volatile alcohols. Subsequently, thermal desorption of the adsorbed analytes was performed in a GC injector for 3 min to ensure efficient transfer onto the analytical column.

Chromatographic separation was achieved using an Agilent HP-5MS capillary column (30 m × 0.32 mm i.d., 0.50-µm film thickness; 5% phenyl-methylpolysiloxane stationary phase), which is commonly employed in ILR analysis and is compatible with ASTM-recommended methods (ASTM E1618). Helium was used as the carrier gas at a constant flow rate of 1.0 mL min^{-1}. To balance resolution, analysis time, and early-eluting alcohol volatility, the oven temperature program was optimized as follows: initial temperature 40°C (0.8 min), ramped to 50°C at 10 °C min^{-1} (0.4 min), then to 100°C at 30 °C min^{-1} (0.1 min), followed by rapid heating to 180°C at 90 °C min^{-1} and a final ramp to 220°C at 120 °C min^{-1}, held for 5 min. This temperature profile enabled efficient ethanol and isopropanol elution while minimizing column bleed and co-elution from matrix components.

The GC injection port was maintained at 220°C with a split ratio of 100:1 and an inlet pressure of 84.9 kPa. Detection was performed using an Agilent 5977B quadrupole mass spectrometer operated in electron ionization (EI) mode at 70 eV. The ion source, quadrupole, and transfer line temperatures were set to 230°C, 150°C, and 220°C, respectively. Full-scan acquisition was performed over an m/z range of 45–300 at a scan rate of 3.6 scans s^{-1}. Instrument performance was verified using the autotune function before analysis, and a solvent delay of 0 min was applied to maximize sensitivity for early-eluting volatile analytes.

All analyses were performed in duplicate to evaluate analytical repeatability. To assess method robustness under realistic post-fire conditions, additional experiments were performed using samples exposed to water and dry chemical fire suppressants (Imperial, Model Dry 2.2 lbs; certified according to TIS 332-2537, Ministry of Industry, Thailand; **Figure 1b**). These experiments were performed under identical analytical conditions to evaluate potential matrix effects arising from suppression media and simulate scenarios commonly encountered in forensic fire investigations [17].

Calibration curve for ethanol quantification

The quantitative determination of residual ethanol was performed using an external calibration curve. Known microliter (µL) volumes of analytical-grade ethanol were dispensed into 20-mL headspace vials, corresponding to absolute ethanol amounts of 0, 171, 343, 856, 1713, 2569, and 3425 mmol. In this study, mmol refers to the total amount of ethanol introduced into each vial rather than a concentration unit, which is appropriate for headspace-based calibration. Each vial was immediately sealed with a PTFE/silicone septum to minimize analyte volatilization and loss.

To ensure methodological consistency, all calibration standards were analyzed under the same optimized SPME–GC–MS conditions as the fire debris samples [8, 21]. The ethanol peak areas were extracted from the chromatograms and plotted against the corresponding ethanol amounts to construct the calibration curve. Linear regression analysis was employed to evaluate the relationship between ethanol amount and detector response, with the regression equation and correlation coefficient (R^2) used to assess linearity and suitability for quantitative determination. Method sensitivity was evaluated by calculating the limit of detection (LOD) and limit of quantification (LOQ) based on calibration statistics, following established forensic analytical practices [9]. These parameters confirmed that the developed method was sufficiently sensitive for detecting trace amounts of ethanol residues in complex post-fire matrices.

Detection of SAF residues on burned substrates

To simulate realistic fire scenarios, controlled combustion experiments were performed in an open-air environment under natural ventilation, without the use of mechanical ventilation or directed airflow, to avoid forced dispersion of combustion gases. All experiments were performed under ambient laboratory conditions (25°C ± 2°C; relative humidity 55%–65%). Fire safety protocols were strictly observed, and appropriate fire extinguishers were readily available throughout the experiments.

