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Evaluation and Improvement of Capillary Microextraction of Volatiles Coupled to Gas Chromatography-Mass Spectrometry for the Analysis of Ignitable Liquid Residues in Fire Debris

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FLORIDA INTERNATIONAL UNIVERSITY

Miami, Florida

EVALUATION AND IMPROVEMENT OF CAPILLARY MICROEXTRACTION OF VOLATILES COUPLED TO GAS CHROMATOGRAPHY-MASS SPECTROMETRY FOR THE ANALYSIS OF IGNITABLE LIQUID RESIDUES IN FIRE DEBRIS

A dissertation submitted in partial fulfillment of the
requirements for the degree of
DOCTOR OF PHILOSOPHY
In
CHEMISTRY
by
Michelle N. Torres

2022

To: Dean Michael R. Heithaus
College of Arts, Sciences and Education

This dissertation, written by Michelle N. Torres, and entitled Evaluation and Improvement of Capillary Microextraction of Volatiles coupled to Gas Chromatography-Mass Spectrometry for the Analysis of Ignitable Liquid Residues in Fire Debris, having been approved in respect to style and intellectual content, is referred to you for judgment.

We have read this dissertation and recommend that it be approved.

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Florida International University, 2022

DEDICATION

I would like to dedicate this dissertation to my mother, Abigail, and my (practically) husband, Xander. The support and the sacrifices came in many forms, but they never wavered. I love you both, dearly and deeply.

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ABSTRACT OF THE DISSERTATION

EVALUATION AND IMPROVEMENT OF CAPILLARY MICROEXTRACTION OF VOLATILES COUPLED TO GAS CHROMATOGRAPHY-MASS SPECTROMETRY FOR THE ANALYSIS OF IGNITABLE LIQUID RESIDUES IN FIRE DEBRIS

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A key aspect of fire debris analysis is the ability to extract the remnants of an ignitable liquid from a matrix with a high degree of reliability and sensitivity. Although there are several robust, standardized methods, there is no single technique universally applicable to casework. In this work a novel extraction technique – Capillary Microextraction of Volatiles (CMV) – has been applied, for the first time, for ignitable liquid residue (ILR) extraction. A 20-minute dynamic sampling laboratory protocol from traditional 1 L paint cans was established and optimized based upon ASTM guidelines. The development of new adsorption phases for CMV use are also reported. A phenyl-modified sol-gel phase demonstrated up to 8-fold higher recoveries of BTEX compounds from headspace sampling compared to previously reported CMV phases and four additional differently functionalized phases were synthesized and evaluated. Preliminary comparisons of the CMV to activated charcoal strips (ACS) and to solid-phase microextraction (SPME) demonstrated equivalent or slightly higher extraction efficiency relative to SPME, and over two orders of magnitude greater extraction efficiency relative to ACS. The versatility of the CMV has also been extended to portable analytical instrumentation. The device was successfully coupled to a TRIDION-9 portable GC-MS when combined with a needle trap, and both were evaluated for their applicability to fire debris analysis. The CMV/NTD technique demonstrated extraction capabilities similar to the CMV alone; however, ILR analysis by the T9 was heavily impacted by the limited chromatographic resolution resulting in complicated data interpretation. The CMV was similarly coupled to a Griffin G510 for dual evaluation. Also presented for the first time is a field ILR headspace sampling protocol involving the use of a paper drinking cup. A five-minute sampling/extraction protocol was sufficient to recover six key gasoline analytes from a 0.01 µL spike of gasoline with typical mass recoveries of 4 – 24 ng. An overall 21-minute analytical method was developed using the CMV/Cup protocol capable of detecting several ILR-associated compounds at up to 10x greater sensitivity than traditional extraction techniques. This body of work demonstrates the overall versatility of the CMV as applied to the entire field of fire debris analysis.

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LIST OF ABBREVIATIONS AND ACRONYMS

ACS	Activated Charcoal Strips
ADC	Accelerant Detection Canines
ASTM	American Society for Testing and Materials
BTEX	Benzene, Toluene, Ethylbenzene, & Xylene isomers
C18	Octadecylsilane
C8	Octylsilane
CMV	Capillary Microextractor of Volatiles
FID	Flame Ionization Detector
FTIR	Fourier Transform Infrared Spectroscopy
GC-MS	Gas Chromatography – Mass Spectrometry
ILR	Ignitable Liquid Residues
LOD	Limit of Detection
LOQ	Limit of Quantitation
MTMOS	Methyltrimethoxysilane
NIST	National Institute of Standards and Technology
PhTMOS	Phenyltrimethoxysilane
PMHS	Polymethylhydrosiloxane
PPM	Part Per Million
RSD	Relative Standard Deviation
SIM	Selected Ion Monitoring
SPME	Solid-phase Microextraction

T9	TRIDION – 9
TFA	Trifluoroacetic acid
TMSPA	N-[3(Trimethoxysilyl)propyl]aniline
Vt-PDMS	Vinyl terminated - polydimethylsiloxane

1. INTRODUCTION

1.1 Project Motivation and Significance

Every year, fire incidents significantly impact multiple aspects of community livelihoods. In the United States alone in 2019, an estimated 1.3 million fires were reported to fire departments. These incidents resulted in over $14.8 billion in property damage, and impacts to human life totaled over 16,600 in civilian injuries and nearly 3,700 deaths (1). Given the extent to which these incidents impact society, investigations into their cause are crucial. Of great importance is determining whether the fire was accidental or intentional – also referred to as arson. A key piece of evidence that could indicate an intentional fire is the presence of an accelerant. Accelerant is a general term for any item or material that can aid in the progression of fire; however, in the context of fire investigations it commonly refers to some type of ignitable liquid (2).

For decades, the investigative process has been limited to surveying the scene and collecting evidence that has the highest probability of containing ignitable liquid residues (ILRs) based on hits by an accelerant detection canine. The confirmation of ignitable liquid presence is dependent on the forensic analyst, who must isolate any resides using robust and validated techniques.

The motivation for this project intends to address both ends of the fire investigation process: on-scene and laboratory analysis. The overall goal for the on-scene aspect is to fill in a gap in the literature regarding instrumental detection capabilities. The sophistication of portable instrumentation - specifically gas chromatography-mass spectrometry (GC-MS) - has grown considerably in the past decade, but thus far applications to fire debris analysis have been limited. This body of work demonstrates the capabilities of two commercially available GC-MS systems, evaluated in the laboratory and out in the field.

On the other hand, laboratory methodologies are much more established, with the majority having standardized protocols designed by researchers and practitioners. A wide number of analytical techniques exist for use at an analyst's discretion. Despite the established state of the field, new techniques and improvements to existing ones are constantly emerging. The second project goal regarding the laboratory aspect of the field is two-fold. First, this work demonstrates the application of a new extraction device, the capillary microextractor of volatiles (CMV) to fire debris analysis for the first time. This application extends to in-field and laboratory use. Second, this new device, along with two popular ones is evaluated using industry standards.

1.2 Specific Project Goals

The whole of this project was divided into three main aims. The first aim was to apply the CMV to the analysis of ignitable liquid residues for the first time. This involved developing and optimizing sampling protocols for laboratory and on-scene analyses. These protocols were developed in accordance with ASTM International standard practice recommendations. A subtask to this aim included the synthesis of additional adsorption phases for use in the CMV. After development, the phases were subject to validation and evaluated for their effectiveness in retaining ILRs.

The second project aim was directed towards the systematic comparison of the CMV as an extraction device to other common extraction techniques. The two techniques utilized for this comparison were activated charcoal strips (ACS) and solid-phase microextraction (SPME). The sampling protocols for these techniques were also optimized according to their respective ASTM methods.

The final aim was a dual evaluation of analytical technologies applicable to the on-scene sampling of fire debris. The capabilities of the CMV were assessed as a fieldable device that could be stored and brought back to the lab for analysis. In addition to its laboratory use, it was also coupled to two different portable GC-MS instruments: the TRIDION-9 and the Griffin G510. These units were assessed on several points of performance, including software abilities, chromatographic resolution, and detection sensitivity.

1.3 Hypotheses

The CMV is hypothesized to match, if not outperform the two extraction techniques evaluated in this study. More specifically, it is hypothesized to achieve higher mass recoveries of ILRs, while doing so in a shorter amount of time and with greater ease. Additionally, it is hypothesized to suffer from less discrimination in chromatographic profiles due to its higher adsorption capacity. The different functionalized adsorptive phases are expected to aid in lessening the degree of discrimination normally seen with charcoal strips and SPME fibers.

It is also hypothesized that the portable GC-MS instrumentation examined in this body of work will prove to have great diagnostic value in fire debris analysis. The quality of data generated will be dependent on the abilities of the individual units as a whole, but can ultimately be a powerful tool for investigators who could benefit from rapid results on-site.

2. FIRE DEBRIS ANALYSIS

2.1 Current State

The field of fire debris analysis can be separated into two areas: that which occurs out in the field at the fire scene, and evidence processing that occurs within the laboratory. Current analytical capabilities within the laboratory significantly outpace what can be done in the field. Analytical methodologies regarding the extraction and analysis of ignitable liquid residues have been established for several decades and evaluated numerous times by the practicing community. Several ASTM International standardized methods exist for the collection and preservation of evidence, ILR extraction via multiple techniques, and the analysis and interpretation of data using GC-MS (3).

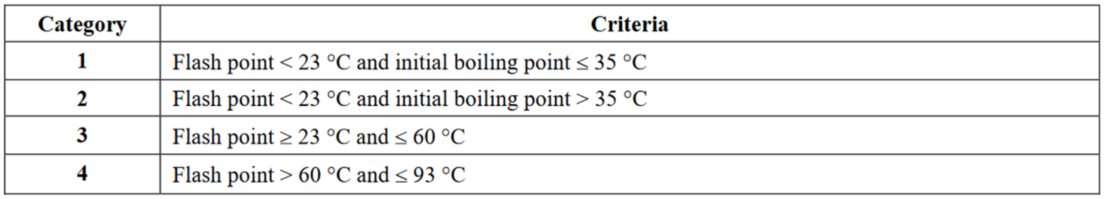
On-site capabilities are mainly concerned with being able to detect and isolate 'hot spot' areas where an ignitable liquid may have been poured. Once the scene has been secured, the investigation will start with a walkthrough in order to visually identify points of origin. Common physical characteristics an investigator may look out for are 'V' patterns, lines of demarcation, and pour patterns (4). While they help narrow down how a fire may have progressed, they should not be taken as confirmation. No two fires behave the same way; a pour pattern at one scene can be legitimate while the other may be the result of intense heat concentrated in that area. Currently, the best method of residue detection fire investigators utilize are accelerant detection canines (ADCs), or arson dogs.

Accelerant detection canines are considered the ‘gold standard’ in residue location for several reasons. They have a naturally heightened sense of smell relative to a human’s; if properly trained, a dog has the capability of detecting as little as 0.005 µL of neat gasoline from a quart paint can (5). ADCs also have excellent scene mobility and detection accuracy as high as 90% (6). There are, however, limitations to their usefulness. For their safety, dogs are limited to non-hazardous scenes, and only for small amounts of time due to the natural endurance of the animal. Their performance can also be unintentionally influenced by the handler, leading to false positives. Lastly, they are unable to communicate beyond their alert signal. This means an investigator has no idea if the spot does have residue and what the residue might be until that evidence is sent for laboratory testing. NFPA 921 specifically states that any canine alerts should not be taken as confirmation of residue presence until a laboratory analysis has validated the call (7).

Given the destructive nature of fire, it is unlikely that any ignitable liquid would have survived on surfaces. If present, the residues would be absorbed into a matrix, thus necessitating extraction. Investigators are responsible for collecting all the suspected debris for transport to the lab, where the forensic analyst handles the extraction and analysis of any ignitable liquid residue. The extraction technique utilized depends on several factors: the nature of the debris, and the suspected class of liquid (8,9).

2.2 Ignitable Liquids

The term ‘ignitable liquids’ refers to a broad collection of liquids that can be further divided into flammable and combustible classifications. These classifications are based upon the liquid’s flash point. The flash point is defined as the lowest temperature at which enough of the liquid has volatilized to form a mixture with the air capable of sustained burning after ignition from an external source (10). Flammable liquids have a flash point of less than 100° F; combustible liquids have a flash point of 100° F or greater [NFPA 30]. A separate scheme created by the Globally Harmonized System of Classification and Labeling of Chemicals (GHS) incorporates initial boiling points into the categories for ignitable liquids. This scheme separates flammable liquids into four increasing grades (11). This scheme is summarized in Figure 1.



Category	Criteria
1	Flash point < 23 °C and initial boiling point ≤ 35 °C
2	Flash point < 23 °C and initial boiling point > 35 °C
3	Flash point ≥ 23 °C and ≤ 60 °C
4	Flash point > 60 °C and ≤ 93 °C

Figure 1: Globally Harmonized System (GHS) criteria for flammable liquids (11)

Routine fire debris analyses can detect ignitable liquids with flash points up to 100° C. This includes most flammable liquids and some combustible liquids. Liquids with flash points higher than 100° C, such as heavy oils and lubricants, can sustain fire but have difficulty initiating one (12).

2.2.1 Chemical Composition

The majority of ignitable liquids are derived from a common source – crude oil, otherwise known as petroleum. Petroleum's composition is primarily carbon-based, followed by much smaller fractions of oxygen, nitrogen, and sulfur, and trace amounts of metals. The carbon fraction can be separated into general groups of alkanes, cycloalkanes, and aromatics. More specifically, there are six major groups: normal (straight) alkanes, branched alkanes, cycloalkanes, aromatics, polynuclear aromatics, and oxygenates (2).

2.2.2 Manufacture/Creation

In its base form, crude oil is not a useful material; therefore, it is put through several refining processes to isolate more valuable fractions. These refinement processes can be summarized as distillation, conversion, or cracking techniques. Fractional distillation is the general process that separates the complex mixture of hydrocarbons into more narrow ranges based on boiling points. This is normally the first step in the refinement process as the end fractions are not pure, single-component fractions, but less complex mixtures relative to the starting material. Fractionation can occur at either atmospheric pressure or under vacuum. Atmospheric distillation utilizes a tall, heated column to induce the separations. The column is hottest at the bottom and gradually becomes cooler along its height. Perforated trays are set up along different temperature zones within the column in order to collect the vapor fractions as recondensed liquid. These fractions can then undergo further refinement to remove undesired components like sulfur and nitrogen or be reformulated for specific liquid blends. The temperature zone cut points will vary depending on the production needs of the refinery. Vacuum distillation is a secondary technique that can be applied to the heavier fractions of crude oil, such as the straight-run residues and heavy gasoil. The lower pressure allows large, high boiling molecules to vaporize, but at a lower temperature. Another benefit to the lower temperatures is that the molecules are at less risk of cracking, or breaking down into smaller molecules (8).

Cracking is another refinement process that is used to form the base material, or feedstock for many commercially used solvents and is extremely important in the manufacture of gasoline blends. Cracking involves the breaking of larger hydrocarbons into smaller, lower boiling molecules. This process can occur during fractionation due to the high temperatures needed to induce vaporization; however, this conversion is poorly controlled. For this reason, a catalyst is introduced to have more control over the reaction and the final products. Zeolites, or molecular sieves, are the most common catalyst employed in these petrochemical processes. They are naturally occurring aluminosilicate crystalline minerals that are microporous due to the interconnected network of SiO_4 and $[AlO_4]^-$ molecules. Synthetic zeolites are preferred for industrial use as their sizes and structures can be tailored to specific needs. In the widely used fluid catalytic cracking (FCC) process, the sieve particle size is extremely small, behaving like a fluid in large amounts. The feedstock is dispersed onto the catalyst surface, causing breakages primarily between carbon-carbon single bonds. This reaction occurs with straight-chain alkanes, cycloalkanes, and aromatic rings (13).

Conversion techniques seek to do the opposite of cracking; these processes take smaller molecules and force a change in their size or structure to obtain more valuable refinement fractions. These processes include alkylation, reforming, and isomerization. Alkylation is used to generate higher weight hydrocarbons by reacting lower weight ones with each other. At least one of the reactants involved is an olefin, or alkene, for the reactive carbon-carbon double bond site(s). While not strictly necessary, as in the cracking process, the addition of a catalyst to the alkylation reaction provides better control and higher efficiency. The product of refinery alkylation is called alkylate, which mainly consists of highly branched alkanes, or isoparaffins, within the C_7 – C_9 range. Alkylate is an important part of gasoline blends worldwide as it greatly improves the octane rating, which is a measure of the performance and stability of the liquid (14).

Reforming and isomerization aim to alter hydrocarbon structure while maintaining the original molecular weight. In both cases the end goal is the same as alkylation: produce fractions with higher octane ratings. The reforming process is primarily applied to converting cycloalkanes into aromatic molecules. The use of a catalyst like platinum causes dehydrogenation of the saturated ring structure, leading to the aromatic ring. Isomerization processes are targeted towards converting straight-chain alkanes into isoparaffins, also using a catalyst to drive the reaction. Additionally, it can occur as a step before reforming. Straight chain alkanes can be cyclized through isomerization into cycloalkanes, and then immediately reformed into aromatics. The incidence of these additional reactions is dependent on the composition of the starting fraction (15).

2.2.3 ASTM Classifications

ASTM International E1618 - 19 (16) outlines a scheme for the classification of petroleum-based ignitable liquids. This scheme is divided into eight major groups. The groupings are based on two characteristics: the hydrocarbon content and its boiling point range. The hydrocarbon content describes what compound classes (discussed in 2.2.1) make up the liquid grouping and their ratios relative to each other. The groupings are further divided by the volatility of the carbon range present. Light product ranges contain compounds that fall between the C_4 – C_9 n-alkane scale, medium between C_8 – C_{13}, and heavy between C_9 – C_{20+}. These classifications translate into characteristic chromatographic patterns when a pure ignitable liquid is analyzed by gas chromatography-mass spectrometry. An arson analyst's main goal in data interpretation is to compare the debris extract with a known reference material for a visual pattern match. If such a match exists, then the liquid's classification and weight subclass are reported.

