

Comparison of portable and benchtop GC–MS coupled to capillary microextraction of volatiles (CMV) for the extraction and analysis of ignitable liquid residues

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HIGHLIGHTS

- CMV was coupled to TRIDION-9 (T9) for first time via CMV/NTD.
- Multiple ILR compounds were sampled from debris at nan grams levels.
- CMV is capable of retaining ILRs in < 5 min of open-air sampling.
- 14 out of 20 ILR components correctly identified at low mass loadings on the T9.

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ABSTRACT

A novel extraction device, capillary microextraction of volatiles (CMV) was coupled to a TRIDION-9 GC–MS with a needle trap (NTD) and evaluated for the analysis of ignitable liquids fire debris. The performance of the TRIDION-9 was compared to a benchtop GC–MS using CMV. A system detection limit of ~10 ng for each of 20 key ignitable liquid residue (ILR) compounds was determined for the T9 GC–MS. Dynamic headspace sampling of simulated ILRs was performed in closed and open-air systems. Closed system evaluations the CMV/NTD technique resulted in extraction performance similar to the CMV alone; however, ILR analysis on the T9 was impacted by limited chromatographic resolution. Compound identification was possible for 14 out of the 20 selected compounds on the T9 when 1 µL of a 1% standard accelerant mixture (SAM) was sampled, compared to 17 compounds on the benchtop GC–MS for the same mass loading. Open-air sampling with a modified vapor source resulted in the retention of most compounds with as low as 5 min. sampling, and equilibrium concentrations were reached after 10 min. No significant differences were observed between CMV and CMV/NTD sampling suggesting that the combined technique does not suffer from affinity bias. While the potential of the CMV/NTD extraction coupled to a T9 GC–MS for fire debris analysis was limited by the chromatographic resolution of the instrument, this study serves as proof of concept for the CMV's potential for the extraction of ILRs in combination with portable GC–MS systems.

1. Introduction

The analysis of fire debris is often essential for criminal investigators when working cases where a fire is suspected of being intentionally set with an accelerant. This can include materials like newspapers, cigarettes, and candles, but the most commonly used accelerants are ignitable liquids. One of the most frequently encountered ignitable liquids in debris from a fire that is suspected as arson is gasoline due to its accessibility and ease of use [1]. Fire debris analysis typically involves the packaging and transport of charred material from the scene to the

laboratory, where it will undergo an extraction process to isolate any ignitable liquid residues (ILRs) not consumed by the fire. Once extracted, analysis is normally performed using gas chromatography–mass spectrometry (GC–MS) to obtain the chromatographic profile and mass spectral data necessary for the characterization [2]. Analysis in this manner has long been an industry standard because it results in repeatable, reliable data; however, it is also a very lengthy process. A complete laboratory report may not be available to investigators for weeks or months depending on the extraction process utilized and the complexity of data interpretation. This can pose a

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problem for the investigation, especially in the identification of potential suspects. The ability to generate presumptive data at the fire scene could significantly aid fire investigators and the investigation as a whole [3].

One potential solution to this need has been the development of field-portable instrumentation. Currently, the most effective tools for on-scene investigations are accelerant detection canines (ADCs). ADCs are considered the gold standard in 'hot spot' identification because of their naturally heightened sense of smell relative to a human's. They are highly mobile and can alert to residues quickly with reported accuracies as high as 90% [4,5]. They are, however, limited in use to non-dangerous scenes for their safety. Overall performance at a scene can also be affected by the natural endurance of the animal, or by subconscious influencing of the handler. Finally, they are incapable of communicating the identity of the residue they hit upon, thus necessitating the collection of evidence for transport back to the lab for confirmation and identification [6–8].

Other technologies such as portable hydrocarbon noses have been applied to onsite detection, however, they generally lack sensitivity and specificity. Another major drawback is their inability to differentiate between legitimate residue components and pyrolysis products, therefore leading to false positives [9–12]. Gas chromatographic systems such as the zNose™ have been evaluated for ILR detection but most have ultimately suffered from the same issues faced by less sophisticated instrumentation, in addition to contamination, poor resolution, and poor fieldable designs [13]. The viability of miniaturized GC–MS has only recently reached a point where several systems exist on the market with true fieldable utility. Instrument companies including Agilent Technologies, Perkin Elmer, Bruker Corporation, and FLIR Systems Inc. have their own versions of portable GC–MS systems that have managed to incorporate design features that would make them amenable to forensic applications like fire scene investigation. The primary advances that have made this growth in portable technology possible are low-thermal mass (LTM) GC systems and smaller, more high-performance batteries. Other features generally include an easy-to-use interface, minimal training requirements, onboard libraries, and generated data reports geared towards non-scientist users. Additionally, many have a range of accessories to couple extraction devices like SPME and desorption tubes, expanding analytical capabilities [3,14,15]. One notable study done by Visotin and Lennard utilized a TRIDION-9 (Torion Technologies Inc., at time of publication) portable GC–MS with a SPME interface for the detection and on-site identification of several ILRs using DVB/PDMS fibers. The optimized methodology involved a three-minute sampling and a two-minute run time which they applied to simulated debris, neat liquids, and live debris sampled on-site from a controlled burn exercise. Out of 49 simulated samples, 38 were presumptively identified [16].

This study further evaluates the TRIDION-9 (specifications found in [16,17]) to the analysis of fire debris. An additional accessory under evaluation includes the Sample Preparation Station (SPS-3), which enables the analysis of large volumes of air using a sorbent tube as the extraction device. The analytes in the tube are thermally desorbed onto a needle trap (NTD) which is then introduced into the T9 injection port [18]. In this study, the sorbent tube apparatus was adapted for use with the capillary microextraction of volatiles (CMV) device. The CMV is a dynamic headspace sampling device that has been applied to several fields of forensic interest, including smokeless powders, methamphetamine vapors, marijuana VOC characterization, and explosives [19–24]. A recent publication detailed the development of a new sol-gel adsorption phase modified with phenyl groups for enhanced retention of several highly volatile aromatics. This new phase resulted in a 2 to 4-fold increase in the group of compounds known as BTEX – highly prevalent in many gasoline formulations [25].