Cotton fabric bundles (20 × 20 × 15 cm^3) were loosely packed and selected as test substrates due to their widespread use in household textiles and their frequent recovery in forensic fire debris investigations. Before ignition, each substrate was weighed to ensure consistency (±2 g). A single pink cubic block of SAF (RIKO brand) was centrally positioned on the fabric surface. Ignition was initiated using a laboratory gas lighter, and auxiliary fuels were deliberately avoided to prevent cross-contamination. The fuel was allowed to burn freely until complete consumption, which typically occurred within approximately 30 min, leaving only the substrate and combustion residues.

Two suppressants were applied to evaluate the influence of fire suppression on residue detectability. For water suppression, 1000-mL distilled water was evenly poured over the burning substrate until complete flame extinction was achieved. For dry chemical suppression, a commercial dry powder fire extinguisher (Imperial, Model Dry 2.2 lbs) was discharged toward the flames from a controlled distance of 2 m to ensure consistency across trials. Each suppression condition was conducted in duplicate to assess reproducibility and account for potential variability in combustion dynamics and residue distribution. Control burns without suppression were also performed to establish baseline residue profiles for comparative analysis [17].

Immediately after extinguishment (0 h), a charred debris sample (1 × 1 cm^2) was excised from the central region of the fabric corresponding to the original placement of the SAF block (**Figure 2**). This sampling location was selected to minimize spatial heterogeneity and to represent the area with the highest expected fuel concentration, consistent with standard forensic fire debris sampling practices [8]. To assess the persistence of volatile residues, additional samples were collected sequentially at 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, and 12 h post-extinguishment, reflecting realistic delays in forensic evidence collection.

Each debris sample was carefully weighed (approximately 0.5–1.0 g) and transferred into a 20-mL headspace glass vial, which was immediately sealed with a PTFE/silicone septum to minimize analyte volatilization. Gloves were changed between each sampling event to prevent cross-contamination. All samples were stored at room temperature (25°C ± 2°C) and analyzed within 24 h to reduce analyte loss and sample degradation.

Samples were analyzed using the optimized SPME–GC–MS method described above. Blank controls (unburned fabric) and negative controls (burned fabric without SAF) were included to confirm analytical specificity. Each experimental condition was performed in duplicate, with instrument blanks analyzed between samples to monitor potential carryover. Calibration verification using ethanol standard solutions was performed after every 10 samples to maintain quantitative accuracy. Given this study's exploratory nature, duplicate analyses were considered sufficient for trend evaluation. To ensure methodological reliability and reproducibility, all analytical procedures followed established forensic guidelines (ASTM E1412; ASTM E1618) [21-22].

The experimental design provides a controlled and reproducible framework for evaluating the detectability and temporal persistence of SAF residues under different fire suppression conditions, generating data directly applicable to forensic investigations involving alcohol-based fuels.

Results and Discussion

The ion chromatogram of SAF obtained by SPME–GC–MS analysis exhibited multiple well-defined peaks corresponding to its chemical constituents (**Figure 3**). The retention times (RTs), chemical identities, calculated and reference alkane indices (AIs), and Qual scores of the detected compounds are summarized in **Table 1**.

Figure 2. Sampling procedure for charred debris collection: (a) cotton fabric ignited with a SAF block, (b) fire extinguished with distilled water, and (c) a 1 × 1 cm^2 debris sample collected from the central region corresponding to the original fuel placement

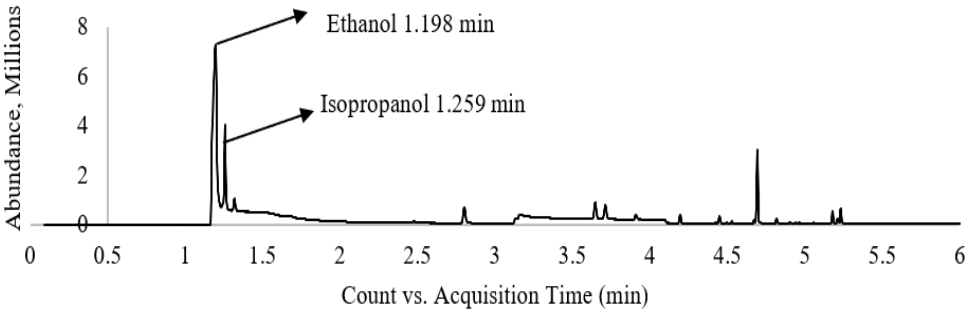

Figure 3. SPME–GC–MS ion chromatogram of SAF showing ethanol, isopropanol, and minor additives

