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TECHNICAL NOTE
Development of an Extraction Technique for Ignitable Liquid Residues (ILR) in the Field using Capillary Microextraction of Volatiles (CMV) and Person-Portable GC-MS

Introduction

Person-portable GC-MS is an advantageous tool for emergency first-responders. It can provide rapid data acquisition, which informs credible leads early in an investigation. This can be especially beneficial for investigators at fire scenes, whose main goal is to determine whether the fire was set intentionally or accidentally. A significant indication of an intentionally set fire would be the presence of ignitable liquid residues (ILR) at the scene (Lam et al., 2018).

The common choice for residue detection is an accelerant detection canine, or arson dog. Their naturally heightened sense of smell can detect trace amounts of residues with a very high degree of accuracy. Their success, however, depends on the comprehensiveness of their training and on natural abilities that vary by individual animal. Finally, despite their accuracy, they cannot communicate the identity of what they found but only that they found something (Almirall, Arkes, Lentini, Mowrer, & Pawliszyn, 2017; Tindall & Lothridge, 1995).

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Knowing this, investigators must still collect any potential evidence and send it for analysis, which can take weeks to months depending on a laboratory's backlog. The use of a portable GC-MS in conjunction with a sensitive extraction technique could be a valuable screening tool, allowing for more efficient scene processing and less evidence sent for confirmatory testing.

The work in this report is an extension of the capillary microextraction of volatiles (CMV) application (M. Torres et al., 2020) by Florida International University, reported by the Forensic Technology Center of Excellence (FTCoE) in April 2020. This technical note details the optimization of a field-sampling protocol originally used with solid phase microextraction (SPME), now adapted for use with the CMV (M. N. Torres & Almirall, 2022). Following the optimization, Florida International University researchers extracted ILRs from simulated fire debris and analyzed the extracted compounds using a portable GC-MS unit. Finally, qualitative sampling researchers conducted at a controlled structural fire for a preliminary field assessment of the sampling protocol and portable unit.

Instrumentation

A FLIR Griffin G510 GC-MS was used to collect all portable-related data. The system was equipped with a PSI-Probe attachment for direct insertion of the CMV device into the GC inlet. The injector temperature was set at 250°C. A DB-5MS (15 m × .18 mm × .18 µm) was used as the analytical column. The oven was programmed with a starting temperature of 40°C and four ramp steps. Step 1 had an end temperature of 40°C with a 0.25 min hold and no split. Step 2 had an end temperature of 80°C at a rate of 7°C min^{-1} and a 20% split. Step 3 had an end temperature of 200°C at a rate of 16°C min^{-1} with no hold or split. Step 4 had an end temperature of 275°C at a rate of 30.10°C min^{-1} with no hold or split for a total run time of 16 min. The MS source was set to 200°C. Data acquisition occurred in Full Scan mode, over the range of 45–400 m/z.

A sub-library of compounds was programmed into the instrument method for qualitative and quantitative purposes. A standard solution of 20 compounds representing residue components was used to determine retention times. Eighteen of the 20 compounds had existing entries in the onboard library, thus only retention time information was added. Entries were manually created for the two missing compounds (4-ethyltoluene and durene) using the standard solution. Calibration curves (5–300 ng µL^{-1}) were constructed via direct spike onto the CMV for all 20 compounds and recorded into the fire debris sub-library.

CMV/Cup Extraction Optimization

A common laboratory practice for ILR extraction is the use of a headspace/adsorption technique to sample volatiles from the debris container, followed by GC-MS analysis. Method choice is based on several factors like the condition of the evidence and the type of container. Generally, most techniques benefit from heating the container for an equilibration period to allow sufficient vapor build-up for efficient extraction. Consequently, many laboratory techniques are not well suited to fieldwork because of the additional apparatus necessary.