In this study, we report the application of the CMV to ignitable liquid residue analysis, for the first time. The device is evaluated in two scenarios: traditional laboratory analysis using a benchtop GC–MS, and

simulated field analysis using the portable T9 unit. As a measure of performance for the extraction device and both instruments, figures of merit were determined for comparison. Individual sampling protocols were developed, resulting in rapid and reproducible results for both instruments.

2. Materials and methods

2.1. Materials

Heptane (27, 051-2, HPLC grade, 99+%), Octane (O-325-7, 99+%), Nonane (N2-940-6, 99%), Decane (D90-1, 99+%), Undecane (U40-7, 99+%), Dodecane (D22, 110-4, 99+%), Tridecane (T5, 740-1, 99+%), Tetradecane (17, 245-6, 99+%), Pentadecane (P340-6, 99+%), Hexadecane (29, 631-7, 99+%), Ethylbenzene (29, 684-8, 99.8%), p-Xylene (24, 045-1, 99+%), 2-Ethyltoluene (E4, 940-1, 99%), 1,2,4-Trimethylbenzene (T7, 360-1, 98%), 1,2,4,5-Tetramethylbenzene (T1,960-7, 98%), Naphthalene (18, 450-0, 99+%), and 1-Methylnaphthalene (M5, 680-8, 95%) were obtained from Aldrich. Toluene (T0260, 99.5%), m-Xylene (X0013, 99.0%), Ethylbenzene (29, 684-8, 99.8%), and 1,3,5-Trimethylbenzene (T0470, 97%) were obtained from TCI America. o-Xylene (AC140990010, 99%) was obtained from Acros. Pentane (P399SK-1, HPLC grade, 99.6%) was obtained from Fisher Chemical.

Calion PV Nix Standard (NTSSMIX011019) was obtained from PerkinElmer. 1-liter unlined round paint cans (02991233) were obtained from Qorpak. 5 mL Transfer pipettes (13-711-5AM) were obtained from Fisher Scientific. Whiskey smoker chips (PN3496224) were obtained from Char-Broil. Bamboo 12-inch skewers (247928) were obtained from goodcook. Class 100 Cleanroom polyester Wipes (S-18512) were obtained from Uline. For the standard accelerant mixture, 87-grade gasoline was obtained from Marathon and diesel fuel was obtained from Exxon. A Bailey Nurture III vacuum pump was used for headspace sampling.

2.2. Instrumentation

A TRIDION-9 (Perkin Elmer Inc.) gas chromatograph-mass spectrometer was used to collect all portable related data. The unit was equipped with a 5 m MTX-5 column (0.1 mm × 0.4 µm). The column parameters were programmed with a 10-second hold at an initial temperature of 50 °C with a ramp rate of 1.8 °C s⁻¹ to a final temperature of 300 °C with a 30-second hold, for a total run time of 178 s. The injector port temperature was set to 300 °C with a desorption time of 10 s. Split ratios were configured as follows: A 10:1 split starting at 0 s to 10 s, followed by a 50:1 split from 10 s to 30 s. A 19-second delay was placed on the filament and a 20-second delay was placed on data collection.

The T9 was used in conjunction with a Sample Preparation Station (SPS-3) (Perkin Elmer Inc.) to facilitate analyte transfer from the CMV to the needle trap for analysis. After CMV sampling the device was inserted into a stainless-steel tube made to fit within the conventional trap holder. The trap holder was then sealed and placed into the SPS-3 slot with the needle trap inserted at the top. Desorption of the CMV occurred as the steel tube heated to 300 °C, while a stream of helium at 30 mL min⁻¹ flowed through and up into the needle trap for a total method time of five minutes. The needle trap was then removed from the holder assembly and introduced into the T9 inlet when prompted by the method.

An Agilent Technologies 7890A gas chromatograph coupled to a 5975C inert mass spectrometer with a triple-axis detector was utilized for all benchtop experiments. The gas chromatograph was equipped with an Agilent Technologies Thermal Separation Probe (TSP) for the insertion of CMVs into the inlet for thermal desorption. A DB-5 ms Ultra Inert (30 m × 0.25 mm × 0.25 µm) was used as the analytical column. The oven was programmed at 35 °C with a 2 min hold, followed by a

Table 1

Retention times, Qualifier ions, & Signal to Noise ratios for Aromatic and Alkane standard compounds on the T9 via CMV/NTD.

Compound	R _t (sec)	Qualifier ions (m/z)	1000 ng S/N	100 ng S/N	10 ng S/N	Compound	R _t (sec)	Qualifier ions (m/z)	1000 ng S/N	100 ng S/N	10 ng S/N
Heptane	26.02	43, 57, 71	83	10	1	Toluene	33.61	91	152	19	3
Octane	36.47	43, 57, 71	118	16	2	Ethylbenzene	44.1	91, 106	177	20	3
Nonane	47.29	43, 57, 71	178	25	2	m&p-xylene	44.88	91, 106	217	24	3
Decane	57.66	43, 57, 71	214	33	3	o-xylene	47.61	91, 106	254	29	3
Undecane	67.23	43, 57, 71	271	38	n/a	1,3,5-TMB	55.42	105, 119, 120	270	36	5
Dodecane	76.21	43, 57, 71	334	49	4	2-Ethyltoluene	56.71	105, 106, 120	308	36	5
Tridecane	84.64	43, 57, 71	350	47	4	1,2,4-TMB	58.05	105, 119, 120	303	39	5
Tetradecane	92.52	43, 57, 71	373	58	5	1,2,4,5-TMB	70.08	91, 119, 134	359	49	6
Pentadecane	99.87	43, 57, 71	395	60	5	Naphthalene	77.28	128	293	36	5
Hexadecane	106.91	43, 57, 71	353	51	5	1-methylnaphthalene	88.17	115, 141, 142	316	44	5

ramp to 200 °C at 7 °C min⁻¹, to 275 °C at 15 °C min⁻¹ for a total run time of 30.57 mins. The inlet temperature was set to 250 °C and run in split injection mode set at a 5:1 ratio. Helium was used as the carrier gas, set at a flow rate of 1.2 L min⁻¹. The transfer line, MS quadrupole, and ion source temperatures were set to 280 °C, 150 °C, and 230 °C, respectively. Data collection occurred in total ion (TIC) over the acquisition range 42 – 300 m/z, and selected ion monitoring (SIM). Monitored ions for analytes of interest are summarized in Table 1. Compound identification was determined from a comparison of retention times and mass spectra obtained from the injection of standard solutions in scan mode. SIM mode was utilized for all quantitative data.