Gasoline is its own distinct group and does not follow the light/medium/heavy sub-categories. This is due to its unique composition; gasoline is a highly refined product, specifically blended in innumerous ways to achieve optimal octane ratings. Thus, the gasoline class encompasses all brands. The main compounds that comprise gasoline are a group of aromatics that produce a specific pattern. These aromatics include m-, p-, & o-ethyltoluene, 1,3,5-trimethylbenzene, and 1,2,4-trimethylbenzene. Polynuclear aromatics are also usually present; naphthalene, 1-methylnapthalene, and 2-methylnaphathlene are most seen. Normal alkanes are present between the C_4 – C_{12}

range but amount and extent can vary by brand. Generally, the aromatic content will predominate the alkane content above C_7. The gasoline class of ignitable liquids also includes all gasohol and E85 blends, which have higher ethanol concentrations than standard gasoline (16–19).

Petroleum distillates are predominated by n-alkanes, present in series depending on the weight sub-class of the liquid. This series typically appears as a Gaussian distribution in a gas chromatogram, apart from some light distillates that may only contain one or two n-alkanes. Unless it is a specifically de-aromatized distillate, aromatic compounds are always present within medium and heavy distillates, and occasionally within light distillates. Also present, but in less abundance relative to n-alkanes are isoparaffins and cycloalkanes. Polynuclear aromatics are not characteristic but can be present depending on the sub-class and peak spread of the liquid. Key liquids that fall into this classification are kerosene, diesel fuel, and cigarette lighter fluids.

Isoparaffinic product compositions are predominately branched alkanes (isoparaffins). Very minuscule amounts of straight-chain alkanes and cycloalkanes may be present, depending on the formulation. Mono- and polynuclear aromatics are absent. Many ignitable liquids from this class have overlap with the petroleum distillate class, such as lighter fluids and kerosene.

Aromatic products are much like isoparaffinic products in that they are composed primarily of their titular compound class. Alkanes (branched and straight) and cycloalkanes are typically absent or present in minor amounts. Polynuclear aromatics may also be present depending on the formulation. Various industrial cleaning solvents are formulated as aromatic products.

Naphthenic-paraffinic products have isoparaffins and cycloalkanes in the greatest abundance. All other compound classes may be present but in minuscule amounts. Charcoal fluid starters, lamp oils, and mineral spirits fall into medium and heavy sub-classes of naphthenic-paraffinic products.

Normal-Alkane products are typically highly refined to comprise of only n-alkane compounds. All other compound classes are not present in significant amounts. Products only fall into medium or heavy sub-groups given the high volatility of lighter n-alkanes. These include lamp and candle oils.

Oxygenated solvent compositions are highly varied as alkanes, cycloalkanes, and aromatics can be present in patterns comparable to other liquid classes. Significant oxygenated components include alcohols, esters, and ketones from C_8 and below. A key consideration in the identification of an oxygenated solvent is if the oxygenated component(s) present are at least one order of magnitude greater than the rest of the mixture. This is because oxygenates can be the result of pyrolysis or combustion which then end up as extraneous components in the debris extract (16).

The Others-Miscellaneous class includes liquids that do not fall into any of the other categories and those that share the characteristics of multiple classes. Products that are considered other-miscellaneous include commercial thinners, specialized gasolines, and fuel additives. In many cases, these liquids are highly refined mixtures of only a few compounds and are synthetic rather than blended distillation fractions (16).

3. INSTRUMENTATION BACKGROUND

3.1 Gas Chromatography-Mass Spectrometry

The premier analytical instrumentation for the analysis of ignitable liquid residues is a gas chromatograph (GC) coupled to a mass spectrometer (MS). The gas chromatograph induces the separation of components in a mixture which are then detected and converted into a signal output by the mass spectrometer. The basis of separation relies on the interactions of the components dissolved in an inert, gaseous mobile phase with the stationary phase they pass over. The stationary phase is a liquid coating of varying thickness supported on an inert solid within a capillary column. A component's interaction with the stationary phase is driven by a combination of factors including its affinity for the phase, its vapor pressure, and the temperature programing of the instrument. The mobile phase, or carrier gas is typically helium or hydrogen (20).

Samples can be introduced into the inlet of the GC in a liquid, gaseous, or solid-state. The most common state is as a liquid, which is vaporized by the heated inlet before it is carried on to the analytical column. Gaseous and solid samples require different apparatus to make them suitable for analysis by GC-MS. The sample amount delivered to the column is controlled by the initial volume injection and the inlet mode. Typical injection volumes are 1 µL but can vary depending on the application. The inlet mode can also be modified to accommodate sample volume and type. In split mode, a designated portion of the whole injection is vented out of the split vent so as not to overwhelm the column and the detector with excess solvent. Splitless mode retains the entire sample; this is most useful for trace analyses (21).

The analytical column is housed in a programmable oven to facilitate the separation of components on the stationary phase. Oven methods can be programmed in one of two ways: isothermal or ramped. With an isothermal method, the temperature is kept at a set point for a specified length of time. Separation of more complex mixtures benefits from a ramped method where the lowest temperature point starts just below the boiling point of the most volatile analyte and ends just past the boiling point of the least volatile analyte. Ramped programs can incorporate isothermal steps and vary the increase in temperature over a unit of specified time. Ignitable liquids in particular benefit from analysis using ramped methods as they are generally composed of numerous compounds with a broad range of boiling points (22).

As individual analytes elute from the GC column they reach a detector, which converts the signal from the analytes into a computer readout. Several detectors can be coupled to gas chromatographs depending on the selectivity of the application. Selective detectors are those that only produce a single response to a single target, such as a flame ionization detector (FIDs). Mass spectrometers (MSD) are capable of multiplexed responses for more detailed outputs. Both detectors are mass-sensitive, thus the generated response is based on the analyte mass as it contacts the detector over a unit of time. Another important factor to consider is the detection limit, which is the minimum amount of analyte that can be reliably converted to a signal distinguishable from instrument noise. FIDs can detect as low as 10 – 100 pg, while MSDs can detect down to 1 ng in full scan mode, and 1 pg in selected ion monitoring (SIM) mode (15,21).

Flame ionization detectors were commonly used as a hyphenated technique for ILR analysis until mass spectrometers became more powerful and widely available. Their utility is due to their selectivity for carbon and hydrogen-containing compounds, which make up the majority of ignitable liquids. It also has a wide dynamic range (10^7), making it suitable for low-level detection of ILRs (15,23).

Mass spectrometers have become the preferred detector for ILR analysis by gas chromatography as it provides structural data necessary for residue classification. While a wide array of mass spectrometers exists, the quadrupole MS is the most applied configuration. When analytes elute off the column and travel into the detector, energy is transferred to the molecules in the form of electrons to induce their ionization and fragmentation. Ionization techniques are considered 'hard' or 'soft'. Fire debris analysis relies on hard ionization, or electron ionization (EI) mode. In EI, a tungsten wire generates a beam of high-energy (70-eV) electrons that are accelerated within a low-pressure ionization chamber. The molecules that interact with these electrons become energized and expel an electron of their own, becoming positively charged. Depending on the stability of the ionized species, the molecule may undergo fragmentation or rearrangement. A repeller within the chamber pushes the ionized species out into the quadrupole mass filter (24).

Quadrupoles are configured with four rods made of a conductive material, with each set of rods oriented across from each other on an x- and y-axis. Direct current (dc) and alternating current (ac) in the form of radio frequency (rf) electric fields are applied to the rods to filter the ions based on their mass to charge (m/z) ratios. After passing through the mass analyzer, the ions strike a detector to convert their abundance into a measurable current. Electron multipliers are commonly paired with quadrupole filters as they are more sensitive and precise compared to Faraday cups. A series of metal plates are arranged in a funnel orientation to collect the incoming ions. As a single ion of a particular m/z hits the first plate, the plate emits electrons that go on to bounce off the next plate. Subsequent strikes produce a cascade of electrons proportional to the original amount of a particular ion (21).

The visual representation of a generated signal is displayed as a mass spectrum. Signals are plotted on an x- and y-axis, where m/z ratios are along the x-axis and the abundance of each signal is along the y-axis. The highest signal – termed the base peak – within the spectrum is normalized to 100%. The abundances of the other peaks are calculated as a percentage of the base peak. Using a conventional 70 eV leads to reproducible fragmentations patterns, giving many molecules characteristic mass spectra (22).

3.2 Portable Instrumentation

Time is a crucial factor in many forensic/emergency scenarios, as evidence can become more difficult to attain the further out it is collected from the initial incident. In a fire scene investigation, the chances of finding any ignitable liquid residues improve the sooner potential evidence is identified and properly packaged for laboratory analysis. However, even if the scene processing is accomplished quickly, full laboratory analysis can take weeks, at minimum. The period between packaging and analysis can incur an unknown loss of analyte and possibly lead to an altered interpretation of data.

Portable instrumentation has been increasingly looked to in the past two decades to improve the efficacy of on-scene investigations (25). First responders, environmental surveyors, and military personnel have benefited from the rapid sampling capabilities and immediate identification of potentially hazardous chemicals. The implementation of such devices for fire scene investigation can provide several advantages over traditional evidence processing. In addition to the quick feedback, the risk of analyte loss from sampling, packaging, and transport is reduced. Demand on the laboratory is also lessened as preliminary screening of evidence can prevent wasting resources on items of no value (26,27). Investigators can make advancements in a case much faster with the information provided by the field analysis instead of waiting for results generated by a full laboratory analysis (28).

Fieldable instrument designs generally compromise between performance and practicality. Miniaturization of hardware is necessary for easy transport in the field but will reduce analytical capabilities relative to their laboratory equivalents. Sensitivity metrics like signal-to-noise ratios and limits of detection tend to be higher to compensate for ruggedness. There is the expectation that many field situations will involve extreme weather or hazards, thus design elements are focused on ensuring functionality while minimizing maintenance. Overall instrument operation is intended to be as simplistic as possible, especially for operators who will likely not have a scientific background. This includes the analysis software capabilities, which are commonly automated to a high degree. The instrument handles the data analysis through a librarysearching algorithm and then generates a concise report to limit the need for data interpretation (26).

3.2.1 Electronic Noses

Non-separation-based instrumentation is focused on the detection of residue vapor ‘hot spots’ for targeted evidence collection. Hydrocarbon noses, or “sniffers” have been utilized as a compliment to visual investigations and as a potential substitute to canine detection. General instrument design is comprised of a sampling probe, a vacuum pump to pull in vapor, the detector, and meter readout. Detector types applied to ILR sampling include flame ionization, photoionization, and catalytic combustion. In flame ionization, the collected vapor is burned in a hydrogen/air flame. The resulting ions/electrons produced by the combustion generate a current proportional to the species concentration. Photoionization detectors similarly produce current readouts to flame ionization, however; the method of ionization is dependent on a UV lamp for irradiation. In catalytic combustion/bead detectors, the collected vapor is passed into a chamber housing a catalyst-coated resistance wire. Vapor combustion induces an increase in resistance, which is converted into a proportional signal (4).

Evaluations of several commercial ‘sniffers’ have demonstrated the ease of use, low maintenance requirements, and low initial cost. The majority, however, lack sensitivity and specificity. Another major drawback is their inability to differentiate between legitimate residue components and pyrolysis products, therefore leading to false positives. This is especially prevalent in modern homes where a significant amount of interior materials are petroleum-derived (29–32). Ultimately, these types of detectors have limited utility during fire scene investigations.

3.2.2 Portable GC-MS

Recent reports have called for the investigation of portable GC-MS applicability to the analysis of ignitable liquid residues in the field (3,25,28,33,34). Person-portable gas chromatograph-mass spectrometry instrumentation has been increasingly sought after as a versatile tool to address in-field analysis needs.

Early GC-MS systems such as the zNose™ and Hapsite® were evaluated for ILR detection, with limited success. Both suffered from limitations of poor chromatographic resolution and temperature programming. The zNose™ was also easily contaminated by carryover and had low vapor detection sensitivity. Data outputs by both systems were too technical for untrained users to interpret. Despite the miniaturization of the systems, the logistics of the designs required further improvement (35,36).

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 individual portable GC-MS systems with 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, high-performance batteries (29). Other features 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 (25,26,28).

A recent study conducted 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 (33). A subsequent study with the same instrument collected air and water samples from fire scenes using SPME and was able to detect a range of combustion-related compounds. Many were presumptively identified to due to a lack of a fire-scene specific on-board library (37).

4. EXTRACTION TECHNIQUES

4.1 Introduction

Following the collection of evidence from the fire scene, an extraction must be performed to prepare the sample for analysis. A piece of debris such as a section of carpet will not likely have remnants of ignitable liquid on the exposed, charred surface, but instead in the underlayers if enough seeped through before ignition. There are several validated techniques an analyst can use to liberate these residues, each with its own benefits and drawbacks (38).

One of the oldest methods is solvent extraction. Solvent extraction involves the immersion of the evidence into a large volume of solvent like pentane or carbon disulfide for the residues to partition out. The extract is then analyzed via GC-MS. This technique has mostly fallen out of favor due to its destruction of the evidence, which is undesirable for an investigation. The large volumes of solvent necessary put demand on laboratory supply, and thus is not considered a 'green' technique. It also poses health risks as most useful solvents, such as carbon disulfide, are incredibly toxic. In some cases, solvent extraction produces a more complete chromatographic profile compared to other extraction techniques. The technique, however, is also very prone to contamination by matrix effects. Many pyrolytic products will partition into the solvent, skewing the overall profile (39).

ASTM E1386 – 15 is the active standard practice protocol for solvent extractions of ILRs. It is currently recommended for situations involving non-porous materials such as glass, or the inside of suspect containers (40).

4.2 Headspace & Adsorption-based

4.2.1 Activated Charcoal Strips (ACS)

Activated charcoal strips are comprised of compressed activated carbon and polytetrafluoroethylene (PTFE). The structure of the carbon strips results in adsorption/absorption of molecules into the micron crevices all along the strip surface. Analytes passively diffuse on and off the strip dependent on the equilibrium reached within a sealed container (39).

ASTM method E1412-19 outlines standard practice procedures for the analysis of fire debris by activated charcoal. Typical sampling protocol involves suspending a single strip within a paint can containing the debris, secured by a safety pin or paper clip on a piece of unwaxed dental floss. Once sealed, the paint can is left to equilibrate at an elevated temperature of between 50 to 80 °C for a certain time frame. The recommended equilibration time is between 2 to 24 hours. The exact combination of temperature and equilibration time will depend on the suspected nature of the ignitable liquid. Once equilibration is complete, the strip is removed from the debris container and extracted using a solvent. Multiple solvents can be utilized for this process; however, many are not as effective as carbon disulfide. Other, less dangerous solvents commonly used are diethyl ether and pentane. If the strip is large enough, half of it can be used for extraction. The other half can be properly stored and archived in the event a reanalysis is necessary. Solvent extraction can be carried out in a GC vial so that the strip may be left in there (41,42).

The limit of detection for this technique is 0.1 µL of ignitable liquid residue within a 1 L paint gas. Despite the high sensitivity, this method has multiple drawbacks. Total extraction times can be excessive and solvent waste is incurred. Additionally, there is potential exposure to the highly toxic carbon disulfide, given it is the most effective solvent for extraction. Charcoal strips also pose issues with profile discrimination for several reasons – one being preferential adsorption of mid-weight and above compounds. The variability in equilibration time and temperature can also lead to the displacement of lighter-weight compounds, skewing the profile (31,43). Despite the drawbacks, ACS is a highly favored technique due to its low costs and sensitivity.

4.2.2 Solid-phase Microextraction (SPME)

Solid-phase microextraction is a technique developed by Janusz Pawliszyn in the 1990s (44). The device consists of fused silica fibers coated with a functionalized polymer. The thin fiber is housed in a needle shaft to protect it and prevent contamination. To sample, the fiber is extended out of the shaft and exposed to the matrix. After exposure, it is retracted back into the shaft until it can be analyzed. GC-MS is the usual instrumental technique used to analyze the extracts, as the fiber can be thermally desorbed in the heated inlet. Other coupled techniques include high-performance liquid chromatography (HPLC) and capillary electrophoresis (CE). The combination of the fiber and polymer allows for adsorption or absorption of organic compounds depending on the mode of exposure. Headspace sampling of solids and liquids is common, but the fibers can also be immersed in a liquid matrix. SPME fibers are commercially available and come coated with a variety of sorbents in different thicknesses. Two popular phases are polydimethylsiloxane (PDMS) and divinylbenzene (DVB) (45,46).

ASTM method E2154-15a outlines standard practice procedures when using SPME as the extraction technique for fire debris analysis. Choice of fiber is left up to the analyst’s discretion as some are better suited to different ranges of compounds. For medium to heavy-range compounds (C_{10} – C_{25}), a 100 µm PDMS phase coating is recommended. Light compounds between C_1 and C_{10} are best recovered using either an 85 µm polyacrylate (PA) or a 75 µm Carboxen/PDMS coating. Much like the practices for ACS, SPME can be used to sample from any kind of container deemed suitable for debris evidence. The container is heated to the desired equilibrium temperature between 60 and 80 °C before sampling; however, one benefit is that it does not have to equilibrate for as long as charcoal strips do. Typical equilibration times range from 20 to 30 minutes but can be longer depending on the temperature and the amount of debris present. Another benefit to SPME is the short exposure time. Like the equilibrium time, the optimal sampling time can vary depending on other factors, but commonly applied times range between 5 to 15 minutes. The sensitivity of this technique is equivalent to that of the activated charcoal strips – as little as 0.1 µL of neat gasoline can be detected from a 1 L paint can (47,48).

Despite the advantages SPME has with regards to its overall sampling time, it also has numerous drawbacks. One that significantly impacts its efficacy as an extraction technique is its limited surface area. This limitation often results in skewed chromatographic profiles, which are also influenced by the specific polymeric coating used in the analysis. The limited adsorption sites also pose problems with the displacement of lighter molecules by heavier molecules, further contributing to skewed profiles. As a result of this, the current ASTM method recommends that SPME be used as a screening technique for fire debris analysis to assess the potential class and concentration of any residues present in the sample. Other drawbacks include the high cost of the fibers, their fragility, and their limited reusability (42,47,49).