In a related study (DeHaan, Byron, Matthew, Jones, & Harper, 2021), the need for a container was accounted for by using a simple paper cup in conjunction with a SPME fiber. High-concentration areas were first marked out with a photoionization detector. The cup, placed upside-down over the suspected "hot spot," concentrated the headspace without the need for external heating. To sample, the fiber was exposed through a hole in the cup for a brief period. Like SPME, the CMV is capable of functioning as an open-air sampling device; however, this is not an optimal way of extracting ILRs from debris. For this study, the same cup concept was applied to the CMV.

Several variables were considered in the optimization of a CMV/Cup protocol, including equilibration time, sampling time, and size (volume) of the cup utilized. The goal was to optimize for both maximum recoveries and the greatest range of analytes possible. Ideally, the technique should be useful for the extraction of every weight class of ignitable liquid. Equilibration time was considered to determine the smallest amount of time possible for sufficient vapor to build up. The sampling time was given the same concern, in addition to limiting breakthrough of relevant analytes. The variable test points were selected in the interest of keeping the overall protocol time under 10 min for high-throughput extractions.

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Figure 1: Photograph depiction of the CMV/Cup apparatus with debris placed on the glass platform (left) and the CMV sampling using the hand-held vacuum pump (right).
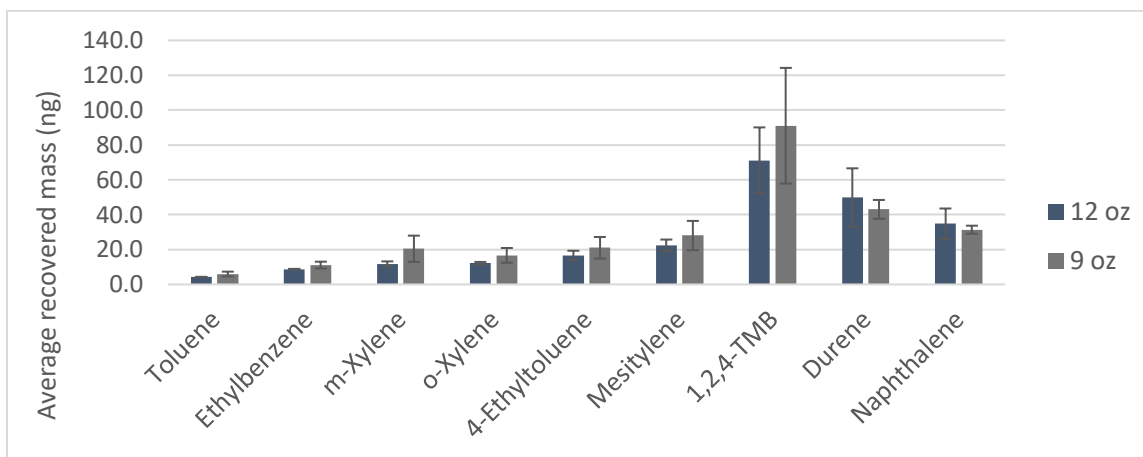
Each set of optimization experiments was carried out twice—one set sampling neat gasoline and the other sampling neat diesel fuel. The sample matrix was prepared by spiking 10 μL of either ignitable liquid onto approximately 4 g of wooden bamboo sticks. The sticks were left uncovered at ambient temperature for 25 min to let most of the liquid evaporate prior to extraction. To sample, the material was transferred to a clean glass platform and immediately covered with a single paper cup. A small hole was made 1.4 cm above the rim before use for the snug insertion of a CMV device.

A single trend found in all optimization experiments was the distinct improvement in aliphatic semi-volatile compound recoveries. Ultimately, the optimal sampling parameters were chosen according to what was the best compromise between increased semi-volatile recovery and minimized loss of the lighter volatiles. A 2-min equilibration time was considered optimal because it produced the lowest variation (%RSD) in the average recoveries of the aliphatic series (decane to tetradecane) found in diesel fuel. Variation at 5 min equilibration time was 10%–26% greater than at 2 min, whereas there was less than 10% variation difference for all eight detected gasoline compounds. A 3-min sampling time resulted in the greatest improvements to the diesel aliphatic series recoveries relative to a 2-min sampling time. On average, recoveries at 2 min were only 7.5 ng greater for gasoline. For the diesel components, semi-volatile recoveries were doubled at 3 min whereas volatile components were equal or up to 10 ng greater. Cup volumes of 9 and 12 oz were evaluated using the previously optimized parameters: 2-min equilibration time and 3-min sampling time. Figure 2 shows the average recovered masses for components detected from each ignitable liquid. Recovery increases for the detected gasoline components from using a 9 oz cup compared with a 12 oz cup ranged between 2–9 ng, with the greatest increase of 20 ng for 1,2,4-trimethylbenzene. All diesel components saw an increase in recovered mass with the smaller cup volume, ranging from 3–17 ng for the aromatics and 13–94 ng for the aliphatics.