2.3. Methods

2.3.1. Solution preparation

All solutions were prepared with pentane as the dilution solvent. Two standard stock solutions were prepared – an n-alkane series and an aromatic series, as well as stock solutions of each individual compound. The individual standards, aromatic, and alkane solutions were prepared using a weight by volume (w/v) procedure. Approximately 0.1 g of each compound was added to a 10 mL volumetric flask and then brought up to volume with pentane for a 10,000 ng µL⁻¹ stock solution. The compounds in the alkane stock were: heptane, octane, nonane, decane, undecane, dodecane, tridecane, tetradecane, pentadecane, and hexadecane. The compounds in the aromatic stock solution were: toluene, ethylbenzene, m and p-xylene, o-xylene, 1, 3, 5-trimethylbenzene, 2-ethyltoluene, 1, 2, 4-trimethylbenzene, 1, 2, 4, 5-tetramethylbenzene, naphthalene, and 1-methylnaphthalene. A serial dilution was then done to prepare solutions with concentrations of 1,000, 700, 500, 350, 100, 35, and 10 ng µL⁻¹. The individual standard solutions were prepared each to 10,000 ng µL⁻¹ and then serially diluted down to concentrations of 1000, 100, and 10 ng µL⁻¹. A standard accelerant mixture (SAM) stock was prepared with gasoline and diesel. Preparation was done using a volume by volume (v/v) method with 50 µL of 87-grade gasoline and 50 µL of diesel fuel in a 5 mL volumetric flask and brought up to volume, for a concentration of 10,000 ng µL⁻¹.

2.3.2. Closed-system headspace sampling protocol

Closed-system sampling was conducted from 1 L unlined metal paint cans. The lid was pre-pierced with two holes which were sealed with rubber septa: one centered for CMV sampling, and one off-center to allow ambient air to enter the can. 1 µL of the sample was spiked into the can, then hammered shut and placed in the heating mantle to equilibrate for 10 min at 70 °C. After equilibration, the septa were pierced through with 16-gauge hypodermic needles to allow sampling with the CMV. The needle used to pierce the off-set septum had a short length of PFA tubing attached for the ambient airflow, preventing the formation of a vacuum inside the can. The center septum was pierced with a needle attached to a longer length of PFA tubing, to which one end of the CMV was inserted inside. The other end of the CMV was inserted inside separate tubing connected to a flowmeter and Bailey

Nurture III vacuum pump. The vacuum pump was set to a flow rate of 0.2 L min⁻¹ using the flowmeter and left to sample for 10 min for a total of 2 L of air. After sampling the CMV was taken out of the tubing and placed in the TSP for analysis with the benchtop GC–MS or placed into the holder for desorption for the needle trap for analysis in the TRIDION-9.

2.3.3. Simulated open-air sampling protocol using a calibrated vapor source

The injector port of a Varian (Palo Alto, CA) CP 3800 gas chromatograph was used to generate analyte vapors from 1 µL injections of solutions at 100 and 1000 ng µL⁻¹ mass loadings. The source parameters were reported previously [25] with two changes: the intermediate column was changed to an 8 m DB-5 (30 m × 0.25 mm × 0.25 µm) and the inlet liner was changed to a splitless 0.4 mm Agilent Ultra Inert Inlet Liner. Two small holes were punctured on the bulb of a 5 mL plastic pipette. In one of the holes, about 2 cm of the column is inserted to allow the analyte vapor to flow through the pipette. The second hole allows the flow of ambient air into the pipette. The tip of the pipette was cut to insert the CMV securely. The other side of the CMV was connected to the flow meter and vacuum pump. A 1 µL sample was directly injected into the inlet with the inlet temperature at 250 °C. Following the injection, the vacuum pump was turned on. The nitrogen carrier gas carries the analyte through the column and into the pipette at a flow rate of 0.05 mL min⁻¹. After sampling for a predetermined length of time at a flow rate of 0.2 L min⁻¹, the CMV was removed from the pipette and then either placed in the TSP for analysis with the benchtop or placed into the needle trap desorption holder for analysis in the TRIDION-9.

3. Results and discussion

3.1. T9 method configuration

A review of the existing fire debris literature was conducted to select compounds for targeted analysis. To evaluate the ability of the software to identify relevant analytes in ignitable liquid residues, solutions of individual standards were introduced to the T9 via directly spiking 1 µL of solution onto a CMV and then desorbed onto a needle trap using the SPS-3. Individual compounds at 100 ng µL⁻¹ were analyzed to determine retention times and any instances of coelution with certain CMV background peaks. The mass spectrum produced by each compound was also examined to see if there were significant differences in the fragmentation patterns relative to those produced by quadrupole mass spectrometers. In all cases the mass spectra did not differ in the fragment patterns; however, in some cases the ratios of the fragments slightly varied. This was mostly seen in the larger n-alkanes. After verifying the spectras and chromatograms, the compounds were then entered into the onboard library which automatically assigned the retention time with a ± 3 sec min-max window. Chromatograms of the individual compounds were overlaid to assess peak resolution; no instances of extreme overlap were encountered.