4.2.3 Capillary Microextractor of Volatiles (CMV)

The Capillary Microextractor of Volatiles (CMV) device was developed by Fan and Almirall (50–52) as a modification to the previously developed planar solid-phase microextraction (PSPME). The PSPME consists of a 4.25 cm circular fiberglass filter that has been activated and coated with a PDMS-incorporated sol-gel polymer, which acts as the adsorption phase. The original PSPME devices were used with portable IMS detectors for the sampling of drugs, smokeless powders, and other explosive residues (53–56). The CMV is constructed by taking approximately seven 2 cm strips of a PSPME filter and inserting them lengthwise into a 2 cm by 2 mm glass capillary tube. This configuration allows for a dynamic sampling device that can be directly inserted into the inlet of a GC-MS for thermal desorption. The dimensions of the tube were selected so that the device could fit in the commercially available thermal separation probe (TSP), available from Agilent Technologies (Figure 2). The CMV configuration has over 5000x greater surface area and 165x greater phase volume than that of a single SPME fiber (51).

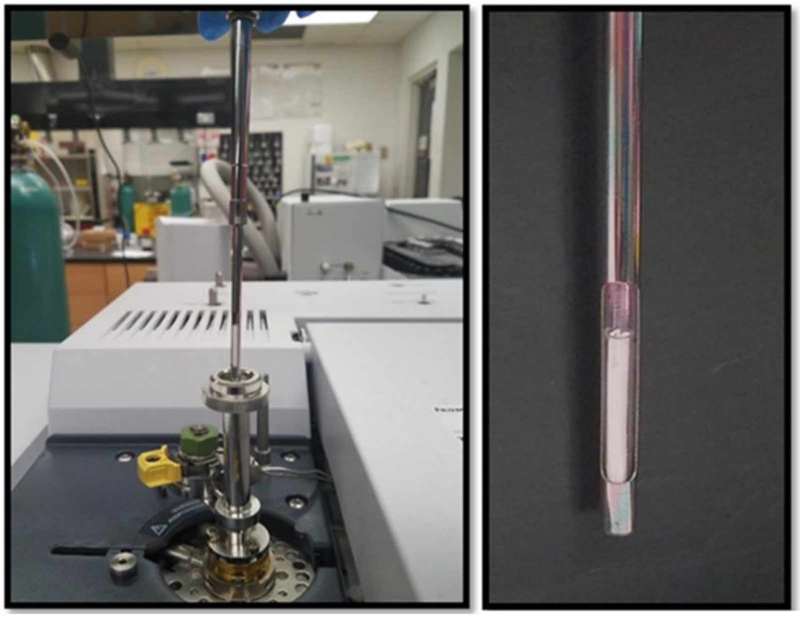


Figure 2: Photograph depiction of the CMV device seated in the Agilent TSP

CMV sampling is conducted by connecting one end of the capillary device to a vacuum pump through a direct adapter or a length of PFA tubing. The free end of the capillary is positioned in proximity with the desired headspace, without direct contact with the matrix. The vacuum pump then pumps air through the CMV for a determined length of time at a constant flow rate. Volatilized compounds make contact with the phase as they are pulled through and adsorb depending on their affinity. Prior applications of the CMV include headspace sampling of marijuana and hemp volatiles, breath sampling of cigarette smokers, and organic gunshot residue swabs from the hands of shooters (57–63).

5. MATERIALS AND METHODS

5.1 Materials

5.1.1. Phase Development and Validation Materials

Methanol (A452-4, HPLC grade, 99.9%), Acetone (A18-4, ACS certified, 99.5%) Methylene Chloride (D151-4, 99.9%), concentrated Sulfuric Acid (A300-500, 95-98%), Hydrogen Peroxide (H325-500, 30%), Sodium Hydroxide (S320-500, pellets 95-100%) were obtained from Fisher Scientific. Vinyl-terminated PDMS (vt-PDMS) (DMS-V22) was purchased from Gelest. Trimethoxyphenylsilane (PhTMOS) (104744, 97%), methyltrimethoxysilane (MTMOS) (246174, 98%), poly (methylhydrosiloxane) (PMHS) (176206), Benzene (270709, 99.9%), Toluene (244511, 99.8%), Ethylbenzene (03079, 99.5%) were purchased from Sigma-Aldrich. o-Xylene (A11358AE, 99%), m-Xylene (L03788AE, 99%) and p-Xylene (A10534AE, 99%) were purchased from Alfa Aesar and Trifluoroacetic acid (TFA) (13972e5000, 99%) from Acros.

G6 glass fiber filter circles (09-804-42A), glass capillaries (Wiretrol II, 21-176-4A), and 5 mL Transfer pipets (13-711- 5AM) were obtained from Fisher Scientific. Branson Ultrasonic bath (model 1510) and WS-400B-6NPP-LITE spin-coater from Laurell Technologies, was used for coating the filters.

5.1.2 TRIDION-9 Experimental 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.

5.1.3 Griffin G510 Experimental Materials

Heptane (99+%), Octane (99+%), Nonane (99%), Decane (99+%), Undecane (99+%), Dodecane (99+%), Tridecane (99+%), Tetradecane (99+%), Pentadecane (99+%), Hexadecane (99+%), Ethylbenzene (99.8%), 4-Ethyltoluene (90%), 1,2,4-Trimethylbenzene (98%), 1,2,4,5-Trimethylbenzene (98%), Naphthalene (99+%), and 1-

Methylnaphthalene (95%) were obtained from Aldrich Chem Co. Toluene (99.5%), m-Xylene (99.0%), and 1,3,5-Trimethylbenzene (97%) were obtained from TCI America. o-Xylene (99%) was obtained from Acros. Pentane (99.6%) was obtained from Fisher Chemical.

The paper cups were 9 oz heavy-duty cold cups (Dixie Consumer Products, Atlanta, GA). Simulated debris materials include cardboard packaging (Victory Packaging, Westfield, MA), plastic wrap packing air pillows (Pregis LLC, Deerfield, IL), and dark-wash jean fabric (93/6/1% cotton/polyester/spandex blend). Neat 87-grade gasoline was obtained from a Marathon gas station. An Escort ELF (Zefon International) air vacuum pump was used for headspace sampling.

5.2 Methods

5.2.1 Benchtop GC-MS 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-5ms Ultra Inert (30m x 0.25mm x 0.25µm) was used as the analytical column. The oven was programmed at 35°C with a 2 min hold, followed by a 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 (SIM) mode.

Comparison experiments involving the G510 resulted in an increase of 50:1 for the split ratio. The length of the analytical column was reduced to 28.9 m.

5.2.2. TRIDION-9 Method

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 x 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 sec^{-1} to a final temperature of 300°C with a 30-second hold, for a total run time of 178 seconds. The injector port temperature was set to 300°C with a desorption time of 10 seconds. Split ratios were configured as follows: A 10:1 split starting at 0 seconds to 10 seconds, followed by a 50:1 split from 10 seconds to 30 seconds. 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.

5.2.3. Griffin G510 Method

A FLIR Griffin G510 gas chromatograph-mass spectrometer 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 x .18 mm x .18 um) was used as the analytical column. The oven was programmed with a starting temperature of 40°C and a total of 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 minutes. The MS source was set to 200°C. Data acquisition occurred in Full Scan mode, over the range of 45 – 400 m/z.

5.3 Sampling protocols

5.3.1 Closed-Sampling Protocols (Can Headspace)

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 minutes 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 minutes 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. Reference picture can be found in Section 7.1.

5.3.2 Open-Air Sampling Protocols (Varian 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 varied mass loadings (Figure 3). The operation parameters for the BTEX experiments consist of a 150°C inlet temperature, a Restek split open liner packed with glass wool, and an 8 cm Megabore intermediate column (DB5-ms, 0.53 mm ID, 0.5 µm film thickness). For all fire debris-related experiments: The intermediate column was changed to an 8 cm DB-5 (30 m x 0.25 mm x 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.

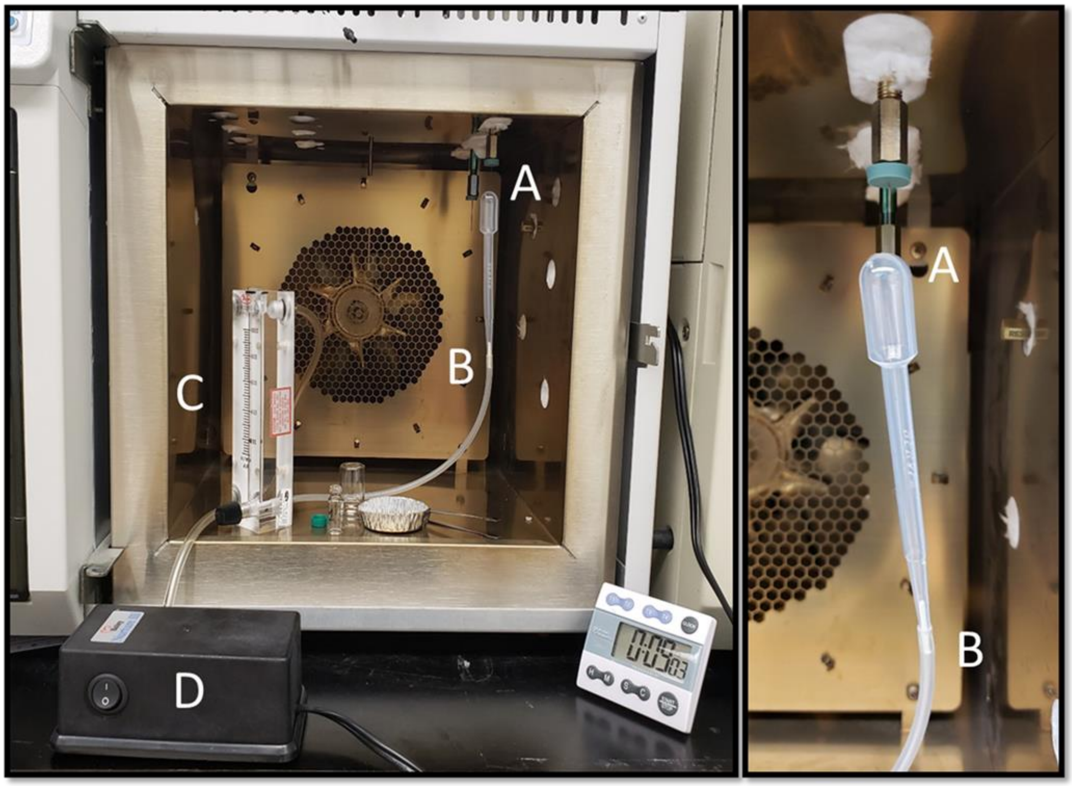


Figure 3: Photograph diagram of the open-air vapor sampling set-up: injection port with intermediate column (A), CMV within pipette tip and vacuum tubing (B), flowmeter (C), air pump (D)

5.3.3. CMV/Cup Sampling Protocol

Simulated debris sampling was carried out using 9 oz ‘heavy duty’ Dixie brand paper cups. Debris material was placed onto a glass platform and immediately covered with a single cup. The cup was pierced with a single hole punch before use, approximately 1.5 cm above the rim. The hole itself was approximately 2 mm in diameter to allow the snug insertion of a CMV device. The other end of the CMV device was inserted into a length of Teflon tubing connected to the Escort ELF vacuum pump. The cup was left over the debris undisturbed for two minutes at ambient temperature to allow vapor equilibration, followed by extraction via CMV for three minutes. The sampling flow rate was maintained at 0.5 L min^{-1} for a total sampling volume of 1.5 L. Reference picture can be found in Section 8.2.1.

Preliminary field sampling of spiked known volumes of ILRs involved an additional 5-minute delay before the equilibration period. The known volume was spiked onto the substrate’s surface and then left uncovered for 5 minutes to mitigate any device saturation.

5.4 Standards Preparations

5.4.1 TRIDION-9 Standards

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 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 1,000, 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}.

5.4.2 G510 Standards

All solutions were prepared using pentane as the dilution solvent. A single stock solution comprised of 20 compounds (20-mix) was 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 for a final concentration of 10,000 ng μL^{-1} (1%) stock solution. 20-mix calibration solutions were prepared in series at a concentration range of 5 - 300 ng μL^{-1}. A stock solution of diluted gasoline was prepared using the Marathon brand gasoline blend. The stock was prepared using a volume by volume (v/v) method with 50 µL of 87-grade gasoline into a 5 mL volumetric flask and brought up to volume, for a concentration of 10,000 ng µL^{-1}.

6. RESULTS AND DISCUSSION

6. CMV ADSORBENT MODIFICATIONS

Some sections published in: Gura S, Tarifa A, Mulloor J, Torres MN, Almirall JR. Capillary microextraction of volatiles device for enhanced BTEX vapors sampling based on a phenyl modified PDMS sol-gel adsorption phase. Anal Chim Acta 2018;1014:27–40. https://doi.org/10.1016/j.aca.2018.01.043.

6.1 Phase A Development

Efforts towards a new adsorbent phase for the CMV were initially focused on incorporating another adsorbent material into the existing methyl-terminated sol-gel. Carboxen particles were desired as their inclusion would theoretically increase the absorption capacity of the strips while still being able to thermally desorb the analytes. Several types of particles were attempted, including granulated powders and single-walled cylinders. Initial attempts used different epoxy formulations to glue the particles on the filters pre- and post- sol-gel coating, but it interfered with the sol-gel's ability to form a covalent bond with the activated filter. Another approach taken was to mix pre-determined amounts of carboxen into the sol-gel. Two issues arose because of this approach. In some instances, the inclusion of the carboxen particles inhibited the polymer gelation or the adhesion of the gel onto the filter. In the cases where filter coating and curing were possible, there was no way to ensure an even distribution of the particles across the filter surface. Some attempts involved coating a filter in nothing but a carboxen suspension. The filters made in this manner were strong enough to cut into strips for CMV assembly; however, this method also resulted in uneven particle distribution. Furthermore, the coating easily sloughed off even with gentle handling and thus was unsuitable for consistent use.

After many unsuccessful attempts at incorporating carboxen, the focus shifted to modifying the existing sol-gel formulation by substituting out certain components of the base reaction. These substitutions included the use of vinyl-terminated diphenylsiloxane-dimethylsiloxane in place of vinyl-terminated polydimethylsiloxane (vt-PDMS), and phenyltrimethoxysilane (PhTMOS) in place of methyltrimethoxysilane (MTMOS). Some formulations also included mixtures of PhTMOS and MTMOS at varying ratios. These modifications to the sol-gels made it through the gelation stage and were used to create CMVs. Preliminary testing of the new adsorption phases' retention capabilities was conducted by directly spiking 1 µL of a known amount of BTEX solution onto the CMV for direct desorption in the GC inlet. Triplicate analyses of each phase type determined the complete substitution of PhTMOS for MTMOS at the original relative ratio yielded the highest relative integrated areas for all five targeted analytes.

The synthesis procedure for the new phase (deemed as CMV-A) was then optimized to account for the overall gelation time. It was determined that a sonication step after the addition of the catalyst was necessary to overcome the steric hindrance created by the bulkier phenyl groups of the precursor. Synthesis trials were performed by following the original phase (deemed CMV-B) procedures, with the sonication step included in the 30-minute waiting period post-catalyst addition. Times tested included

10-minute intervals up to 30 minutes, and no sonication as a control group. Following the waiting period, all the sol-gel solutions were applied to filters for spin coating. The control group was the least viscous of all the trials, indicating the reaction had been significantly slowed. As the sonication time increased, so did the working viscosity. The 30-minute solution had a thick gel consistency which made it difficult to dispense an adequate amount onto the filter; this likely affected the uniformity of the final coat. Ultimately, a 10-minute sonication time allowed the sol-gel to reach a workable viscosity, resulting in evenly coated filters. The CMV devices made from those filters also demonstrated the highest volatile trapping performance.

6.2 Phase A Validation

6.2.1. Phase A Characterization

The coated glass fiber filters were characterized by SEM. Figure 4 shows images of glass fiber filters before (Fig.4a) and after coating with both sol-gel adsorption phases at the same magnification (Fig.4b, Fig.4c) (2000X, 15.5 mm WD, 10 Kv). Homogenous porous film coatings were consistently achieved for the original PDMS as well as for the new PhPDMS with no visual morphological differentiation. The appearance of the coatings is a combination of both the substrate fiber texture and the sol-gel process, being known for the creation of pores in sites where the solvent involved is trapped (64). The porosity of the adsorption phase coatings increased the capacity of surface area for the extraction of compounds and contributed to lower air flows restriction while pumping. Figure 4d illustrates a cross-section image of the new PhPDMS adsorption phase, evidently demonstrating the homogeneity of the coating throughout the interior fibers of the filter, over its complete thickness, corresponding to an average of ~210 mg increased weight to the filter.