Table 1. RTs, chemical composition, calculated and reference AIs, and Qual scores of compounds detected in the SAF by SPME–GC–MS

RT (min)	Compound	Molecular Weight	AI (Calculated)	AI (Reference)	Qual Score
1.198	Ethanol	46	480	421	9
1.259	Isopropyl alcohol	60	496	496	5
2.804	Toluene	91	709	751	90
3.648	Ethylbenzene	106	1316	1024	50
4.197	α-Pinene	136	977	937	94
4.450	β-Pinene	136	1508	943	94
4.674	*o*-Cymene	134	950	1015	92
4.694	*D*-Limonene	136	1062	1018	99
4.820	γ-Terpinene	136	1213	1240	97
5.179	Cyclohexanone, 5-methyl-2-(1-methylethyl)-, *cis-*	154	1334	1165	97

Notes: Qual score: indicates the similarity of the experimental mass spectrum to the NIST17 reference spectrum. AI: linear retention index calculated from RTs and compared with reference values from NIST17

Quantitative evaluation revealed that ethanol was the predominant component in the SAF, accounting for approximately 51.26% of the total detected signal, whereas isopropanol represented 15.52%. The remaining fraction (33.22%) comprised minor additives, such as aromatic hydrocarbons and terpene-based compounds, such as α-pinene, β-pinene, o-cymene, and D-limonene. These compounds are commonly used as stabilizers, fragrances, or coloring additives in commercial SAF formulations and have been reported in previous consumer alcohol-based fuel analyses [2-3]. The results confirm that SAF primarily comprises short-chain alcohols supplemented by minor organic additives.

Spectral matching against the NIST17 mass spectral library indicated that the peaks at RTs of 1.198 and 1.259 min corresponded to ethanol and isopropanol, respectively. Although the Qual scores for these substances were below the conventional acceptance threshold (<80), this observation is consistent with the known limitations of EI mass spectral library matching for low-molecular-weight alcohols, which typically generate simple and nondistinctive fragmentation patterns [8-9]. Therefore, for short-chain alcohols, compound identification in forensic GC–MS practice relies more strongly on retention behavior and AI agreement than on library match scores alone. To further strengthen compound identification, AI values were calculated and compared with reference values. The calculated AIs for ethanol (480) and isopropanol (496) closely matched the corresponding reference values reported in the NIST17 database. In addition, analytical-grade ethanol and isopropanol (>99.8% purity) were analyzed under identical SPME–GC–MS conditions to confirm retention behavior. This concordance among RT, AI values, and reference standards provides robust confirmation of ethanol and isopropanol as the principal SAF constituents. Some discrepancies between the calculated and reference AI values (e.g., β-pinene) are attributable to differences in column dimensions, temperature programming, and early elution effects, which are well-documented for monoterpenes. Nevertheless, high Qual scores (>90) and consistent retention behavior support reliable compound identification. To assess potential analytical interferences, blank samples and substrate controls were analyzed under the same SPME–GC–MS conditions and chromatographic column. The resulting chromatograms showed no background peaks overlapping the characteristic signals of ethanol and isopropanol. Further, baseline resolution was achieved for all target compounds, with resolution values ≥1.5, indicating adequate chromatographic separation from neighboring matrix components. These findings demonstrate that the developed analytical method is selective and reliable for identifying SAF constituents.

Collectively, the results establish ethanol (RT = 1.198 min; AI = 480) and isopropanol (RT = 1.259 min; AI = 496) as characteristic SAF chemical markers. Their consistent detection across replicate analyses, supported by spectral matching, alkane index confirmation, and interference-free chromatograms, provides a strong analytical basis for the forensic identification of SAF residues in post-fire debris. The findings further support the suitability of SPME–GC–MS as a sensitive and selective method for forensic fire debris analysis involving alcohol-based fuels.