Following the library additions, 10, 100, and 1000 ng μL^{-1} mixtures of the aromatics and n-alkanes were analyzed via 1 μL direct spikes to verify the resolution of compounds with retention times within 1 s of each other. Signal-to-noise ratios were calculated as a measure of instrument sensitivity. This was also done to assess the accuracy of the onboard library to 'call' and integrate each peak. Unfortunately, the CHROMION software had issues calling at least half of all the compounds within each mixture at all three levels. Only compounds that had already been included as a part of the library such as tetradecane and naphthalene were matched by the library consistently with < 99% accuracy. Most other compounds were either 'split called' or were completely misidentified. Split calls were due to the deconvolution function built into the software, resulting in two or three smaller integrated peaks within one peak. This threw off the entire integrated area for the compound and could not be reassigned as a single peak. Misidentification was seen most consistently with the aromatic cluster of 1,3,5 - trimethylbenzene, 2-ethyltoluene, and 1,2,4 - trimethylbenzene, and the whole series of n-alkanes. The software seemed to give ID preference to compounds already apart of the library over those that have been added, as every compound in the aromatic cluster was identified as any other substituted benzene ring that had a retention time within 0.2 s of the true compound. For the n-alkanes, with the exception of heptane and tetradecane, all others were identified as 'unknowns' with suggested matches of their true identity. Undecane and all alkanes onwards had an additional suggestion of the next largest alkane in the series.

The CHROMION software does not have an integrated S/N function like traditional benchtop data analysis software, therefore the signal-to-noise for each compound was determined by hand. The signal was taken as the highest point of the peak (referred to as abundance), and the noise was averaged from 10 randomly selected points along the baseline, per replicate. The average baseline abundance was cross-referenced with the baseline produced from CMV blanks to ensure the noise would not be over or underrepresented. Direct spikes of the aromatic and alkane mixes at each concentration were performed in triplicate. The averages of the signals and the noise averages were used to determine the S/N, shown in Table 1. As can be seen for all 20 analytes the S/N increases by roughly a factor of 10, in line with the increases in mass loading. Additionally, all compounds with the exception of heptane, octane, nonane produce signals at least three times higher than the CMV background noise, leading to an estimated method detection limit of 10 ng μL^{-1} .

Calibration curves were built to assess the T9 software's quantitative capabilities and that of the CMV/NTD retention capacity. Direct 1 μL spikes of either the aromatic or n-alkane '10-mix' in a concentration range of 35–500 ng μL^{-1} were deposited onto the CMV, followed by desorption onto the needle trap for analysis by the T9. The analysis was done in triplicate for each solution mixture, and curves were built for each individual compound using the CHROMION software quantitative features. The initial response type in the program was set to utilize the integrated areas of each compound, however; the same identification issues seen during the S/N determination resulted in highly variable integrated areas and overall poor linearity for many of the compounds. As a result, the response type was set to use the peak height which had better signal reproducibility. Table 2 shows the R^2 values for all compounds the software was able to construct curves for. Compounds without curves due to misidentified/split called include ethylbenzene, 1,3,5 - TMB, 2-ethyltoluene, decane, undecane, 1,2,4,5-TMB, dodecane, naphthalene, and 1-methylnaphthalene.

3.2. Benchtop method comparison

For direct comparisons, the same standard individual solutions and mixes were run on the benchtop using the CMV. Signal-to-noise determinations and calibration curves were built using peak areas obtained in the SIM. All ten aromatic compounds and eight of the n-

Table 2

R^2 values produced by CHROMION software.

Compound	R^2
Toluene	0.9258
Octane	0.8537
m&p-xylene	0.8286
Nonane	0.7730
o-xylene	0.8834
1,2,4-TMB	0.9846
Tridecane	0.8254
Tetradecane	0.8222
Pentadecane	0.8418
Hexadecane	0.8217

alkanes produced signal 10-fold higher than the baseline noise at 10 ng μL^{-1} , with the lowest being nonane with an S/N ratio of 13. Octane was just below the minimum at S/N = 2, and heptane could not be extracted due to its elution within the tail-end of the solvent peak. Calibration curves were constructed in the same manner as on the T9; examples of several curves shown in Fig. 1 a and b. The alkane series C_8 through C_{16} curves all exhibited linear performance between 0.9845 and 0.9969; for the aromatics between 0.9405 and 0.9893. Only compounds with S/N greater than 10 were plotted against the relative peak areas.

3.3. Simulated fire debris – closed-system sampling

Simulated fire debris experiments were carried out on the benchtop and the T9 to evaluate the extraction capabilities of the CMV and the software performance of the T9. The closed-sampling protocol was used for CMV and CMV/NTD extractions. Three different materials were utilized: polyester cloth strips, wood chips from whiskey barrels, and bamboo skewer shafts. Approximately 4.0 g of material was added to the bottom of individual 1 L paint cans, then burned for two minutes by direct exposure to a propane torch. The cans had been conditioned at 300 °C for approximately 24 h to allow the hydrocarbon-based oils used during the manufacturing process to evolve off. Immediately after burning, the can was then set aside for ~30 s to allow any smoke to dissipate. Once the smoke had dissipated the can was sealed with its pre-punctured lid and set aside again for an additional two minutes so that the walls of the can would cool to room temperature. Finally, the closed-system protocol detailed in Section 2.3.2 was carried out. This protocol was carried out twice using the same cans: first to sample the debris background alone, and second, to sample a spiked volume of standard accelerant mixture (SAM) in the presence of the background. At the completion of background sampling, the can was removed from the heating mantle and set aside with the lid popped open to disrupt the equilibrium. A 2.4 cm fiberglass filter circle was then placed at the bottom of the can carefully as to not be overlapped by any of the charred material. A 50/50 gasoline (Marathon) and diesel fuel (Exxon) SAM made up at 1% concentration was used as the spike solution. Volumes of 1, 3, and 5 μL were spiked onto the glass filter using a 5 μL gas-tight syringe. The lid of the can was left on top, leaving just enough room for insertion and withdrawal of the syringe in order to minimize the evaporation of the solution. The can was immediately resealed after the spike and put through the close-sampling protocol. The same series of CMVs were applied to the same cans and the same materials after reconditioning at 250 °C for a 30-minute period.