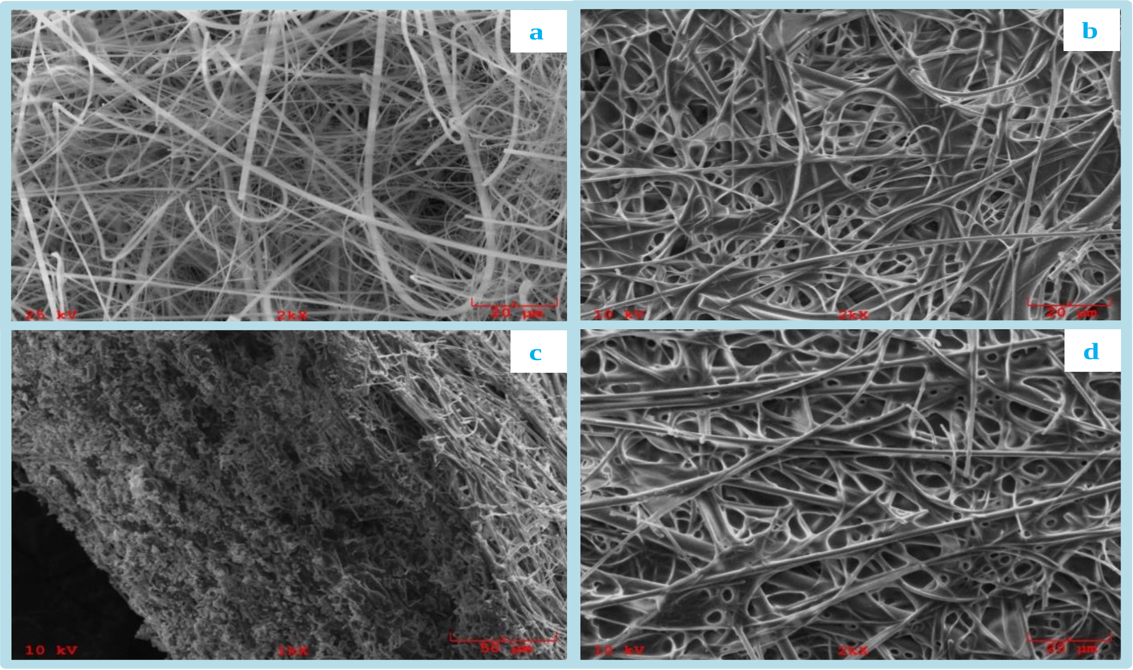


Figure 4: Scanning electron microscope (SEM) surface images of the glass fiber of the filter substrate before (a) and after (b) being coated with the original PDMS (X 2000). The cross-section of the new PhPDMS CMV is shown in (c) (X 1000), and the surface of the new PhPDMS is shown in (d) (X 2000)

The infrared spectra of the PhPDMS sol-gel sample in comparison to the original PDMS are presented as an average of three replicates in Figure 5, within the absorption screening range of 600-4000 cm^{-1} (Fig. 5a). To distinguish between the two coatings the ranges 1400-1650 cm^{-1} and 600-900 cm^{-1} were enlarged (Fig.5b and Fig.5c, respectively). The analyses for the two samples were performed for the remaining bulk sol-gel solutions, which were initially used for coating the activated filters and later allowed to complete the gelation process inside the tube under the same ambient conditions. The common absorption peaks in the figures around 1018, 1085, 1136, and 1260 cm^{-1} are attributed to Si-O stretching bonds, the peak around 2970 cm^{-1} is attributed to the methyl C-H stretching, all matching with the library spectra for PDMS and with literature reports (64). The peaks around 2202 and 907 cm^{-1} are attributed to Si-H stretching originating from the PMHS component of both coatings (64). The absorption peaks present on the PhPDMS spectrum and not found on the PDMS spectrum are emphasized in the enlarged figures. The peak at around 700 cm^{-1} and the weak ones at 750 and 726 cm^{-1} may be attributed to the mono aromatic sp2 C-H bond and the peaks around 1600 and 1430 cm^{-1} are attributed to the C=C stretching bond, thus pointing to the presence of phenyl groups in the new sol-gel coating (65).

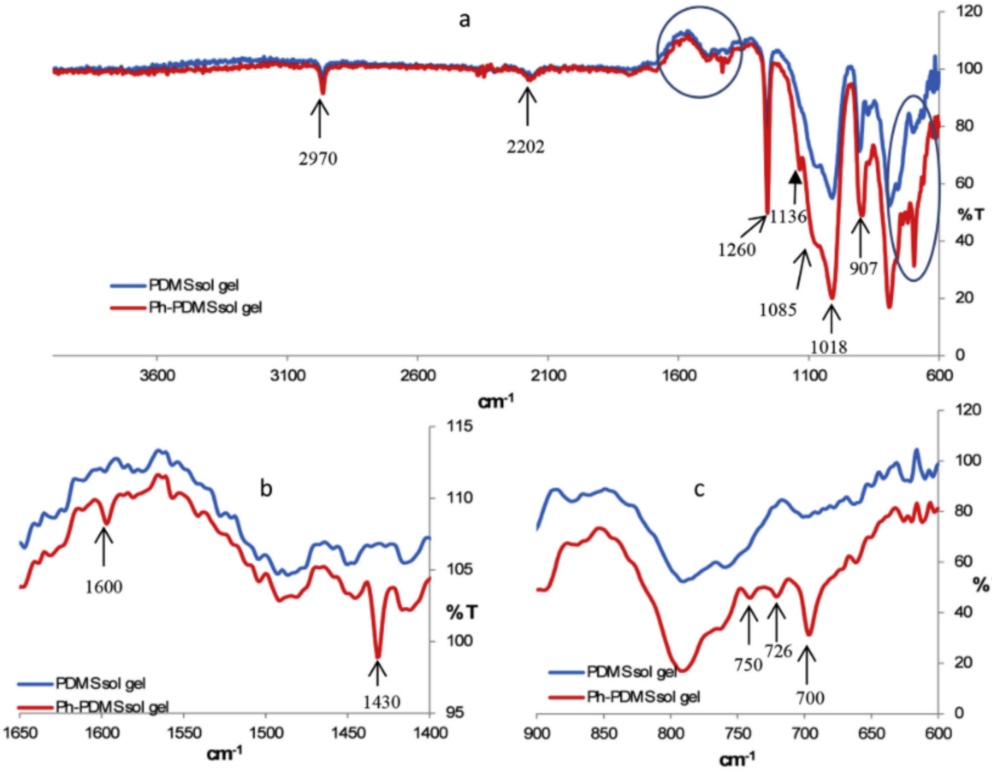


Figure 5: FTIR-ATR transmission spectrum of the PDMS (blue) and the PhPDMS (red) sol-gel coatings in the scan range 600-4000 cm^{-1} (a) sign with circles for directing the enlarged area ranges of 1400-1650 cm^{-1} for pointing the C=C stretching bond (b), and 600-900 cm^{-1} for pointing the mono aromatic sp^2 C-H bond (c) of the phenyl groups in the new PhPDMS coating

6.2.2. Phase A Experimental Evaluations

The performance of the new active sampler PhPDMS-CMV was evaluated in this study using an experimental setup that simulated an outdoor field sampling scenario. The more challenging outdoor scenario represents an open space where a continuous emitting source may be randomly diluted with air. It would be unable to reach equilibration, thus yielding inconsistent vapor concentration during sampling. A calibrated GC injector port was used to generate instant vapor pulses for sampling (Section 5.3.2), with the introduction of ambient air for dilution. Additionally, an aging test was also performed to evaluate the CMV's retention capabilities. Known quantities of headspace vapor were sampled and then the devices were left in different storage conditions for up to 18 hours before GC-MS analysis. Knowing the extent of retention stability and optimal storage conditions are important for the success of the CMV as a field sampler. Immediate analysis is not always feasible after sampling; thus, delays should be accounted for when using the device.

In both studies, the new PhPDMS-CMV (CMV A) was measured in comparison to the original PDMS-CMV (CMV B) to gauge any performance increases. Calibration curves were constructed for both CMV devices to quantitate the recoveries/retention amounts from each experiment. The curves were built via 1 µL direct spikes of BTEX solution in the concentration range of 1.6 – 500 µg mL^{-1} and analyzed in triplicate by GC-MS. A linear trend equation was obtained for each compound. Linearities better than 0.968 were determined for the most volatile compound (benzene) and higher than 0.993 for the rest. The average signal intensities for all the concentration ranges are similar for both CMV adsorption phases, indicating similar desorption efficiencies for BTEX compounds inside the GC-MS injection port during analysis.

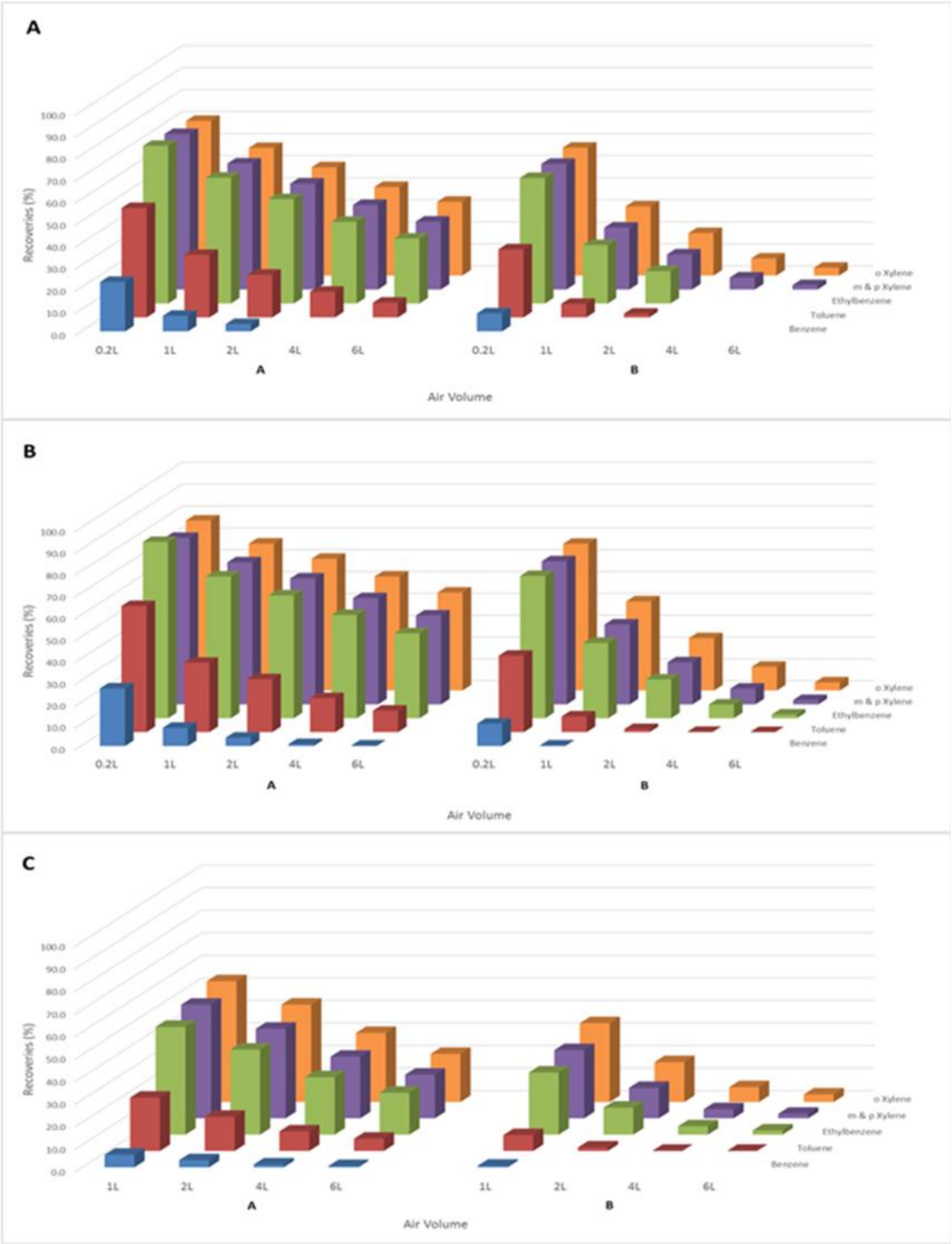


Fig. 6. Retaining capabilities measurement using the GC injector vapor source for generating instant immediate pulse of BTEX vapors followed by surrounding air pumping up to 6 L, for 100 ng BTEX vapor at 0.2 L min^{-1} flow rate (a), 1000 ng BTEX vapors at 0.2 L min^{-1} flow rate (b), 1000 ng BTEX vapors at 0.5 L min^{-1} flow rate (c)

Fig. 6 demonstrates the results in averaged % recoveries (n = 3) for three experimental series within the simulated open-air scenario. The retention capability for each compound was calculated per CMV, per varied sampling conditions. The three parameter variations include: (i) vapor concentrations, for sampling an instant vapor pulse of 100 ng (Fig. 6a) and 1000 ng (Fig. 6b) mixture amounts at a gradual increase of air volume; (ii) flow rate, sampling in a constant optimized flow of 0.2 L min^{-1} (Fig. 6b) compared to a higher flow of 0.5 L min^{-1} (Fig. 6c); (iii) total air volumes, all three series were subjected to a gradual increase of sampled air pumping volume, up to 6 L. The overall analytical precision achieved was within 17% between replicate measurements for the less volatile compounds in the mixture for both CMV phases across all three sampling setups. For the highly volatile benzene and toluene, the analytical precision was measured within 26% for CMV A. Due to the weaker retaining capabilities of CMV B, trace detection levels were quickly reached as air volumes increased, leading to poor repeatability between replicates.

A general decrease in recoveries is observed as the sampled air volume increases through both CMV devices in all three experimental series, indicating a breakthrough effect (Fig. 6). However, a clear faster, and steep decrease for all the compounds is observed for CMV B in all the conditions studied: compound concentration, pumping flow rate, and total air volume. The highest recoveries were measured at the lower flow rate for both CMV's, at the lowest air volumes sampled (0.2 L air in Fig. 6a and b). However, recoveries were consistently greater for CMV A over CMV B, with average absolute values of 24% and 9% for benzene, 54% and 33% for toluene, and above 70%

and 60% for ethylbenzene and the isomers of xylenes, respectively (Fig. 6b). With the increase in air volumes, significant gaps between the recoveries of the two adsorption phases were emphasized. At 6 L sampling volume, xylene isomers were detected at all levels, but with residues of 2-4% using CMV B versus 20-40% using CMV A. When sampling the higher mass loadings of 1000 ng (Fig. 6b and c), less than 2% ethylbenzene was retained on CMV B whereas 20-40% was retained on CMV A. This was also seen at the higher flow of 0.5 L min^{-1}. Toluene had a minimal percent recovery of only 0.1% in sampling 4 L and 6 L air volumes using CMV B, whereas 5-9% was retained at the same volumes with CMV A.

As seen in Fig. 6a and b (100 and 1000 ng BTEX concentration), complete breakthrough was observed with benzene using CMV B from 1 L and 2 L air volumes onward, respectively. Benzene retention was greater with CMV A; breakthrough did not occur until 4 L at the lower mass loading and remained detectable through all volumes at the higher loading. Similarly, at the faster sampling flow rate (Fig. 6c), benzene was lost from 2 L onwards using CMV B, whereas CMV A retained all the compounds through 6 L of sampling.

Higher absolute recoveries were consistently measured for all the compounds sampled by CMV A at the 0.2 L min^{-1} flow rate compared to 0.5 L min^{-1} (Fig. 6b vs 6c) at the same total air volumes. This trend indicates that the retaining capability of the adsorption phase is influenced more by the pumping flow rate than by the total air volume sampled. Similar trends were also obtained with CMV B mostly for the less volatile compounds.

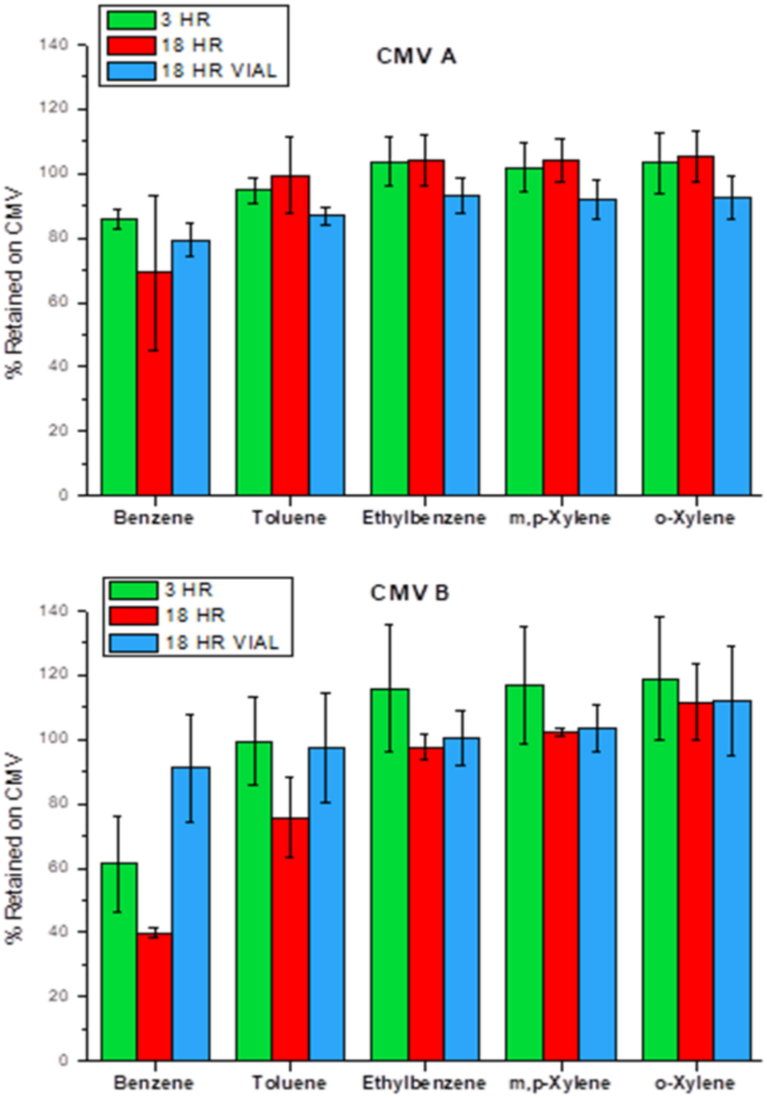


Figure 7: Retained recoveries (%) of BTEX: comparisons of immediate analyses vs. aging time (3 and 18 hours), and storage conditions (wrapped aluminum foil with and without vial), sampling of 100 ng BTEX, 0.2 L air with GC vapor source, with CMV-A (top) and CMV-B (bottom)

Fig. 7 demonstrates current aging test results. Both CMVs A and B retain the lower volatile compounds - ethylbenzene and the xylene isomers - without any losses through all tested conditions. However, better retention performance was demonstrated for benzene and toluene with CMV A than with CMV B. The average results (n = 3) indicate that CMV B experienced 25% loss after 18 h storage in aluminum foil, while no loss was observed for the same test with CMV A. For the most challenging compound benzene, loss was seen from both CMVs. An average loss of 15% was measured for CMV A versus 40% for CMV B after 3 h when wrapped only in the aluminum foil for storage, and 30% versus 60%, respectively, after 18 h. For both CMVs, storing wrapped devices in closed GC vials improved recoveries significantly.

6.3 Additional Adsorption Phase Development

Following the success of the A-phase validation, consideration was given to developing additional adsorption phases using the sol-gel formulation. Specifically, it was hypothesized similar success could be achieved if only the functional group on the precursor were changed. This would allow the affinity of the phase to change, but still retain the favorable properties of a sol-gel polymer. The result would be a greater degree of customization for the CMV; the device could be tailored with phase combinations for specific applications, including drug and explosives detection, environmental sampling, etc.