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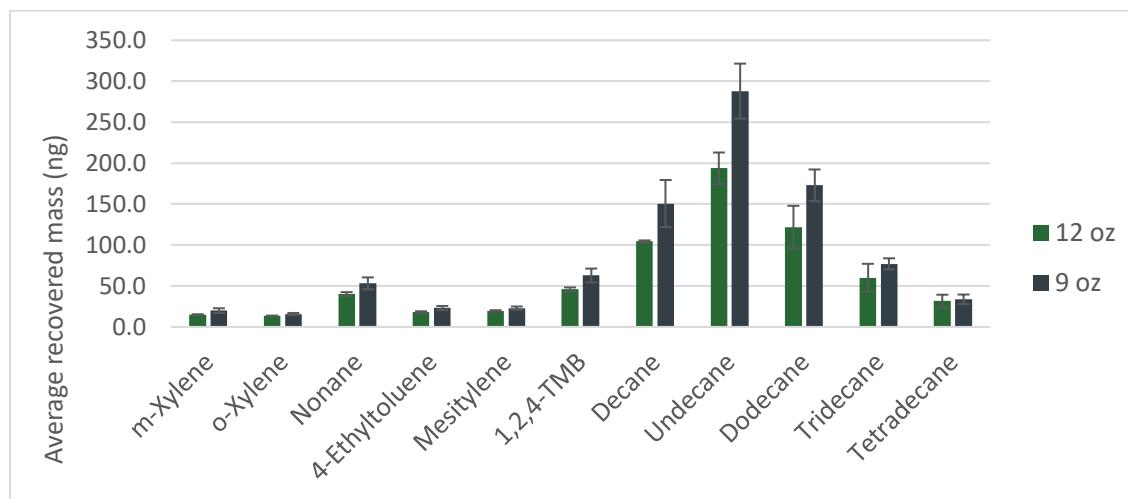
(a)

(b)

Figure 2: Average (n = 3 extractions) masses of gasoline (a) and diesel (b) components using the CMV/Cup protocol to determine the optimal cup volume.

Extractions from Simulated Debris

Several experiments involving sampling and extracting ignitable liquids from simulated debris were performed following the completed optimization of the CMV/Cup protocol. Three different materials were selected as the matrices: blue jean fabric, cardboard, and plastic bubble wrap. Approximately 4 g of each material were burned within a ceramic crucible via direct contact with a propane torch. The material burned for 2 min and was then extinguished by covering the container with a metal lid for

30 sec. Before sampling, the material sat uncovered at ambient temperature for 4 hours to simulate the sampling delay that would occur at a fire scene. After 4 hours, all remaining debris was transferred to a clean glass platform and covered with a new cup to carry out the CMV/Cup protocol (Figure 1). Analysis was performed by directly inserting the CMV into the inlet of the G510.

Debris sampling was a two-part process. First, the debris was sampled on its own to characterize the background combustion/pyrolysis products. The resulting profiles were

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evaluated visually and ion-extracted for any analytes of interest contained in the sub-library. The same charred material was then spiked with a known volume of diluted gasoline. Volumes of 1, 3, and 5 µL of a 1% gasoline solution (diluted in pentane) were spiked onto a 2.4 cm glass-fiber filter placed at the base of the debris pile. A new cup was immediately placed over the material, and the protocol was carried out once more. The same CMV was applied in both instances, after a 15-min conditioning period between the first and second sampling. The integrated areas of any analytical signals found in the matrix blanks were subtracted from those in the spiked samples prior to quantification.