Chromatograms from all the materials pre-solution spike were evaluated for any analytical signal contributions made by pyrolysis/combustion products. The peak abundances for those signals were determined from the selected ion mode and subtracted from those measured from the spiked materials. Overall, the chromatograms produced on the T9 were heavily impacted by the limited resolution caused by the 5-meter column. At the 1 μL spike level quantitation was not

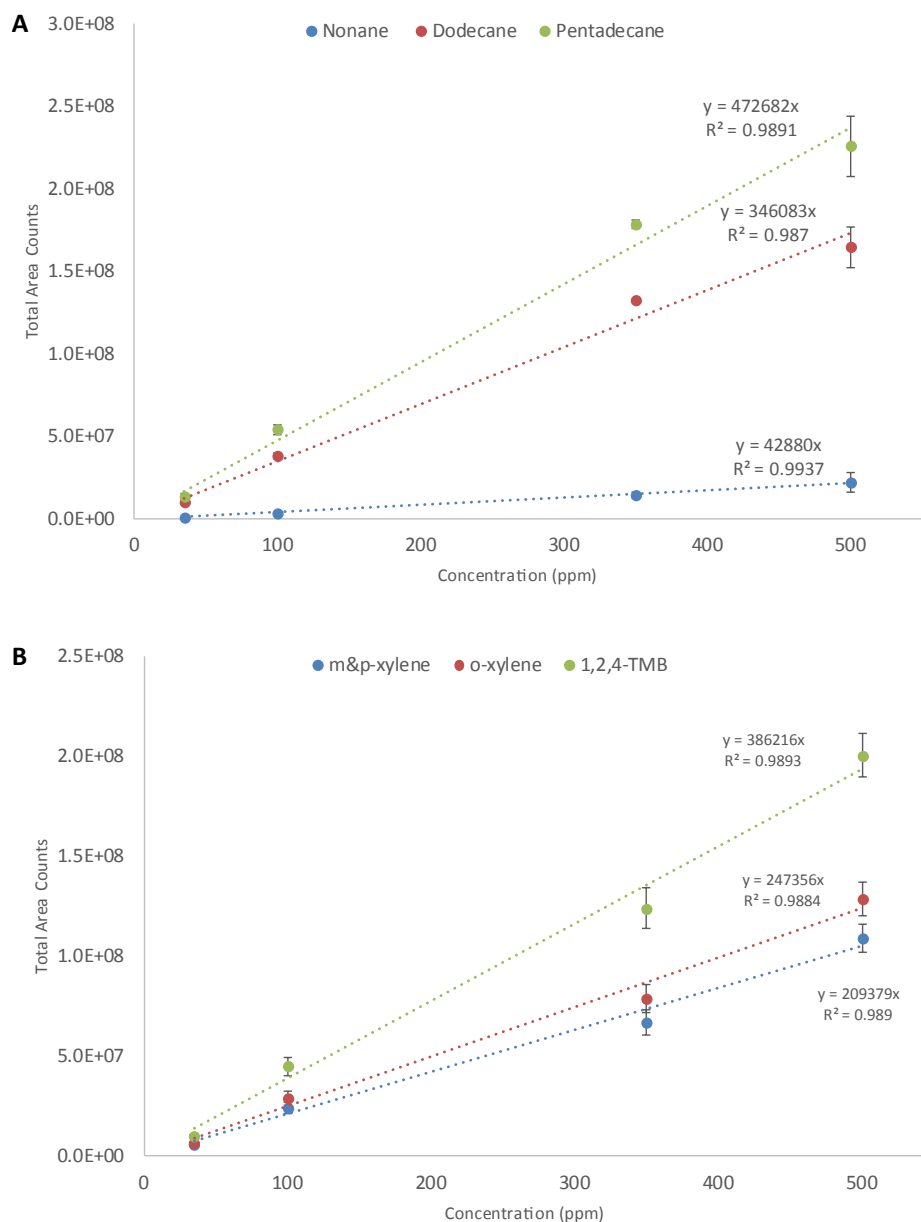


Fig. 1. a and b: Calibration curves built on the Agilent benchtop – a. CMV direct spikes; n-alkane curves (left) and b. aromatic curves (right).

possible for any of the 20 target analytes from any of the debris types. Detection by the software and by hand was also very limited. Fourteen compounds could be identified using extracted ions, but all corresponding signal-to-noise ratios were below three. Some improvements were seen at the 3 μ L and 5 μ L spike levels, but not for every material (Fig. 2 a and b). The wood chips produced high levels of background interference, limiting detection and quantitation to the n-alkanes undecane through pentadecane. Signal-to-noise ratios for most of the 14 detectable compounds ranged between 6 and 16, with the most prevalent compounds being m,p-xylene, 1, 2, 4 -TMB, and undecane – pentadecane. This was true for the extractions from both the polyester cloth and the bamboo skewers. Lighter aromatics such as toluene and ethylbenzene were identifiable with extracted ions but did not meet minimum signal requirements. Signals at the 5 μ L level for both materials increased in overall abundance, but the signal-to-noise ratios only improved for the same compounds by a single point in some cases.

A separate set of materials were burned and extracted under the same conditions for benchtop GC–MS analysis using the CMV. Overall, the chromatographic resolution and detection sensitivity were much

better compared to the T9. All compounds with the exception of heptane, 1, 2, 4, 5-tetramethylbenzene, and 1-methylnaphthalene were baseline resolved in SIM mode. At the 1 μ L spike level for all three materials, the minimum signal-to-noise in SIM mode was \sim 12 times higher than the baseline and subsequently increased with the increase in solution volume. Background products generated by the debris resulted in high amounts of interference in the TICs. The wood chips and the bamboo produced the highest levels, followed by the polyester cloth at a whole order of magnitude lower than both (Fig. 3). The interference from the wood chips and bamboo obscured all but the medium-range n-alkanes peaks, while all targeted peaks were visible above the polyester background at 1 μ L.