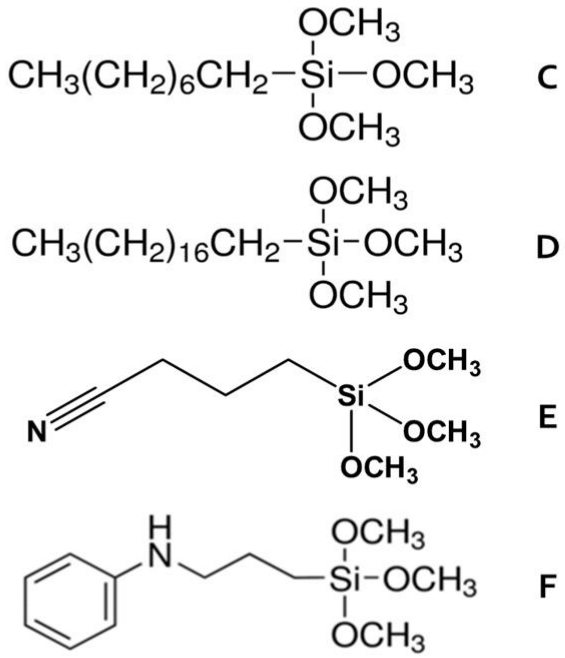


Figure 8: Molecular structures of the experimental precursors: trimethoxyoctylsilane (C), trimethoxy(octadecyl)silane (D), 3-cyanopropyltrimethoxysilane (E), and N-[3(Trimethoxysilyl)propyl]aniline (F)

For this objective, 4 precursors were chosen for experimentation: trimethoxyoctylsilane (C8), trimethoxy(octadecyl)silane (C18), 3-cyanopropyltrimethoxysilane, and N-[3(Trimethoxysilyl)propyl]aniline (TMSPA) (Figure 8). The cyano-substituted precursor was desired for the improvements in thermal stability and efficient extraction of highly polar molecules, including phenols and alcohols, without additional analyte manipulation (66). Octadecyl (C_{18}) and Octyl (C_8) inclusions into sol-gel coatings have demonstrated significantly enhanced extractions of both polar and non-polar compounds, relative to a methyl-based phase. Octadecyl was the most effective, followed by the octyl sorbent. It is posited that the improvements in extraction are due to the increase in chain length. The longer chain length provides more sites for molecular interactions with the analytes, which are simultaneously interacting with the silanol groups (67). TMPSA was selected to explore the possibility of future electrochemical applications of the PSPME. An additional prospect of its use was as a solvent, culminating in another approach to carbon nanotube incorporation into the adsorbent phase (68).

Initial attempts at synthesis kept the molar ratios of all components used for the B-phase (methyl-substituted) the same. Only the calculations for the substituted precursors were adjusted to account for their molecular weight and density. The synthesis/gelation procedure developed for CMV A was followed for all four experimental phases; sonication for 10 minutes after catalyst addition and then an additional 20 minutes of gelation before coating. This was done in consideration of the bulky functional groups that would hinder adequate contact between the precursors for effective condensation. The reactions were observed over a 30-minute period in five-minute intervals for signs of reactivity and consistency.

Early attempts resulted in viscous gelation for the octyl-substituted precursor; the three other reactions resulted in solutions unsuitable for the coating phase. The octadecyl preparation solidified into clumpy white chunks within 10 minutes of catalyst addition. Even with the removal of the 10-minute sonication step in a second synthesis attempt, the solution was too solidified to properly coat an activated filter. The propylaniline preparation resulted in a 2-layer formation: a semi-opaque watery top layer and a pink-tinted, viscous bottom layer. It was later determined that the propylaniline precursor was immiscible with the vt-polydimethylsiloxane (vt-PDMS) and the polymethylhydrosiloxane (PMHS). Through FTIR analysis of the layers, it was found that the top layer was comprised of only vt-PDMS. The bottom layer had a meld of PDMS and propylaniline character; thus, it is suspected that some degree of gelation reaction took place with a small portion of the precursor. Initial preparation of the cyanopropyl formulation resulted in a watery, single-layered solution that did not develop more viscosity even with additional wait time. A second attempt increased the sonication time to 20 minutes, which resulted in the formation of a second, milky white layer. FTIR analysis of the bottom layer was inconclusive.

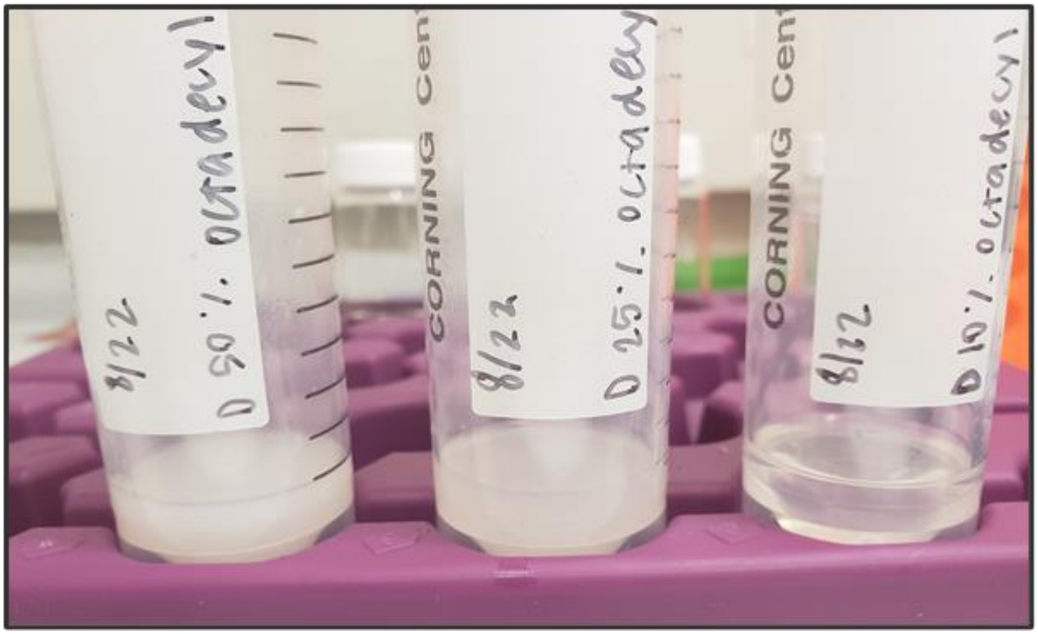


Figure 9: Octadecyl formulations (D-phase) at 50, 25, and 10%, ten minutes after catalyst addition

Subsequent sol-gel syntheses for the unsuccessful precursors involved the reduction of the original molar ratios by percentages, with the difference made up in the amount of solvent added to the total reaction. The cyanopropyl precursor concentration was reduced to 75% of the original amount, and an additional change was made to the solvent medium. The original solvent medium, methylene chloride, was switched to acetonitrile. These two changes resulted in a single layer formation that had a level of viscosity characteristic of the A- and B- phases and was thus suitable for filter coating. The octadecyl phase was evaluated at three different concentrations – 50, 25, and 10% - simultaneously in a timed trial. The gels were carried through the full reagent addition and were left to sit for only five minutes after the catalyst was added, with no sonication step (Figure 9). After the five-minute mark, 150 µL of each solution were pipetted onto strips of activated filter to gauge the mixture consistency. Gel spikes were done for each concentration every five minutes, up to 15 minutes. The 50% solution had a very thick consistency and solidified almost immediately at the first filter spike. The 25% solution was the most promising formulation, as the consistency at 10 and 15 minutes was easily absorbed by the filter without congealing on the surface. The 10% concentration remained very watery at the 5 and 10-minutes marks, with some viscosity improvement at 15 minutes.

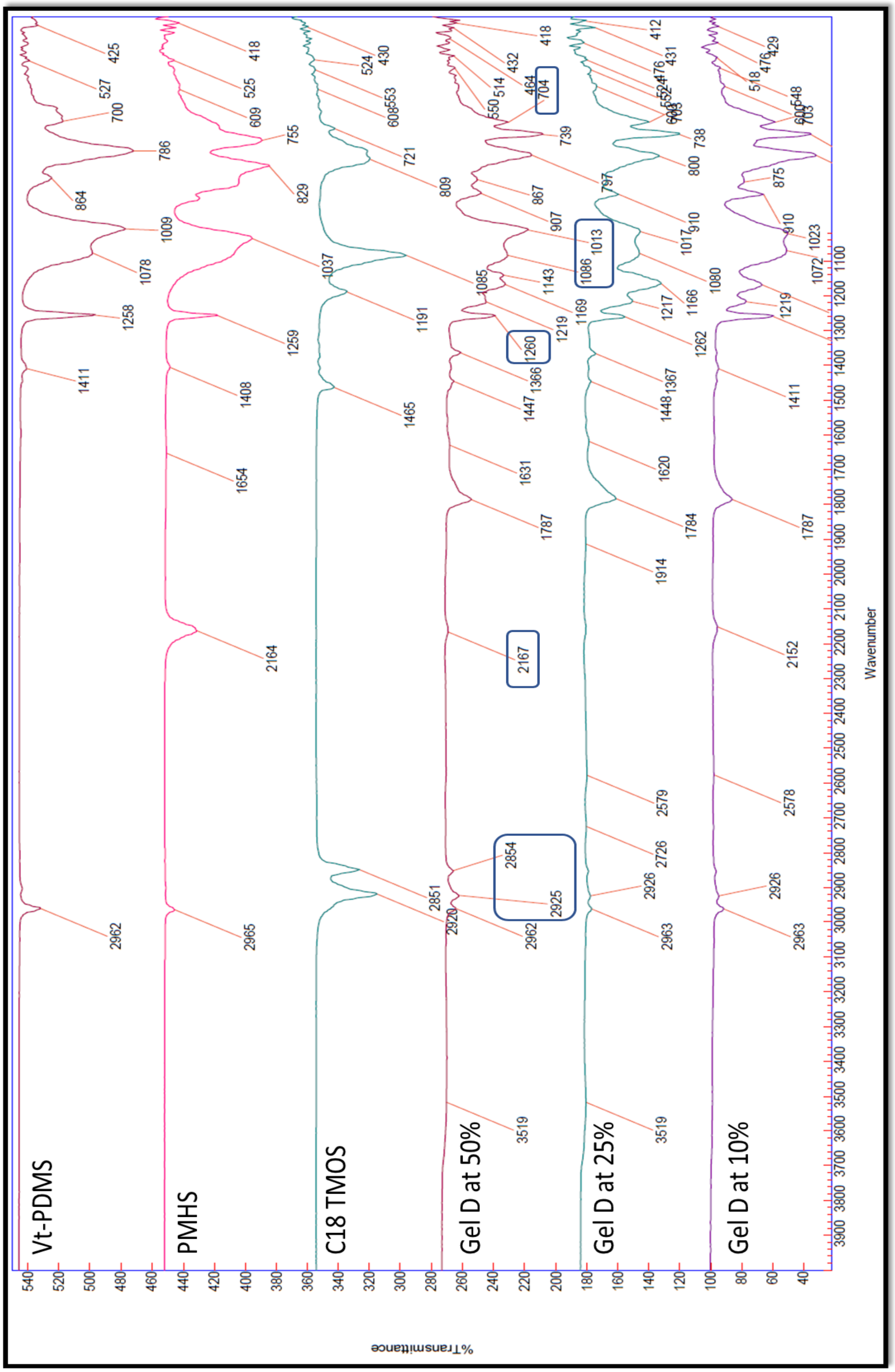


Figure 10: FTIR-ATR transmission spectra of single sol-gel components and Gel D formulations at 50, 20, and 10%

FTIR-ATR analysis was performed on a portion of the remaining gels and the individual sol-components to determine gelation success at each concentration (Figure 10). The gels at all three concentrations displayed character from the individual components, supporting the visual observations during the spiking tests. Of the three concentrations, 10% octadecyl had the weakest gelation character. The spectrum does not contain the peaks at 2854, 1448, and 1367 cm$^{-1,}$ which are present in the C18 precursor and the 25 and 50% concentrations. These peaks are attributed to bending and stretching C-H bonds, likely from the octadecyl functional groups. Other gelation character in all formulations is seen with the Si-O stretch peaks at 1017, 1080, and 1260 cm^{-1}, and the PMHS Si-H stretch peaks at 2167 and 907 cm^{-1}.

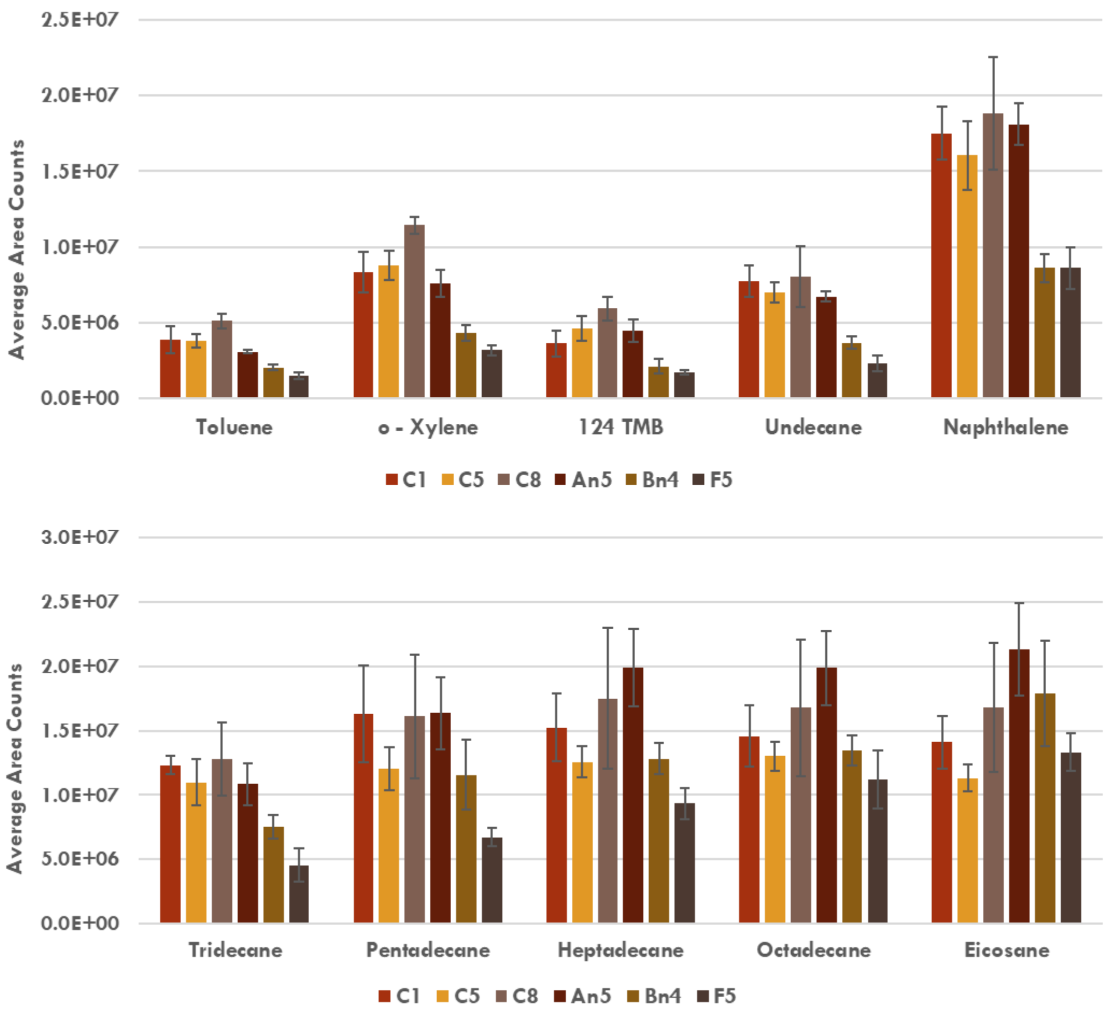


Figure 11: Average area counts (n = 3) of 1 µL 30 ng mL^{-1} '10-mix' (direct spike) onto CMVs for desorption trials

Currently, two of the four precursors are considered CMV prototypes – trimethoxyoctylsilane (Phase C) and 3-cyanopropyltrimethoxysilane (Phase F). Both have undergone gelation, coating, and curing without charring. CMVs made from several test batches exhibited analyte retention and desorption when assembled into a capillary (Figure 11). The other two precursors – N-[3-(Trimethoxysilyl)propyl]aniline and trimethoxy(octadecyl)silane – remain in the gelation stage.

7. FIRE DEBRIS APPLICATIONS AND TECHNIQUE COMPARISONS

Some sections included in: Torres M., Gura S., Tarifa A., Mulloor J., Valdes N., Grabenauer M., & Almirall J. Forensic Technology Center of Excellence 2020. Technical Note: Modifications to Capillary Microextraction of Volatiles (CMV) for the Extraction of Ignitable Liquid Residues. U.S. Department of Justice, National Institute of Justice, Office of Investigative and Forensic Sciences.

7.1 Optimization of Sampling Protocols for laboratory analysis

The approach taken was a univariate assessment of parameters critical to dynamic headspace sampling. Parameters considered for optimization were sample equilibration time, the heating temperature during equilibration, and the air pumping flow rate. Also considered was the GC inlet temperature for the CMV desorption. The levels of testing for each of the parameters were devised from several ASTM methods, including ASTM 1618, 1412, and 1413 (16,40,41). Consideration was given to one of the two available phases potentially exhibiting significantly enhanced performance over the other for ILR extraction, thus optimization experiments were carried out for both. A literature review was conducted to select compounds common to ignitable liquids for targeted analysis. A finalized list includes 20 compounds, ranging from toluene to eicosane; however, for optimization experiments, this was limited to just 10 compounds. This representative ’10-mix’ incorporated compounds from all available chemical classes, including aromatic, aliphatic, and naphthenic. Compound identification was determined from a comparison of retention times and mass spectra obtained from injections of standard solutions. The sampling vessel chosen for the closed-system protocol was a 1 L stainless steel unlined paint can, as it is a commonly used container for storing fire debris evidence.