The quantification of residual ethanol in burned debris was achieved using an external calibration curve constructed by plotting ethanol peak area against concentrations of 0, 171, 343, 856, 1713, 2569, and 3425 mmol. Linear regression analysis yielded the equation $y = 979340x - 738428$ with an R^2 of 0.9993, indicating excellent linearity over the examined concentration range. Based on the calibration data, the LOD and LOQ were determined to be 12 and 41 mmol, respectively. These values are comparable to those reported by Hesham et al. (2025), who achieved an LOD of approximately 10.8 mmol for ethanol using headspace GC–MS in forensic applications. The comparable sensitivity confirms that the developed method is sufficiently robust for detecting trace amounts of ethanol in complex post-fire matrices.

To further evaluate analytical specificity, materials used in the experimental setup were analyzed under identical SPME–GC–MS conditions. No interfering peaks corresponding to ethanol or isopropanol were observed at the RTs, including in samples previously exposed to suppressants (**Figure 4**). This observation confirms that neither the substrates nor the suppressants introduced analytical interferences that could compromise SAF residue identification or quantification.

The effect of different fire suppressants on the detectability of SAF residues in burned materials was systematically evaluated. SAF was placed on a cotton fabric pile (20 × 20 × 15 cm^3), ignited, and allowed to burn freely for approximately 30 min under controlled conditions. Subsequently, fire suppression was performed using either distilled water or a red dry chemical powder extinguisher until complete extinguishment was achieved. Charred debris samples (1 × 1 cm^2) were then collected from the central region of the burned substrate and analyzed using the optimized SPME–GC–MS method.

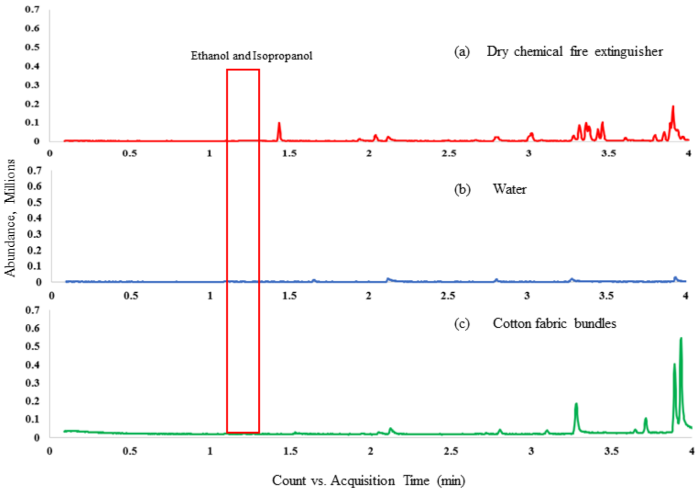

Figure 4. Comparison of ion chromatograms showing no ethanol detection in the materials: (a) dry chemical fire extinguisher, (b) water, and (c) cotton fabric bundles