An evaluation of the CMV and CMV/NTD extraction techniques involved calculating estimates of recovered mass amounts at the 3 μ L spike level using the previously generated calibration curves. Table 3 includes recovered amounts in nanograms for both techniques per debris material. Mass recoveries were directly influenced by the degree of background interference encountered. Recovered mass was greatest from the polyester cloth, ranging from approximately 30 ng to as high

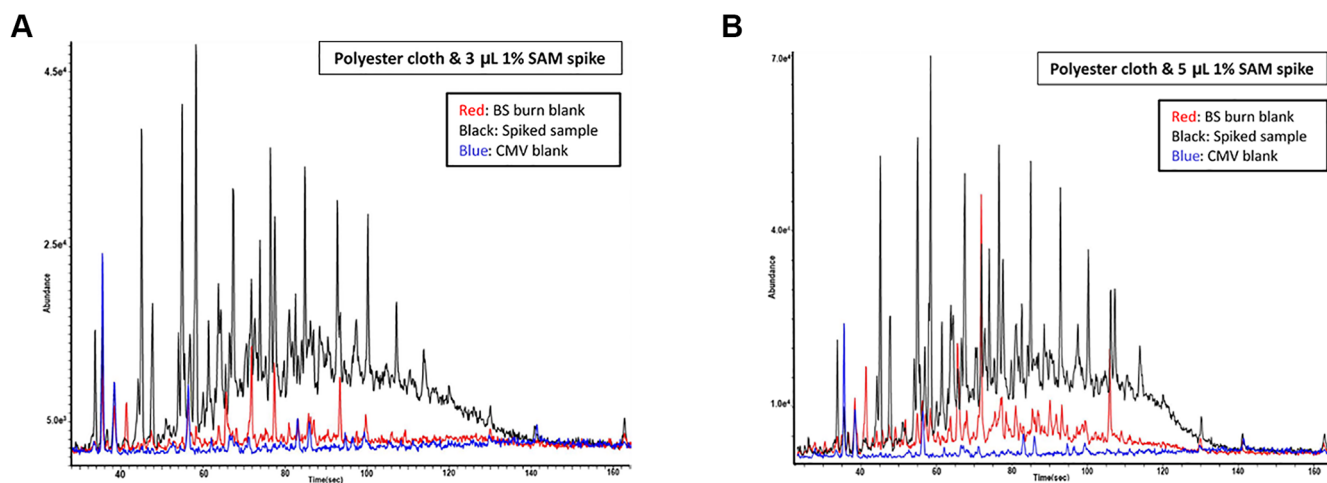


Fig. 2. a and b. Chromatographic overlays of CMV blanks (blue), burned substrate background (red), and spiked SAM solution (black) from closed-system sampling using CMV/NTD on the TRIDION-9 for polyester cloth at the 3 µL (top) and 5 µL (bottom) level.

as 500 ng. The lowest analyte recoveries were from the bamboo skewer material, reaching a maximum of 16 ng with an average recovery of 7 ng. Estimates on the T9 were only possible for half of the final compounds, due to a combination of non-detection by the software, poor signal-to-noise, and inability to quantitate without a generated calibration curve. In general, the recoveries of tridecane through hexadecane were consistent, with mass amounts ranging between 35 and 250 ng.

3.4. Simulated fire debris – open-system sampling

The CMV's performance was also evaluated in simulated open-air conditions on both instruments. Two main goals for this experiment were the evaluation of the CMV's extraction efficiency and an

examination of the analyte transfer between the CMV and the needle trap. The adsorbent within the needle shaft is comprised of three different types, arranged in a 'weak to strong' affinity order. Consideration was given to the idea that despite the multiple adsorbents, discrimination might affect the profile obtained by the T9. Sampling was performed according to the procedure detailed in Section 2.3.3 at time intervals of 5, 10, and 20 min for total sampled air volumes of 1, 2, and 4 L.

Fig. 4 a and b shows the relative abundances/peak areas against the sampling times for the high mass loading alkane injections extracted using CMV (benchtop) and CMV/NTD (T9). The highly volatile aromatics (toluene, ethylbenzene, and m,p-xylene) experienced the most loss as sampling time/air volume increased, which was seen on both the benchtop and the T9. This is also seen on both instruments with the