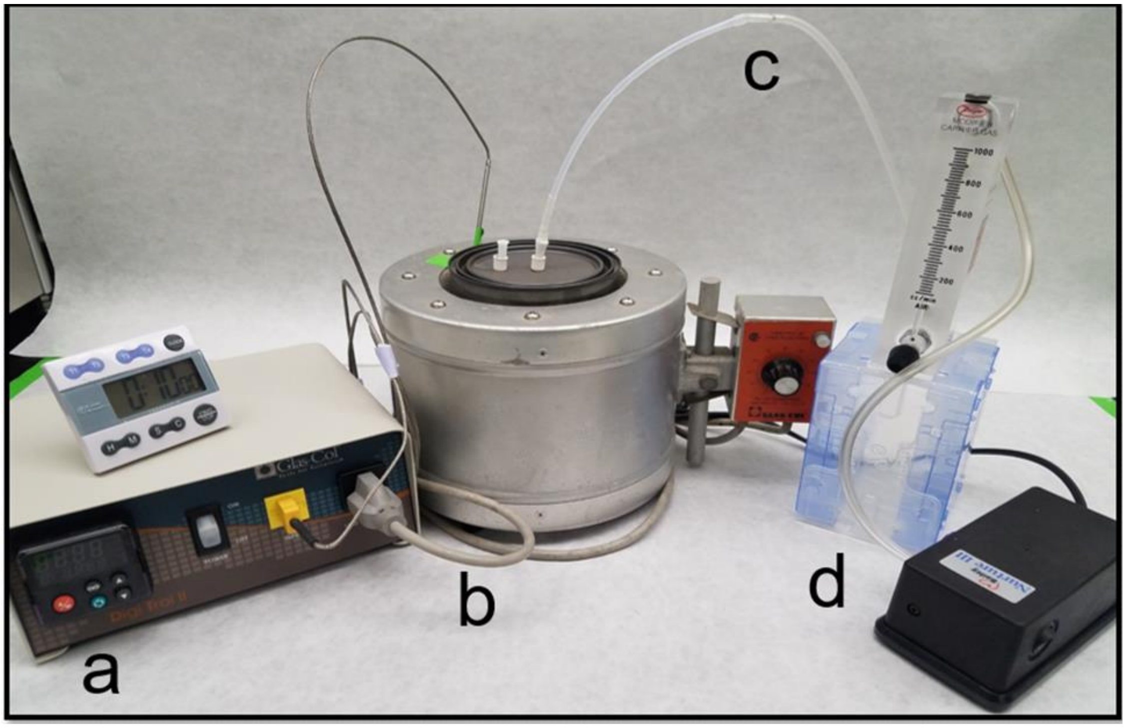


Figure 12: Image of the active headspace sampling apparatus; a) Glas-Col temperature modulator, b) Glas-Col heating mantle, c) PFA tubing with housed CMV, d) Nurture III vacuum pump with Dwyer cc/min flowmeter

The sampling parameters chosen for evaluation were the pumping flow rate, sample equilibration time, and temperature of the can heating mantle (Figure 12). Also of importance was the GC inlet temperature, as that would affect the desorption and recovery of analytes. To optimize the sampling parameters, 1 µL of a 100 µg mL^{-1} ’10-mix’ solution was spiked directly onto the bottom of a 1 L can. The lid of the can was pre-punctured with two holes; one directly in the center and one off-center, sealed with rubber septa. After spiking, the can was immediately covered with the lid and hammered shut to minimize volatile loss, then placed in the can heating mantle. To sample the headspace a 16-gauge hypodermic needle was used to pierce through the center septum. Connected to the needle is a short length of PFA tubing, to which one end of the CMV is connected. The other end is connected by tubing to a flowmeter and a Bailey Nurture III vacuum pump. The tubing seals around the CMV are air-tight to prevent analyte loss while sampling. Another hypodermic needle with open-ended tubing was used to pierce the off-center septum simultaneously to allow ambient air in, preventing a vacuum inside the can. During the course of optimization, it was determined that the use of a kimwipe within the can caused high levels of background interference, making the quantitation of late eluting analytes difficult. Thus, it was replaced with a 2.4 cm glass microfiber filter. The levels examined for each parameter were as follows: the air pumping flowrate at either 0.2 L min^{-1} or 0.5 L min^{-1}; the heating mantle temperature at 60, 70, or 80°C; the equilibration and sampling times at either 5, 10, or 20 minutes; and finally, the GC inlet temperature at 250, 270, or 290°C.

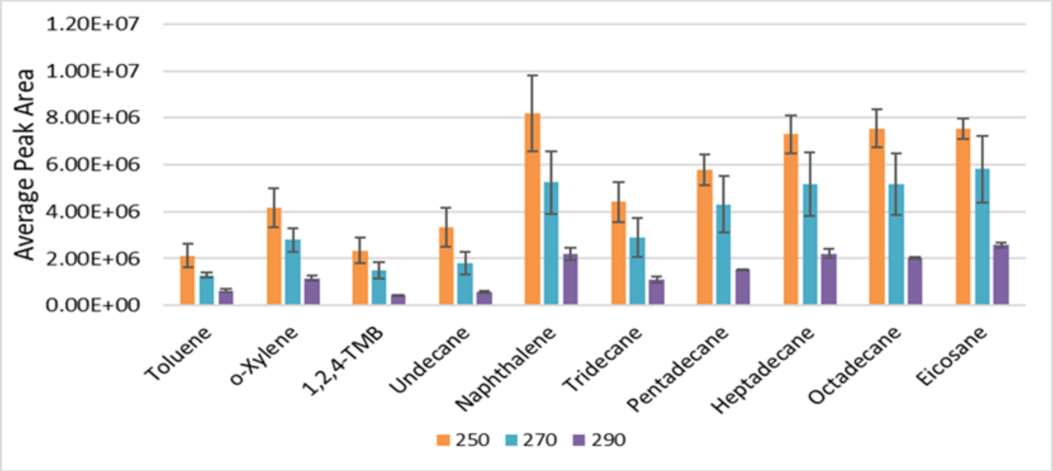


Figure 13: Averaged peak areas (n=3) from 1µL direct spikes of 30 µg mL^{-1} 10-mix onto CMV A to determine the optimal desorption temperature

Due to the diversity of compound volatilities in the 10-mix and more generally in ignitable liquids, the best set points for the parameters of interest were found in the mid-range of guidelines from the ASTM methods. For the mantle temperature, 70 °C was considered optimal as it produced the highest recoveries for semi-volatiles like naphthalene and acceptable recoveries for the highly volatile and non-volatile compounds in the series. This was also true for the equilibration time. A ten-minute equilibration time made significant differences in aromatic recovery compared to five minutes, and for undecane (C_{11}) through pentadecane (C_{15}) compared to 20 minutes. Comparison between flow rates of 0.2 L min^{-1} and 0.5 L min^{-1} showed that the lower flow rate produced the best recoveries, in agreement with results from Gura et al. (69). The higher flow rate showed a slight improvement in the recoveries of the heaviest compounds, but at the cost of the lightest compounds. Some replicate measurements using CMV B resulted in zero recoveries of toluene from the sample mixture. This is thought to be the result of breakthrough, or the loss of originally retained analyte. The higher flow rate likely caused an insufficient amount of contact time between the compound and the phase to allow adsorption or was so strong that it carried off any analyte that may have adsorbed.

The GC inlet temperature was considered an extremely important factor in the analysis, as too low of a temperature would result in inadequate desorption and ultimately, discrimination. Discrimination is very important to avoid, considering the classification of ILRs is partly dependent on the appearance of the chromatographic profile. Figure 13 shows the recoveries at three different inlet temperatures for CMV A.

Sampling was done by directly spiking 1 µL of a 30 µg mL^{-1} ’10-mix’ solution onto one end of the CMV followed by immediate introduction into the inlet. Despite the hypothesis that higher inlet temperatures would favor the lower volatility compounds, decreases in the recoveries were seen across the entire series for CMVs A & B at 270 and 290 °C compared to 250 ˚C. It is likely that some degree of thermal degradation occurred, lowering the recoveries. Siloxane background given off by the sorbent phase was also considered. A set point of 250 °C gave the lowest sorbent background and an increase in analyte recovery between 29 – 85% for CMV A, relative to 270 ˚C. The finalized parameters for the CMV closed-system sampling protocol are listed in Table 1.

Inlet Temperature	250 °C
Equilibrium Time	10 mins
Sampling Time	10 mins
Pumping Flow Rate	0.2 L min^{-1}
Mantle Temperature	70 °C

Table 1: CMV Dynamic Sampling Parameters (Closed System)

7.2 Multi-phase device evaluation

Reports in the literature have shown that SPME fibers functionalized with more than one sorbent have achieved improved extraction efficiencies for different ignitable liquids. This is in contrast to SPME fibers with a single sorbent, which tends to perform best for limited ranges of compounds (70). Considering the success of the phenyl-modified phase, this concept was applied to the CMV. This evaluation utilized the optimized sampling protocol, apart from the desorption temperature which was set at 230 °C before reoptimization. Three separate 50/50 A/B phase CMVs were created and compared to three devices of 100% A phase and three devices of 100% B phase. Triplicate measurements were made by all three types sampling 300 ng of a ‘7-mix’ solution (Figure 14). To determine the amount recovered, calibration curves were built by directly spiking 1µL of standard ‘7-mix’ solution at concentration ranges between 15 - 300 µg mL^{-1} in triplicate.

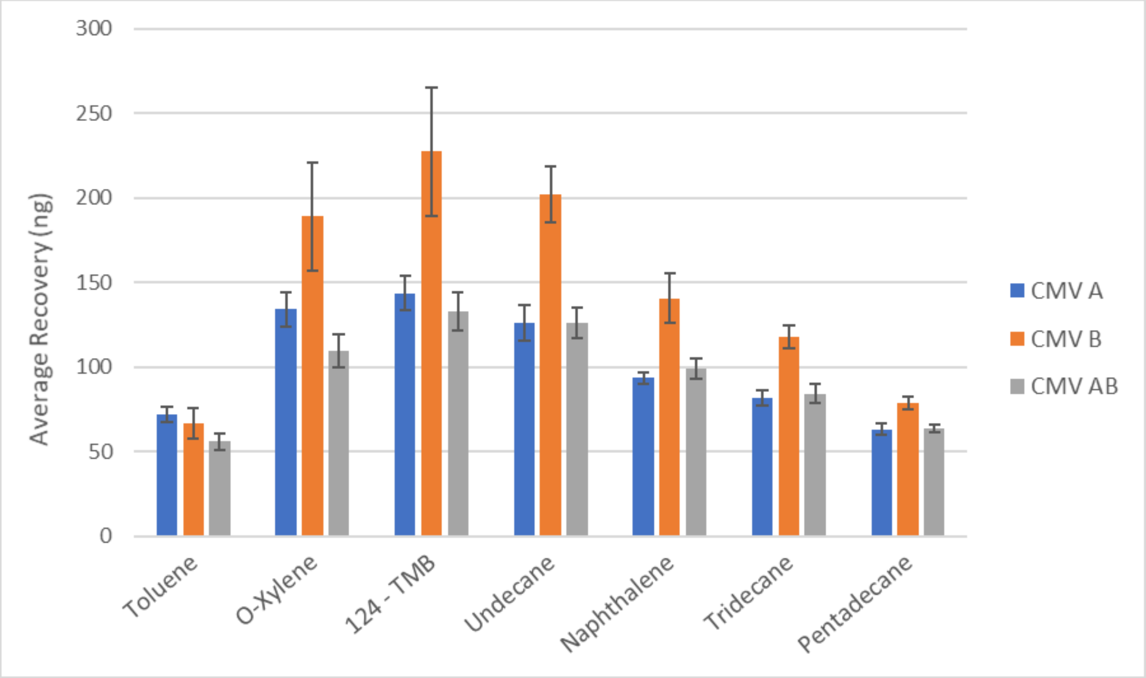


Figure 14: Average recoveries (ng) of a 300 ng '7-mix' solution by CMVs A, B, and AB (n =3) from a 1 L steel paint can

It was hypothesized that the AB CMVs would have had recoveries between what was possible for either individual phase; however, it was seen that CMV B performed better than what was expected, even for compounds it does not have as strong of an affinity for compared to CMV A. One reason for this might have been due to the omission of the three largest compounds present in the ’10-mix’, which were excluded from the solution because of heavy background interference. Their absence may have left more surface area available for greater amounts of the smaller molecules to adsorb, increasing the recoveries despite weaker affinity. The inlet temperature may have also played a role, as the 20 °C difference may have prevented some decomposition of the lighter molecules or caused incomplete desorption of the heavier ones.

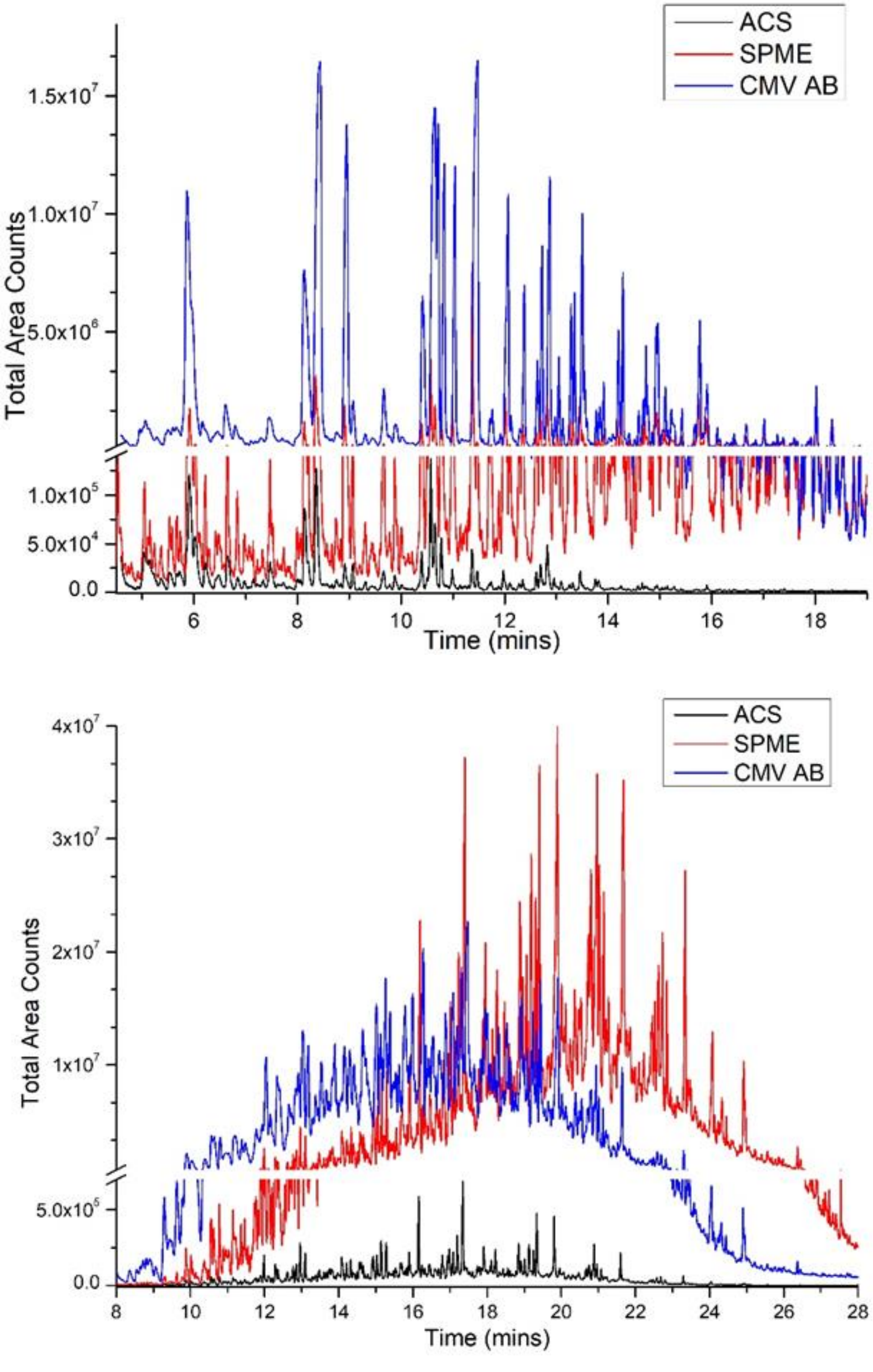
7.3 Comparison Experiments

To ensure as fair a comparison as possible, sampling parameters for all three techniques were adapted from several ASTM methods. The finalized parameters for CMV sampling were discussed in Aim 1.1 and were applied in the subsequent comparison experiments. Parameters for activated charcoal strips and solid-phase microextraction were taken exclusively from their respective ASTM methods. SPME experiments were conducted using a 100 µm PDMS fiber. The only parameter for the SPME protocol that was optimized was the sampling/fiber exposure time, set at 15 minutes. The equilibration time was kept at 10 minutes to stay consistent with the CMV protocol. The use of splitless mode and a splitless liner were the only adjustments made to the GC-MS method. The charcoal strip size employed was a 100mm^2 square which was conditioned before use for ~4 hours in an oven at 325°C. The extraction solvent utilized was pentane in the interests of safety and in minimizing variation in standard sample preparations. For the preliminary comparison, the equilibration time was set at 24 hours and the equilibration temperature at 70°C. The physical setup for closed-system sampling was kept the same for all three techniques except for the paint can lids: two holes with septa were pierced for the CMV, one for the SPME fiber, and none for the activated charcoal strip. The charcoal strips were suspended in the paint cans near the top of the lids using unwaxed dental floss and a safety pin.