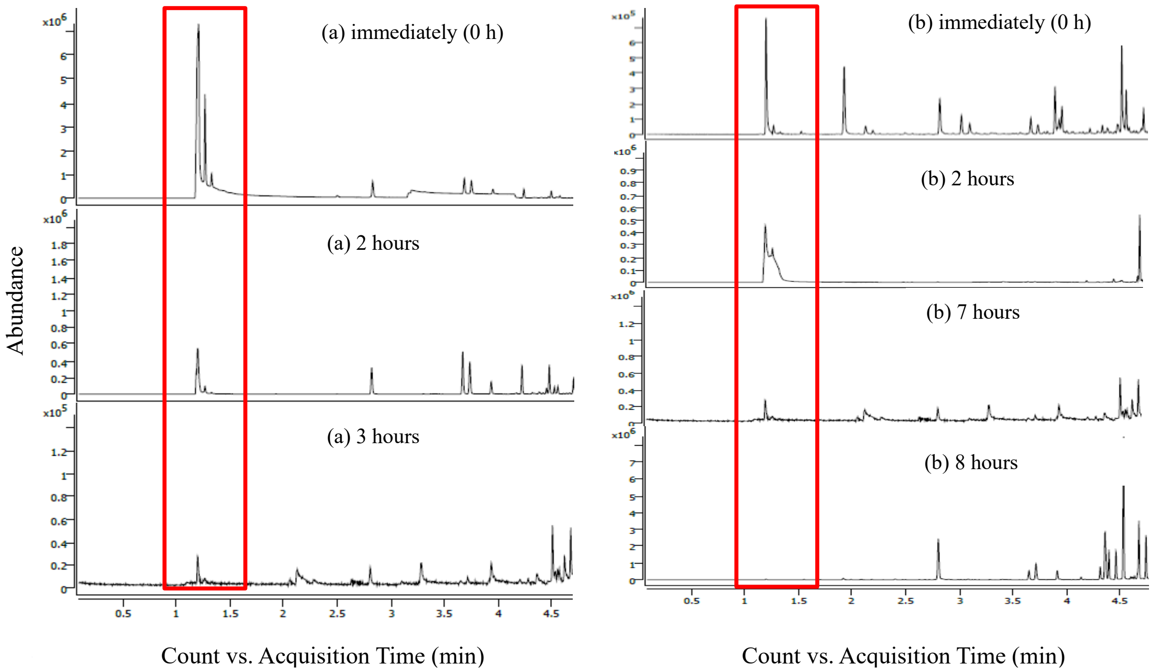

Figure 5. Comparison of ion chromatograms showing ethanol detection in fire debris under different suppression conditions: (a) fire suppression with water and (b) fire suppression with a dry chemical powder extinguisher.

Ion chromatograms obtained immediately after extinguishment (0 h) revealed distinct peaks at RTs of approximately 1.198 and 1.259 min, corresponding to ethanol and isopropanol, respectively, which are the principal SAF constituents. These characteristic peaks were observed following both water and dry chemical powder suppression, confirming the presence of SAF residues in post-fire debris regardless of the suppressant used (**Figure 5**). The consistent detection of ethanol and isopropanol immediately after fire suppression demonstrates that neither suppressant interfered with the initial chromatographic identification of the target compounds. However, differences in peak intensity and subsequent persistence trends highlight the influence of suppressants on residue survivability and detectability, as discussed in the following sections [17, 20].

Effect of fire suppression on temporal persistence of ethanol residues

When water was used as the suppressant, ethanol residues were detectable for up to 2 h post-extinguishment (**Table 2**). Relative to the reference sample collected immediately after suppression (0 h, defined as 100%), the ethanol content decreased to 46% (1,509 mmol) after 2 h. No detectable peaks of ethanol or isopropanol were observed at 3 h post-extinguishment. Although the decline does not strictly follow first-order kinetics, the pronounced reduction during the early post-extinguishment period, followed by nondetectable levels, is consistent with evaporation-dominated loss rather than substrate-limited diffusion, particularly in the presence of water-based suppression. These results are consistent with previous findings reported by Gonzalez et al. [19], who observed that ethanol residues on burned cotton fabrics following water-based suppression were detectable only within a short post-fire interval using headspace-based analytical techniques.

Meanwhile, when fire suppression was performed using a red dry chemical powder extinguisher, ethanol residues remained detectable for a substantially longer period, up to 7 h post-extinguishment (**Table 2**). At this time point, the relative ethanol content was reduced to approximately 4% (282 mmol), which remained above the LOD. The minimum quantifiable ethanol concentration (41 mmol) was also detected within this interval. No ethanol or isopropanol residues were detected beyond 8 h post-extinguishment (**Table 2**). Compared with hydro carbon-based fuels, Dhabbah et al. [20] reported gasoline residue detection on burned carpet up to 5 h post-extinguishment, and Hodálik et al. [17] observed gasoline persistence up to 6 h. Therefore, the present results highlight the greater volatility and lower persistence of ethanol relative to hydrocarbon fuels while simultaneously demonstrating that the choice of fire suppressant plays a pivotal role in residue survivability.