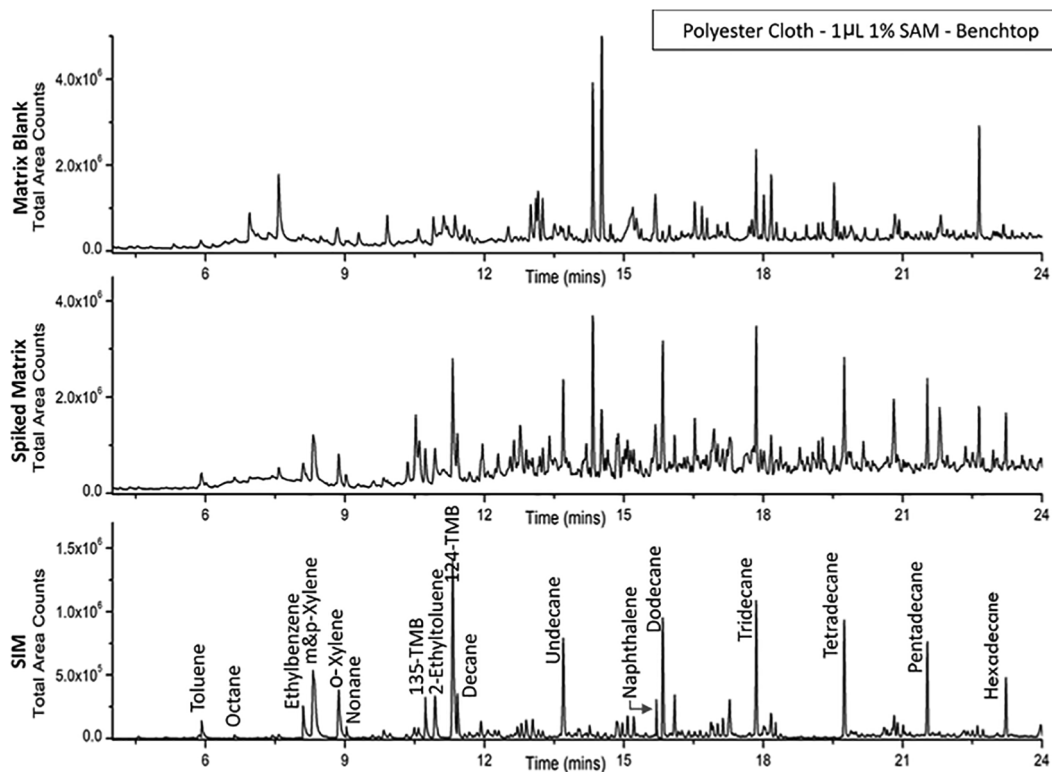


Fig. 3. Chromatograms obtained by CMV-GC-MS from closed-system sampling of polyester cloth at the 1 µL SAM spike level

Table 3Estimated recovered mass (ng) from simulated fire debris at the 3 μ L Level using CMV and CMV/NTD extraction techniques.

Compound	Polyester Cloth		Wood chips		Bamboo skewers		Compound	Polyester Cloth		Wood chips		Bamboo skewers	
	Benchtop	T9	Benchtop	T9	Benchtop	T9		Benchtop	T9	Benchtop	T9	Benchtop	T9
Octane	84	–	18	–	1	–	Toluene	146	113	11	–	3	63
Nonane	120	–	19	–	1	–	Ethylbenzene	180	–	30	–	6	–
Decane	200	–	36	–	4	–	m&p-xylene	505	404	71	36	8	408
Undecane	256	–	–	–	6	–	o-xylene	207	226	33	27	4	205
Dodecane	168	–	61	–	6	–	1,3,5-TMB	133	–	27	–	4	–
Tridecane	147	131	60	35	10	141	1,2,4-TMB	374	481	70	48	9	483
Tetradecane	117	246	57	78	16	243							
Pentadecane	26	98	51	30	14	85							
Hexadecane	28	61	41	24	8	64							

lightest n-alkanes (heptane through decane), although the loss is more pronounced on the T9. Heptane, octane, and nonane were not detected on the T9; likely due to a combination of factors including a lack of instrumental sensitivity, increased background interference from the complex matrix of the SAM, and breakthrough during analyte transfer

from the CMV onto the needle trap. Medium-range volatility compounds (undecane through tetradecane) exhibited the greatest stability on the adsorption phase, reaching equilibrium concentrations at the 10-minute mark. Minor increases in retention occurred between 5 and 15% for the benchtop analysis, and loss of analyte on the T9 ranging

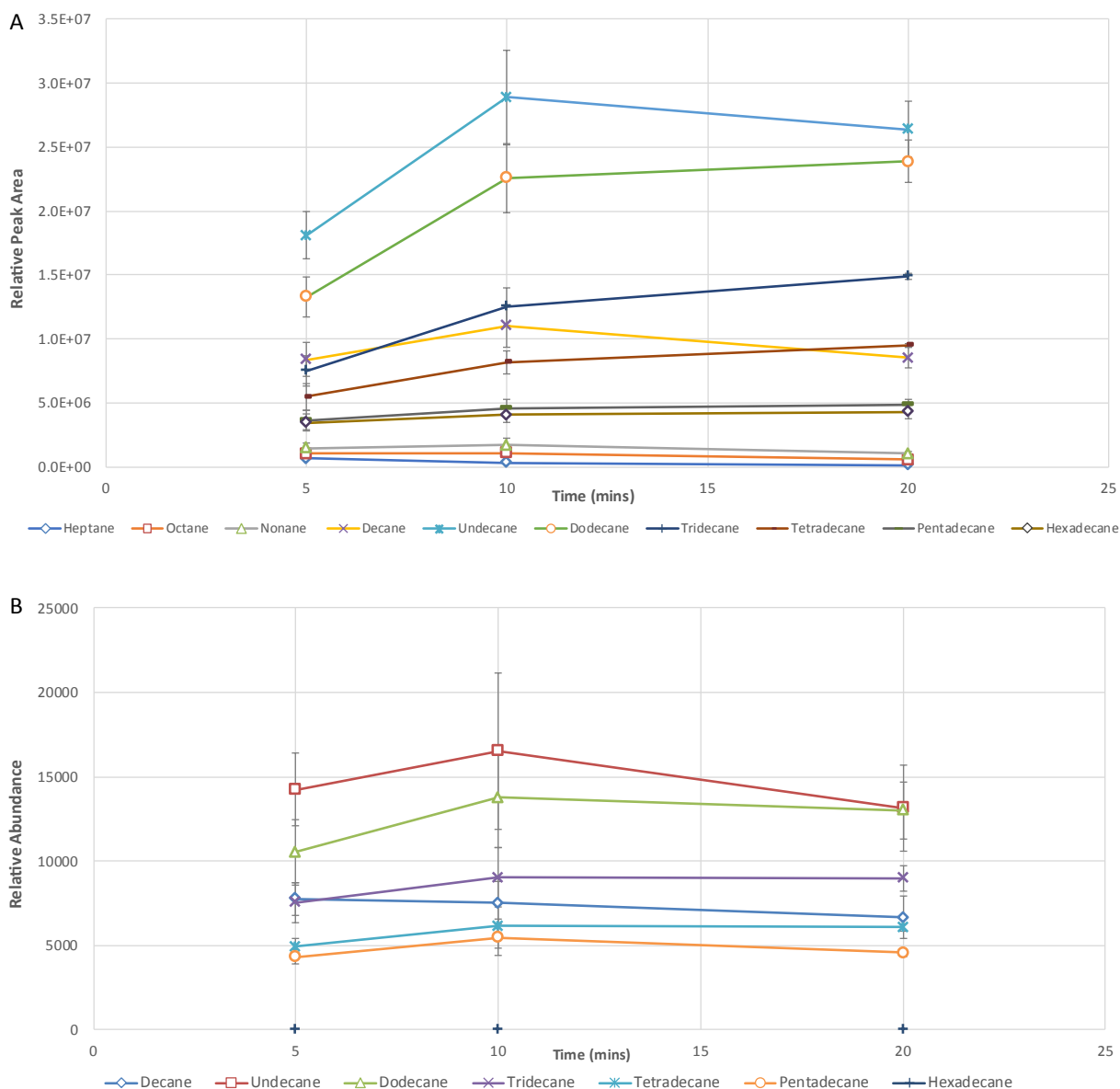


Fig. 4. a and b: Response curves of the relative abundance/peak area for high mass loadings of the n-alkane mixture using CMV (top) and CMV/NTD (bottom) extraction with open-system sampling.

between 1 and 20% after 20 min of sampling. The opposite trend was seen with the heaviest analytes - pentadecane, hexadecane, and naphthalene.