Ignitable Liquid	**Abundance Range**		
	ACS	**SPME**	**CMV (AB)**
Exxon Diesel	1.0 - 3.0x10^5	1.0 - 3.6x10^7	3.0x10^6- 1.6x10^7
Marathon Regular Gasoline	4.0x10^4- 1.3x10^5	2.0 – 8.0x10^6	2.0x10^6- 1.6x10^7
Kleanstrip Kerosene	2.0 – 7.0x10^5	1.0 – 4.0x10^7	2.5x10^6- 2.4x10^7
Kingsford Lighter Fluid	5.0x10^6- 2.5x10^6	2.0x10^6- 1.6x10^7	3.0x10^6- 1.6x10^7

Table 2: Abundance ranges per sampling technique for 1 µL neat ILR extractions

Preliminary comparisons were done by sampling 1 µL spikes of several neat ignitable liquids using the closed-system protocol. Chromatographic profiles for all three techniques were overlaid to scale and analyzed for any instances of discrimination. Additionally, relative response ratios were calculated between the techniques for several prevalent compounds in gasoline as a measure of their sensitivity. The liquids analyzed included 87-grade gasoline (Marathon), diesel fuel (Exxon), charcoal lighter fluid (Kingsford), and kerosene (Kleanstrip). Figures 15a & 15b show the overlays for gasoline and kerosene. Table 2 summarizes the abundance ranges for each technique and ignitable liquid.



Figures 15a & 15b: Chromatographic overlays of neat gasoline (top) and kerosene (bottom); sampled by each technique. Scales have been broken to display all three profiles accurately

From the visual comparisons of all four liquids both SPME and CMV generated profiles with peak intensities at least one to two orders of magnitude higher than those produced by charcoal strips. The profile shapes for all three techniques were similar, and key analytes could be identified. Relative retention ratios between SPME, ACS, & CMV were calculated for six compounds in gasoline: toluene, ethylbenzene, the xylene isomers, 1, 3, 5-trimethylbenzene, & 1, 2, 4-trimethylbenzene (Table 3). For SPME relative to ACS, response ratios ranged between 6 - 45 times greater for compounds up to 1, 3, 5-trimethylbenzene, and 150 times greater for 1, 2, 4-trimethylbenzene. CMV sampling relative to SPME was more consistent with 7 – 23x higher response ratios. Interestingly, the ratios decrease with increasing ring substitution. The greatest increases in response ratios are seen with CMV relative to ACS, ranging between 141 – 1000 times higher for all compounds.

Compound	Retention Time (RT)	Relative Response Ratio (SPME/ACS)	Relative Response Ratio (CMV/ACS)	Relative Response Ratio (CMV/SPME)
Toluene	5.95	6.1	141.0	23.0
Ethylbenzene	8.13	10.1	223.8	22.2
m & p Xylene	8.35	20.5	250.2	12.2
o-Xylene	8.92	45.0	618.7	13.7
135-TMB	10.78	31.8	322.4	10.1
124-TMB	11.37	150.0	1004.4	6.7

Table 3: Relative response ratios per sampling technique for 1 µL neat gasoline

Overloaded profiles were one issue identified when sampling with CMV and SPME for the heavier ignitable liquids. This is likely due to the high concentration of liquid spiked into the can despite the short sampling times. Additionally, the split ratio for the CMV is something that may have to be adjusted when sampling neat liquids. The split ratio utilized for the comparisons was 20:1; an increase from the original 5:1 split.

8. EVALUATION OF PORTABLE GC-MS USING CMV

8.1 TRIDION-9

Some sections published in: Torres M.N., Valdes N.B., Almirall J.R. Comparison of portable and benchtop GC–MS coupled to capillary microextraction of volatiles (CMV) for the extraction and analysis of ignitable liquid residues. Forensic Chem 2020;19 (January):100240. https://doi.org/10.1016/j.forc.2020.100240.

8.1.1 Coupling of the CMV to the T9

The Tridion-9 (T9) gas chromatograph's sample introduction configuration was designed only for headspace vapors from solid, liquid, or gaseous materials. The devices compatible with the inlet port were Custodion® syringes, with three technique models available: solid-phase microextraction, coiled microextraction, and needle trap desorption (71). As a result of the incompatible injection port, a sampling protocol was devised to transfer CMV extracts onto an existing commercial accessory to facilitate analysis. The most appropriate syringe to accomplish this objective was the needle trap, as its configuration would allow for 'air sampling' of the CMV extracts onto its internal sorbents (72). The needle trap sorbents are described as a 'tri-bed' gradient of weak to strong, capable of adsorbing a broad range of compounds. The sorbent bed dimensions are approximately 2 cm long with a < 2 mm diameter, which is roughly equivalent to CMV dimensions (73).

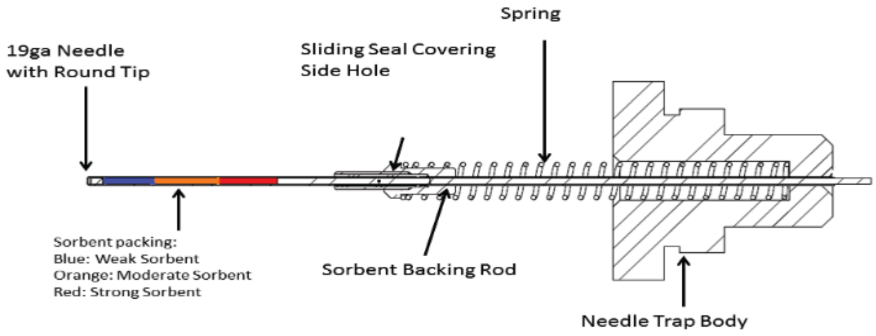


Figure 16: Schematic of the Custodion® needle trap syringe (73)

An additional sampling unit – the Sample Prep Station 3 (SPS-3) – was needed to make the transfer possible. The SPS-3 is a thermal desorption module, meant to thermally desorb analytes collected with conventional air sampling traps onto the needle trap syringes. The trap is secured into a trap holder, which is septum-sealed at both ends. At the top end of the holder, a specific cap is attached which allows the needle shaft of the needle trap through the seal for exposure into the trap tube. Once sealed, the holder is placed into the SPS-3, where another needle on the bottom of the interface pierces the bottom holder seal to deliver a stream of carrier gas (helium) through the tube at a constant rate. As the helium is carried up through the tube and into the needle trap, the module simultaneously heats the exposed tubing all along its length for a pre-programmed time frame. Once the desorption method completes, the needle trap is removed from the holder and can be directly injected into the T9 inlet port (73).

Figure 17: Picture scheme of the CMV/NTD sampling protocol. CMV is inserted into the stainless-steel tube and sealed with the NT adapter (1). Holder with inserted needle trap is placed into SPS-3 for desorption method (2). Top view of the T9 portable GC-MS (3). Injection of the needle trap into the T9 after CMV desorption (4)

To couple the CMV to the needle trap, the conventional trap holder was adapted. In place of an actual air trap, stainless steel tubes were fabricated in the same dimensions (89 mm long x 6.4 mm OD) to house the CMV without additional adsorbent interfering with transfer to the needle trap. Method blank testing of the tubes did not show evidence of carryover between runs, indicating that any potential active sites within the tube interior did not pose an issue to the overall analysis. To ensure the tubes were free of any other contaminants like solvents or skin oils, they were oven-conditioned at 300 °C for approximately 30 minutes before every round of analysis. The desorption method used throughout the study set the module heaters at 300 °C with the helium stream delivered at a rate of 30 mL min^{-1}, for a total method time of five minutes.

8.1.2 T9 Method Configuration

A review of the existing fire debris literature was conducted to select compounds for targeted analysis (74). 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 spectra 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.

8.1.3 Instrumental Figures of Merit

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 second 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 originally included in the library over those that had 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 seconds of the true compound. For the n-alkanes - apart from 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.

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

Table 4: Retention times, Qualifier ions, & Signal to Noise ratios for Aromatic and Alkane standard compounds on the T9 via CMV/NTD

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 signal averages and the noise averages were used to determine the S/N, shown in Table 4. 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 apart from heptane, octane, and 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}.

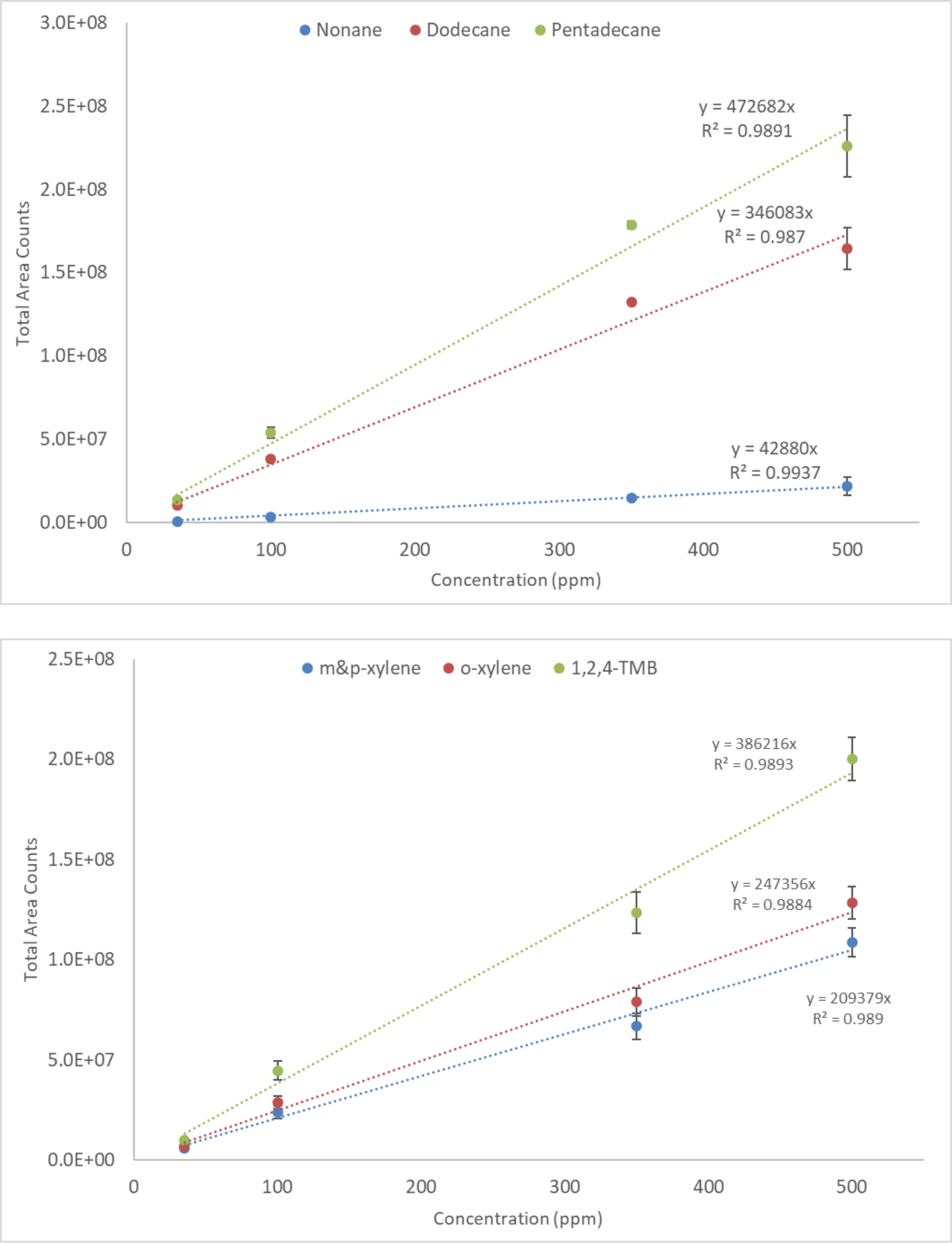
Compound	R^2
Toluene	0.9258
Octane	0.8537
m&p-Xylene	0.8286
Nonane	0.7730
o-xylene	0.8834
1,2,4-TMB	0.9846
Tridecane	0.8254
Tetradecane	0.8222
Pentadecane	0.8418
Hexadecane	0.8217

Table 5: R^2 values produced by CHROMION software

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 individual compounds 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 5 shows the R^2 values for all compounds the software was able to construct curves for. A curve was considered usable if each concentration point had all replicate measurements incorporated from their data files. 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.

8.1.4. Comparisons to Benchtop Performance

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-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 are shown in Figures 18a and 18b. 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.

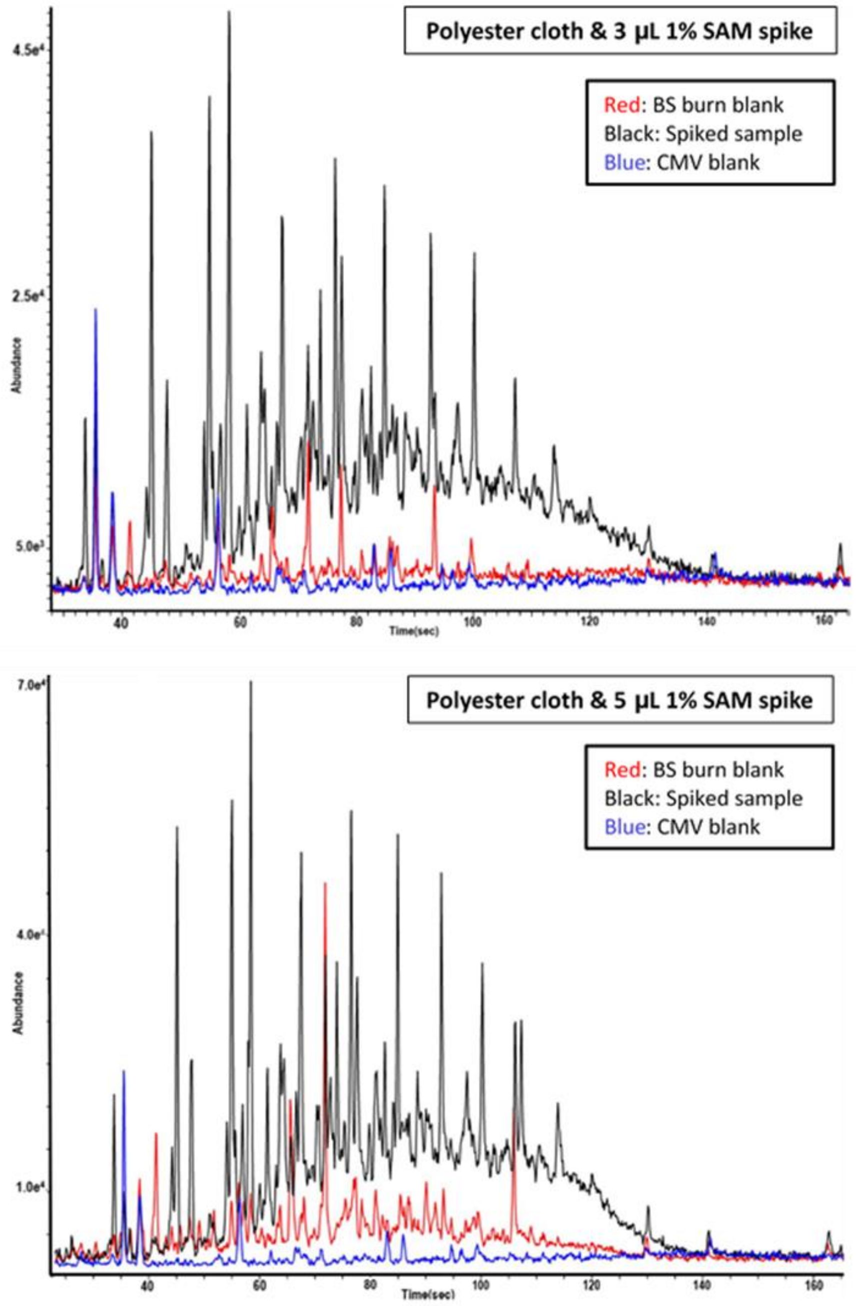


Figures 18a and 18b: Calibration curves built on the Agilent benchtop – a. CMV direct spikes; n-alkane curves (top) and b. aromatic curves (bottom)

8.1.5 Simulated Closed-system Debris 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 grams 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 hours 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 seconds 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 5.3.1 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. After 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 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 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 µL and 5 µL spike levels, but not for every material (Figure 19a and 19b). 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 µL 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.



Figures 19a and 19b: 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 5µL (bottom) level

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 except for heptane, 1, 2, 4, 5-tetramethylbenzene, and 1-methylnaphthalene were baseline resolved in SIM mode. At the 1 µL spike level for all three materials, the minimum signal-to-noise in SIM mode was ~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 (Figure 20). 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 µL.

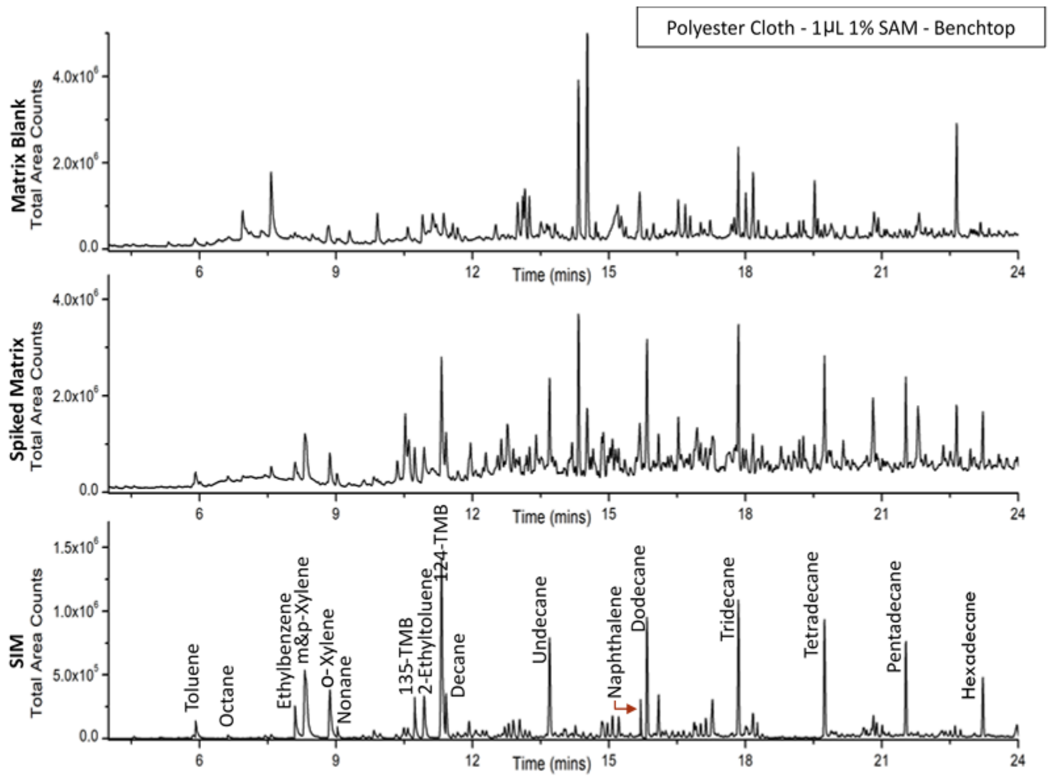


Figure 20: Chromatograms obtained by CMV-GC-MS from the closed-system sampling of polyester cloth at the 1 µL SAM spike level – Benchtop analysis

An evaluation of the CMV and CMV/NTD extraction techniques involved calculating estimates of recovered mass amounts at the 3 µL spike level using the previously generated calibration curves. Table 6 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 as 500 ng. The lowest analyte recoveries were from the bamboo skewer material, reaching a maximum of 16 nanograms with an average recovery of 7 nanograms. Estimates on the T9 were only possible for half of the final compounds, due to a combination of nondetection 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 nanograms.