The observed differences between water and dry chemical suppressants can be explained by physicochemical interactions between the suppressants and ethanol residues. Water-based suppression likely accelerates ethanol loss through dilution, dissolution, and capillary absorption into porous substrates, followed by enhanced evaporation and diffusion. Meanwhile, dry chemical powders, primarily comprising monoammonium phosphate with minor additives, such as silica and magnesium stearate can form a particulate coating on charred surfaces. This coating may partially shield ethanol residues from ambient airflow, thereby reducing volatilization and prolonging residue persistence. Localized changes in surface chemistry and microenvironmental conditions may further contribute to delayed evaporation, resulting in an extended detection window of up to 7 h following dry chemical suppression.

Overall, these findings confirm that although ethanol and isopropanol are less stable than hydrocarbon-based fuels in post-fire environments, SAF residues remain detectable within a limited but forensically relevant timeframe. In particular, dry chemical suppression markedly extends the persistence of detectable ethanol residues compared with water suppression. These results underscore the relevance of considering the type of fire suppressant when interpreting fire debris evidence involving alcohol-based fuels (**Table 2**).

Regarding the detection of SAF residues in burned materials, neither water nor dry chemical suppression interfered with the chromatographic identification of ethanol and isopropanol. However, the effective detection window for SAF residues was limited, generally not exceeding 4–6 h post-extinguishment under the suppression conditions investigated (**Table 2**). This limited persistence is primarily attributed to the physicochemical properties of ethanol, the main SAF constituent, which is highly volatile at ambient temperature, exhibits increased evaporation rates upon heating, and is readily soluble in water. Consequently, delays in firefighting response or prolonged intervals between fire suppression and evidence collection can considerably reduce the likelihood of detecting residual ethanol in post-fire debris.

Conclusion

This study systematically evaluated the influence of fire suppressants either water and dry chemical powder on the detectability of SAF residues in burned substrates using SPME–GC–MS. Ethanol and isopropanol were consistently identified as the principal SAF constituents and served as reliable chemical markers for confirming the presence of alcohol-based fuels in post-fire debris. Neither suppression method interfered with chromatographic identification, as both ethanol and isopropanol exhibited well-resolved, early-eluting peaks.

Quantitative results demonstrated that ethanol residues persisted for up to 2 h following water suppression and became undetectable thereafter, whereas dry chemical suppression extended the detection window to 7 h at trace amounts (approximately 4% of the initial concentration, 282 mmol). These findings indicate that dry chemical suppressants may partially retard ethanol volatilization, likely by forming a physical barrier on charred surfaces, thereby enhancing short-term residue preservation. The results provide practical forensic insight for optimizing evidence collection strategies in arson investigations involving alcohol-based fuels, particularly with respect to the timing of post-fire sampling.

Table 2. Comparison of ethanol detection in fire debris under different suppression conditions

Extinguishing Agent	Detection Time (h)	Ethanol Remaining (% of Initial)	Ethanol Concentration (mmol)
Water	0 h	100%	3,282 mmol
	2 h	46%	1,509 mmol
	3 h	ND	–
Dry chemical powder	0 h	100%	3,282 mmol
	3 h	~40% (est. from reduction)	~1,300 mmol
	7 h	~4%	282 mmol
	8 h	ND	–

ND = not detected

Overall, this study demonstrates the applicability of SPME–GC–MS as a selective and sensitive analytical method for the identification and temporal assessment of SAF residues in fire debris and contributes to the limited body of literature addressing alternative fuels in forensic fire investigation.

Limitations

This study was conducted as a preliminary investigation under controlled laboratory conditions using a single substrate type and two fire suppressants. Duplicate analyses were performed to assess repeatability; however, increased replication and broader substrate diversity would improve statistical robustness and generalizability. Method validation focused on calibration, repeatability, and qualitative matrix interference assessment. Future studies should incorporate additional substrates, suppressants, and expanded validation to better reflect real fire scene conditions.

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