Six key analytes were consistently identified by the instrumental method from all three materials at all spike volumes. Table 1 lists these compounds, the average recovered mass, and the %RSD for the materials over three replicate measurements at the 1 µL spike volume. Mesitylene became detectable at the 3 µL volume for all materials with an average signal-to-noise of 11. Average mass recoveries at all volumes were highest from the jean fabric samples, followed by the plastic wrap and cardboard. Enhanced recoveries with increased spike volume were also consistent among all sampled materials. Increases of 500%–950% were attained with the 5 µL spike volumes relative to the 1 µL spikes. The precision of the technique improved with the increase in spike volume; the 16%–47% RSD range at the 1 µL volume decreased to between 2 %20% at the 5 µL volume for the same set of compounds. This is thought to be the result of the imperfect seal between the cup lid and the surrounding environment, which could allow ambient air in. This would dilute the headspace vapors during the entire equilibration/sampling time.

Table 1: Average mass recoveries (ng) and %RSD from simulated fire debris at the 1 µL spike level using the CMV/Cup protocol and portable GC-MS

Compounds	Cardboard		Plastic Wrap		Jean Fabric	
	Average mass recovered (ng)	%RSD	Average mass recovered (ng)	%RSD	Average mass recovered (ng)	%RSD
Toluene	7±2	30	12±3	22	19±2	9
Ethylbenzene	4±0.1	2	5±2	33	8±1	19
m-Xylene	8±2	26	16±6	37	24±5	21
o-Xylene	6±0.4	6	7±2	29	10±2	19
4-Ethyltoluene	6±1	21	7±3	47	10±2	22
1,2,4 - TMB	8±1	16	8±3	38	13±3	24

Qualitative Field Testing

The optimized cup protocol and G510 unit were taken for preliminary field testing in a controlled structural burn in Carrboro, North Carolina. An old farmhouse scheduled for demolition had been utilized by the local fire department for several small-scale burns conducted for fire investigation training. Two furnished rooms post–full involvement were used for testing at the conclusion of training. Within each room, two sampling scenarios were implemented. The first was random detection sampling of a surface doused with a variable volume of gasoline prior to ignition (Ethanol-free 87

grade). The gasoline deposition in both rooms was limited to a twin mattress, with a small trail leading off one corner and out to the closest doorway. In the second instance, known microliter volumes of gasoline were spiked onto a blank area to determine the sampling sensitivity in the presence of pyrolysis/combustion products. For high-throughput analysis, multiple CMVs were used for headspace sampling of select areas with simultaneous operation of the G510. CMVs were wrapped in a small sheet of aluminum foil and placed into individual amber GC vials for storage until analysis (see Figure 3).

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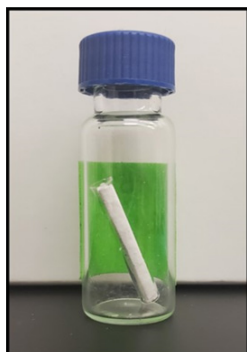
Figure 3: Photograph of the portion of the CMV stored in a vial until analysis. To aid in visualization, the CMV is in a clear, not amber, vial and does not include the aluminum foil.