Analysis by CMV-GC-MS resulted in the retention of all three compounds at each sampling time interval. Relative peak areas for all three only increased by 5% between 10 and 20 min, suggesting equilibrium concentrations were reached. Additionally, displacement of the lighter alkanes likely occurred over the 20-minute period. Four-fold greater peak areas were seen for pentadecane and hexadecane relative to the lightest n-alkanes, in conjunction with analyte loss between 30 and 80% for heptane, octane, and nonane.

Similar trends were seen on both instruments at the low mass loading, although the loss of more compounds at faster rates was greater with the CMV/NTD technique. The lightest compounds underwent continuous loss through all three time intervals, and the heaviest (pentadecane and hexadecane) were not retained at all. Despite losses in retention for even the mid-range aromatics and n-alkanes, matching distributions of analytes for both techniques were observed. This suggests that the combination of adsorbents within the needle trap does not retain analytes at ratios different from the phase combination in the CMV. Any potential profile discrimination can more likely be attributed to low concentrations of sample, displacement of the lightest components at larger air volumes, and the SPS-3 desorption method. Technique precision remained consistent between the high and low concentration samplings on both instruments. Low mass loading replicates ($n = 3$) for all detectable compounds were between 5 and 30% and 5 – 36% on the T9 and benchtop, respectively. The high mass loadings ranged between 8 and 35% and 7 – 37%, respectively.

4. Conclusions

This study reports, for the first time, the application of the CMV to the extraction and analysis of ignitable liquid residues from fire debris. One goal of this study was to determine the capabilities of the sampling device as a routine extraction tool both in the laboratory and as a field sampler and preconcentration tool coupled with portable GC-MS systems. The versatility of the CMV allowed for the successful coupling to the TRIDION-9 for the first time by incorporating the SPS-3 unit accessory. Use of the needle trap holder facilitated analyte transfer between the devices, enabling fast analysis (~3 min) within 5 min of sampling with the CMV. The secondary transfer to the needle trap did not appear to affect the final chromatographic profile, suggesting that affinity bias would not be a disadvantage to this technique.

Another goal of this study was to compare the analytical performance of the TRIDION-9 to a traditional benchtop GC-MS using CMV as the extraction technique. Many key components found within ignitable liquid formulations were retained and analyzed by both GC-MS systems, reaching sub-nanogram detection levels. The recovery of compounds characteristic of ILRs from the closed-system sampling resulted in detection limits well below the guidance (1 μ L spike of a 0.1% neat gasoline sample) provided in the ASTM methods for the solid-phase microextraction (SPME) and activated charcoal strip (ACS) extraction techniques. Furthermore, while not a standard practice for fire debris analysis, quantitation with the CMV is possible with the proper reference and calibration standards. The CMV was also shown to be a fast (~5 min. sampling) and sensitive fieldable device through the open-air system followed by fast analysis using a portable GC-MS.

The TRIDION-9 did suffer from some limitations compared to a benchtop GC-MS. Most notable was the 5-meter column. The total method benefited from a faster analysis time; however, the chromatography was negatively impacted. ILR pattern recognition was poor, decreasing the overall instrument sensitivity. Additionally, compound identification by the software was consistently incorrect for almost half of the analytes of interest due to the narrow 3-second retention time windows. Identification through extracted ions was possible but also proved difficult because of many coeluted peaks, especially in the

interpretation of highly complex mixtures like a SAM, or ILRs in the presence of matrix background/pyrolysis combustion products. Inexperienced operators with little or no analytical chemistry background may be at a disadvantage if they only have the reports generated by the CHROMION software to rely on.

Overall, the combination of the CMV with the T9 as an approach to ILR analysis overcomes some limitations that currently exist with other available tools. As an extraction technique the CMV is a faster, dynamic sampling tool that is easier to handle than a SPME fiber and also benefits from a greater surface area resulting in enhanced recoveries. The necessity of the SPS-3 for analyte transfer is a limitation for field use when compared to the direct desorption of SPME into the T9 inlet. However, both units (SPS-3 and T9) are compact enough that transport to and from the field should not be cumbersome. High throughput is possible given the rapid (1–3 min) sampling and rapid (3 min) analysis including blanks post-sampling. Finally, previous applications of the CMV to field sampling have shown that analytes exhibit stability on the adsorption phase for at least 18 h. If necessary, extracted samples are easily stored for transport to the lab, meaning presumptive and confirmatory results can be achieved with a single extraction device. The most significant limitation of this instrumental setup was found to be the limited chromatographic resolution but a longer column and different chromatographic conditions should be able to overcome this limitation.

Future work regarding the use of the CMV/NTD technique with the TRIDION-9 would aim to improve upon the SPS-3 desorption method to limit overloaded chromatograms, thereby improving pattern recognition and the instrumental sensitivity. Method parameters were kept at the manufacturer's recommendations; future work would consider optimization of the maximum heating temperature, total desorption time, and helium flow rate. Further work with the CMV would include its application to other portable GC-MS systems to evaluate their potential for on-site fire debris analysis. Finally, on-site evaluations of selected portable systems would be conducted following instrumental optimization within the laboratory.

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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