Random samplings of both mattresses produced high variation in the intensities of detected compounds. In all samples taken from the first (i.e., back) room's mattress, background interference was minimal with respect to the number of compounds present (Figure 4). Two compounds—furfural and limonene—were presumptively identified. Limonene predominated the samples taken from the charred mattress top but was seen in amounts relative to other gasoline markers in the less damaged, exposed foam samples. Neither background product coeluted with any other analyte of interest. Nine gasoline markers were detected in similar amounts from both areas, with peak intensities reaching between 0.6–1.3 M. The nine compounds are the same nine consistently detected in the aforementioned protocol optimization experiments (Figure 2a). In contrast, headspace sampling of the mattress in the second (i.e., front) room produced significantly overloaded chromatographic profiles. Recoveries were heavily skewed in favor of the lightest aromatics (e.g., toluene, ethylbenzene, and the xylene isomers); however, closer examination of the entire profile shows detection of other gasoline identification markers as per ASTM 1618–19 criteria (ASTM International, 2019), up to and including 1- and 2-methylnaphthalene. The time window of substrate exposure to ambient conditions after fire extinction is thought to be the cause of the detection sensitivity variability. For the first mattress, the gasoline deposition, room ignition, and extinction happened within a 20-min window in the early afternoon the day prior to sampling, when the window of substrate exposure to ambient conditions was approximately 18 hours. In contrast, the second mattress only had an approximately 30-min exposure window before the sampling/extraction.
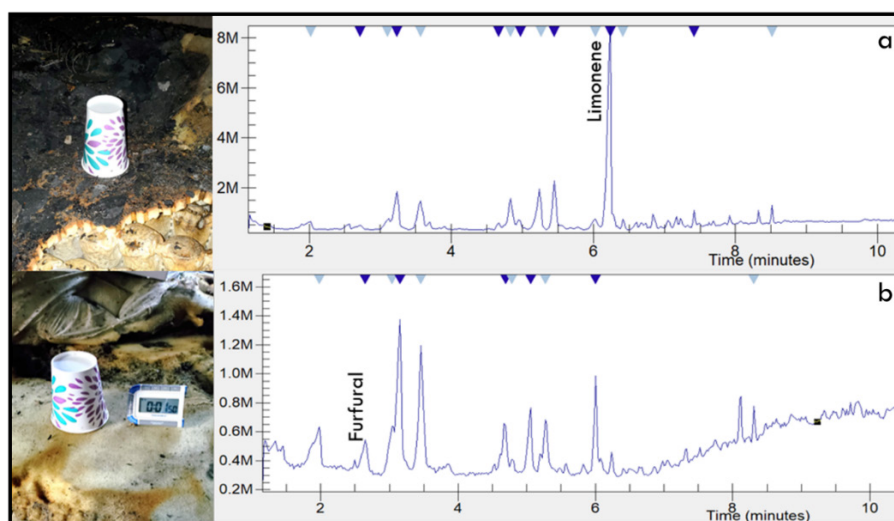

Figure 4: G510 Chromatograms from (a) charred mattress top and (b) exposed mattress foam from the first (back room) mattress.

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The sampling protocol for known volume spikes in both rooms incorporated a 5-min delay prior to the 2-min equilibration period. This was in an effort to prevent oversaturating the CMV device and the instrument. Despite this delay, initial volumes of 50 µL proved too concentrated for good qualitative data. Spike volumes were then reduced to 10 µL, in addition to increasing the inlet split to 50% as another preventative measure. Blank extractions of the carpet area contained only minor contributions of light aromatics with S/N < 10, thought to be from the heavy concentration of soot in the air or transfer from foot traffic through the scene. Replicate samplings from the 10 µL spikes onto the carpeted area resulted in clear profiles consistent with ASTM E1618–19 criteria for gasoline identification (Figure 5a and 5b). All analytes of interest were identified based on their retention times and mass spectra.
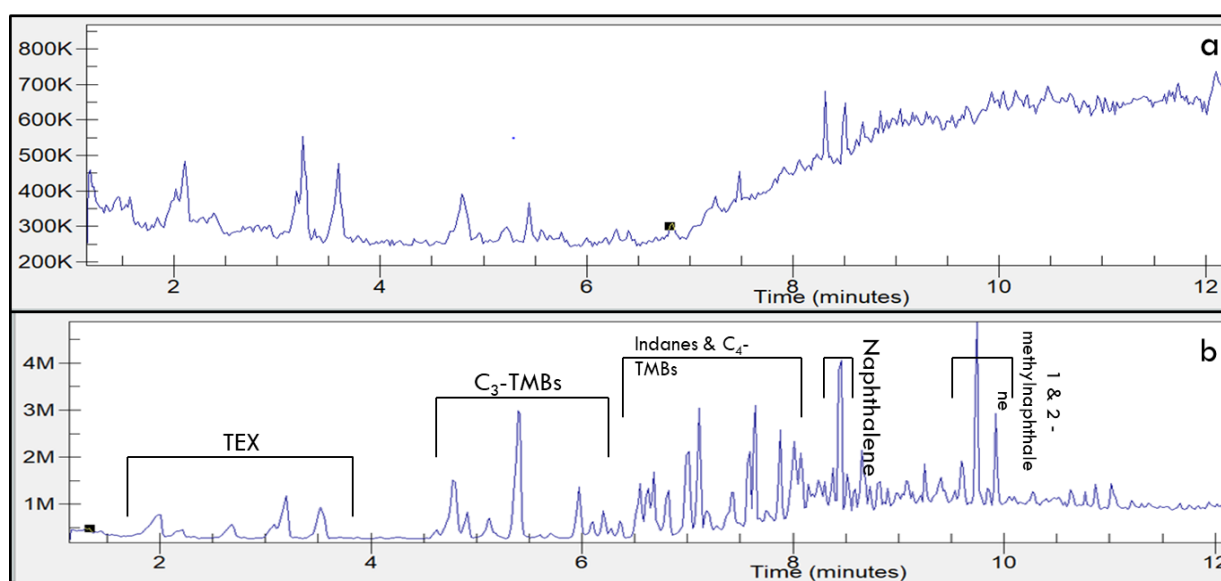

Figure 5: G510 chromatograms of (a) second (front room) carpet blank and (b) 10 µL spike of 87-grade gasoline onto front room carpet with labeled analytes of interest

Conclusions

A fast, easy, and inexpensive method to screen for ILR at an active fire scene would greatly benefit he advancement of an investigation. The work in this report details the development of a 5-min sampling/extraction protocol (2-min equilibration, 3-min sampling) using the CMV and a simple paper cup as the extraction vessel. Results are obtained within 20 min using the sampling protocol in conjunction with the portable G510 GC-MS method. Multiple key ILR components are reproducibly detected within a low nanogram range. Ongoing work involves continuing to evaluate the cup as an extraction vessel, including the design of an external attachment to improve the extraction efficiency of less volatile analytes found within heavier ignitable liquids. Additional fieldwork will also be conducted to evaluate the current protocol's efficacy and determine if further optimization is needed.

Acknowledgments

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References

Almirall, J., Arkes, H., Lentini, J., Mowrer, F., & Pawliszyn, J. (2017). Forensic science assessments: A quality and gap analysis—fire investigation.

ASTM International. (2019). ASTM E1618 - 19: Standard test method for ignitable liquid residues in extracts from fire debris samples by gas chromatography-mass spectrometry.

DeHaan, J. D., Byron, D., Matthew, D., Jones, R., & Harper, R. (2021). Advancing fire scene investigations with field portable technologies.

Lam, R., Lennard, C., Kingsland, G., Johnstone, P., Symons, A., Wythes, L., . . . Spikmans, V. (2018). Person-portable equipment in environmental forensic investigations: application to fire scenes. *Australian Journal of Forensic Sciences*, 1-10. doi:10.1080/00450618.2018.1424242

Tindall, R., & Lothridge, K. (1995). An evaluation of 42 accelerant detection canine teams. *Journal of Forensic Sciences, 40*(4). doi:10.1520/jfs13825j

Torres, M., Gura, S., Tarifa, A., Mulloor, J., Valdes, N., Grabenauer, M., & Almirall, J. (2020). *Modifications to capillary microextraction of volatiles (CMV) for the extraction of ignitable liquid residues (ILRs)*. Washington, DC: U.S. Department of Justice, National Institute of Justice, Office of Investigative and Forensic Sciences.

Torres, M. N., & Almirall, J. R. (2022). Evaluation of capillary microextraction of volatiles (CMV) coupled to a person-portable gas chromatograph mass spectrometer (GC–MS) for the analysis of gasoline residues. *Forensic Chemistry, 27*, 100397. doi:https://doi.org/10.1016/j.forc.2021.100397

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