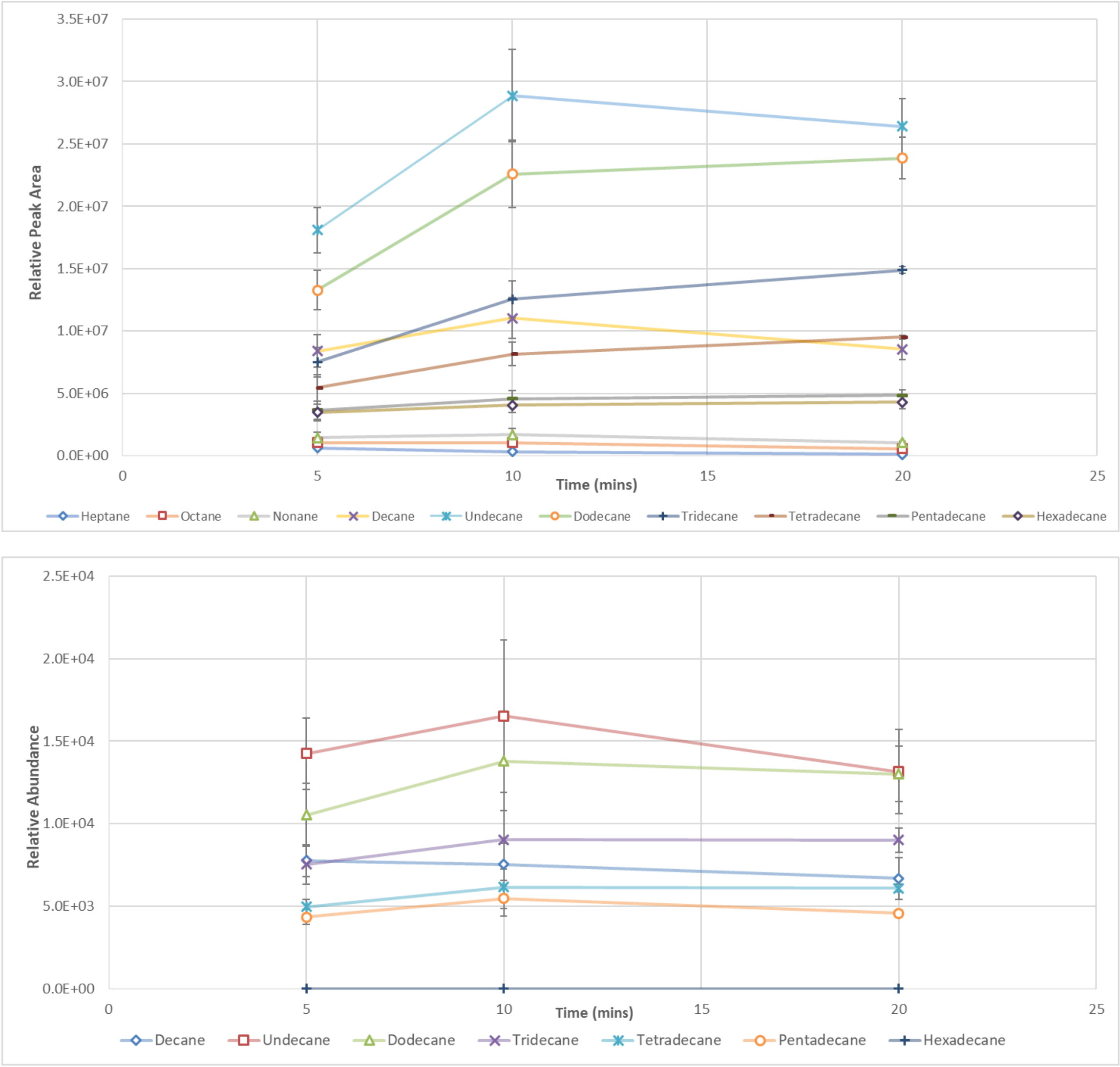
Compound	Polyester Cloth		Wood chips		Bamboo skewers	
	Benchtop	T9	Benchtop	T9	Benchtop	T9
Octane	84	-	18	-	1	-
Nonane	120	-	19	-	1	-
Decane	200	-	36	-	4	-
Undecane	256	-	-	-	6	-
Dodecane	168	-	61	-	6	-
Tridecane	147	131	60	35	10	141
Tetradecane	117	246	57	78	16	243
Pentadecane	26	98	51	30	14	85
Hexadecane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

Table 6: Estimated recovered mass (ng) from simulated fire debris at the 3 µL Level using CMV and CMV/NTD extraction techniques

8.1.6 Simulated Open-air 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 5.3.2 at time intervals of 5, 10, and 20 minutes for total sampled air volumes of 1, 2, and 4 L.

Figures 21a and 21b show 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 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 - 15% for the benchtop analysis, and loss of analyte on the T9 ranged between 1 - 20% after 20 minutes of sampling. The opposite trend was seen with the heaviest analytes - pentadecane, hexadecane, and naphthalene.



Figures 21a and 21b: 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

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 minutes, 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 - 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 – 30% and 5 – 36% on the T9 and benchtop, respectively. The high mass loadings ranged between 8 – 35% and 7 – 37%, respectively.

8.2 Griffin G510

Some sections published in: Torres M.N., Almirall J.R., 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 (2021), doi: https://doi.org/10.1016/j.forc.2021.100397

8.2.1 CMV/Cup Protocol 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. Choice of method 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 equilibrium period to allow sufficient vapor build-up for efficient extraction. Consequently, many laboratory techniques are not well suited to fieldwork due to the additional apparatus necessary.

A related field-analysis study (75), accounted for the container need by using a simple paper cup in conjunction with a SPME fiber. High concentration areas were first marked out using a photoionization detector. The cup was placed upside-down over the suspected ‘hot spot’ and served to concentrate 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 the purposes of this study, the same cup concept was applied to the CMV (Figure 22).

Figure 22: 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)

Several variables were considered in the optimization of a CMV/Cup protocol. These variables were the equilibrium time, the sampling time, and the 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. Consideration for the equilibrium time was 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 the breakthrough of relevant analytes. The variable test points were selected in the interest of keeping the overall protocol time under 10 minutes for high throughput extractions.

Each set of optimization experiments were carried out twice – one set sampling neat gasoline and the other neat diesel fuel. The sample matrix was prepared by spiking 10 µL of either ignitable liquid onto approximately four grams of wooden bamboo sticks. The sticks were left uncovered at ambient temperature for 25 minutes to let most of the liquid evaporate before 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. All analyses were conducted on the G510, with recoveries based on the method calibration curves constructed in Section 8.2.2.

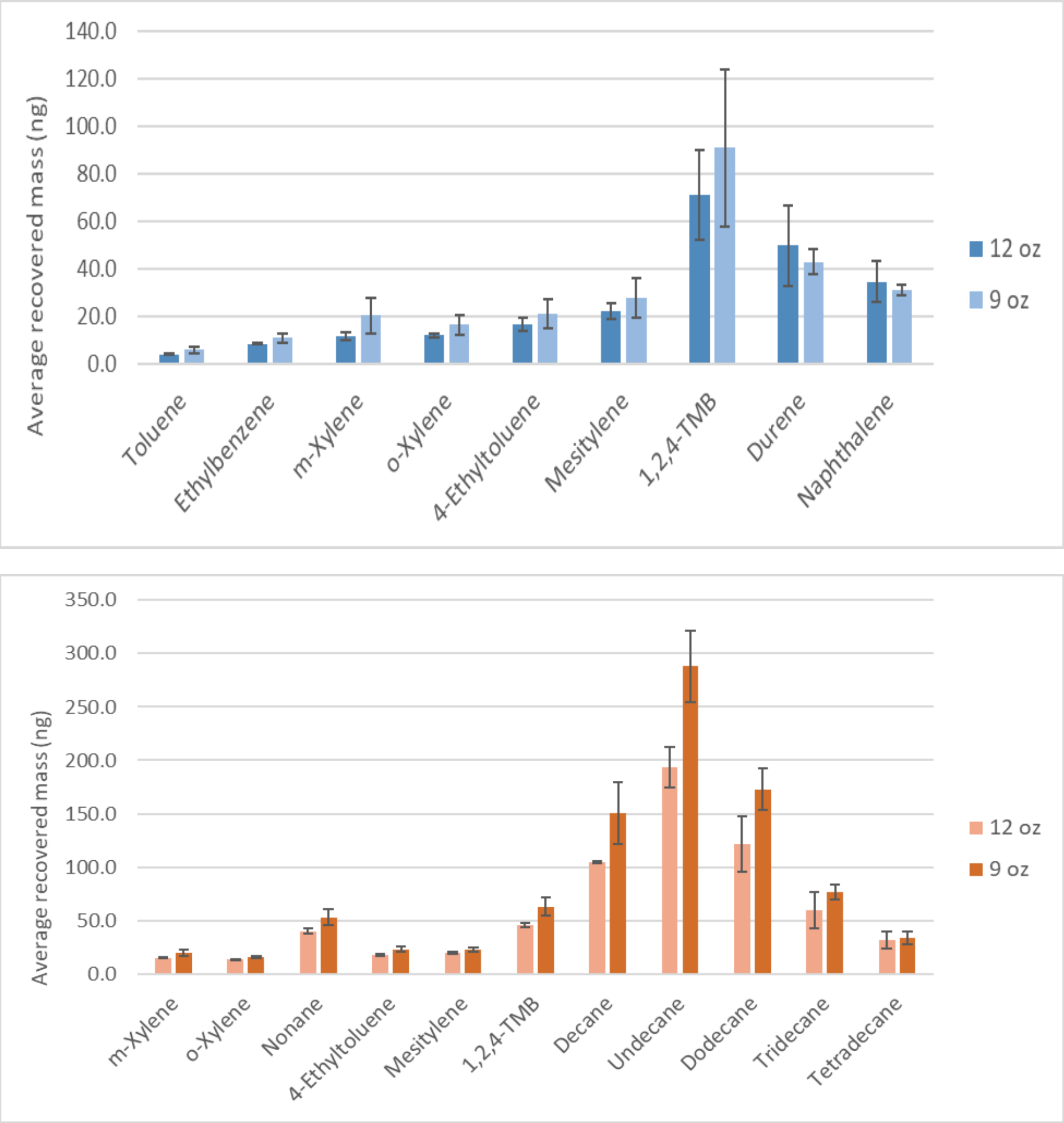


Figure 23a and 23b: Averaged extractions (n=3) of gasoline (top) and diesel (bottom) components using CMV/Cup protocol to determine the optimal cup volume

A single trend found in all the 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 two-minute equilibrium time was considered optimal as it produced less variation (%RSD) in the average recoveries of the aliphatic series (decane – tetradecane) found in diesel fuel. Variation at five minutes equilibrium time was 10 – 26% greater than at two minutes, while there was less than 10% difference for all eight detected gasoline compounds. A three-minute sampling time resulted in the greatest improvements to the diesel aliphatic series recoveries relative to a two-minute limit. On average, recoveries at two minutes were only 7.5 ng greater for gasoline. For the diesel components, semi-volatile recoveries were doubled at three minutes while volatile components were equal or up to 10 ng greater. Finally, cup volumes of 9 and 12 ounces were evaluated using the previously decided parameters (2-minute equilibrium & 3-minutes sampling). Figures 23a and 23b show the average recovered masses for components detected from each ignitable liquid. Recovery increases for the detected gasoline components ranged between 2 – 9 ng, with the greatest increase of 20 ng for 1,2,4-trimethylbenzene using the 9 oz cup. 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.

8.2.2 Software Assessment and Instrument Sensitivity

Two versions of the operating software are found on the instrument – termed as level 1 and level 2. The level 1 software is more inexperienced-operator friendly. The method wizard feature allows users to select a pre-set method based on several parameters such as the sample type, phase, and quantity. The analysis results are generated in real-time with the chromatogram and the mass spectrum on display. The level 2 software contains all the features of the level 1 software, in addition to method development options and greater data analysis capabilities. The entirety of the laboratory-based evaluation was carried out in the level 2 software.

One aspect of the instrument evaluation was to determine the extent of the software's qualitative and quantitative capabilities. For this purpose, a sub-library was created specifically for the analytical method, to which the 20 common target compounds were added. Of the 20 compounds, 18 were already included in the onboard GriffinLib chemical library. The missing two (4-ethyltoluene and 1,2,4,5-tetramethylbenzene) were manually added in with the inclusion of their CAS numbers, chemical formula, retention time, and major fragmentation peaks. Following the creation of the sub-library, calibration curves were built using the method software. A diluted series of a 20-mix standard solution was directly spiked onto CMVs in 1 µL volumes and then inserted into the GC inlet for thermal desorption. Spikes were done in triplicate for each calibration point, with a total of 7 points in a 5 – 300 ng μL^{-1} range. CMV blanks were used as the blank runs. For any analyte signals not called by the method, the targets were manually identified at their specific retention times and quantifier ion (found in Table 7) before they were added to the list of calibration files.

Compound	Retention time (Rt)	Quant ion	Portable LOD	External LOD
Heptane	1.41	57	2.0	74
Toluene	1.89	91	0.3	67
Octane	2.16	57	0.7	65
Ethylbenzene	2.89	91	0.7	70
m-Xylene	3.01	91	0.8	70
o-Xylene	3.34	91	1.4	69
Nonane	3.45	57	0.8	67
4-Ethyltoluene	4.49	105	0.2	87
Mesitylene	4.59	105	0.8	81
124-TMB	5.03	105	0.3	77
Decane	5.17	57	1.0	71
Undecane	6.94	57	1.0	73
1,2,4,5-TMB	7.17	119	1.7	84
Naphthalene	8.07	128	0.4	94
Dodecane	8.25	57	1.5	74
Tridecane	9.30	57	1.0	78
1-methylnaphthalene	9.44	142	0.4	98
Tetradecane	10.21	57	1.2	79
Pentadecane	11.06	57	1.8	84
Hexadecane	11.81	57	2.1	94

Table 7: Limits of Detection and Retention times (G510) for selected analytes

In addition to the curve generation, the level 2 software also calculates values for the correlation coefficient, the limit of detection, and the limit of quantitation. To verify all the instrument outputs and determine what calculation approach the instrument relies on, the curves and limit values were recalculated separately using spreadsheet software. Table 7 summarizes the limits of detection for the compound sub-library, determined using two different approaches. The portable LODs (generated by the method) is defined as 3.3 times the standard deviation of the blank over the slope of the regression. The external LODs (spreadsheet calculations) are defined as 3.3 times the standard deviation of the response of the curve over the slope of the regression. Curves were forced through zero in both the portable method and in the spreadsheet calculations. The sub-nanogram limits of detection calculated by the portable method are attributed to the extraction of the quantifier ions specified in the library, so greater sensitivity is achieved even when the signal is not visually higher than the baseline. The external LOD values are a better representation of the signal amount necessary for the method to reliably integrate a peak. Visually, all 20 compounds are distinguished from the baseline in the TIC at a concentration of 50 ng μL^{-1} despite the method not integrating the peaks during the runs. All 20 compounds exhibited good linear performance with R^2 values between 0.9803 and 0.9909.

8.2.2.1 Benchtop Sensitivity

Calibration curves were constructed on the benchtop in the same manner as the portable GC-MS. The limits of detection for these curves were defined as 3.3 times the standard deviation of the response of the curve over the slope of the regression. Linear performance for all analytes besides heptane was between R^2 0.9996 and 0.9934. Heptane could not be extracted from the tail-end of the solvent peak. Limits of detection for the aromatic analytes ranged between 10 – 30 ng μL^{-1} and between 22 – 41 ng μL^{-1} for the aliphatics.

8.2.3 Simulated Debris sampling with CMV/Cup Protocol

Simulated debris experiments were carried out using the CMV/Cup protocol outlined in Section 5.3.3. This protocol was applied to all sample replicates analyzed using the G510 and the benchtop GC-MS. Three different materials were utilized for this experiment: blue jean fabric, packaging plastics (bubble wrap), and cardboard. The bulk substrates were first cut into manageable sizes so that approximately 4.5 grams of material fit into a 150 mL porcelain crucible. The material was then ignited by direct contact with a propane torch flame for 15 seconds and allowed to burn and/or smolder for an additional minute and 45 seconds. Following the two-minute burn time, a metal lid was used to suffocate any existing flames for 30 seconds. All burned substrates were then set aside and left uncovered for three to four hours. This was done to simulate the sampling delay that would occur at a fire scene from the point the fire was put out to where investigators can begin processing. Debris sampling occurred in two stages. The first stage was a sampling of the substrate alone. The charred remnants were removed from the crucible and arranged in a pile on a glass platform. A new, unused cup was placed over the pile and the protocol was immediately carried out. The second sampling stage was of the spiked ignitable liquid solution in the presence of the debris. Spikes were in volumes of 1, 3, and 5 µL. A 2.4 cm fiberglass filter circle was added to the debris and placed at the base of the pile, partially covered by the material. A new cup was immediately placed over the pile and the protocol was carried out once more. The same set of CMVs was used for both sampling stages after a 15-minute condition period at 250 °C. The matrix blank chromatograms were assessed for any pyrolysis/combustion products produced that were the same as or would interfere with the quantitation of the analytical signals of interest. The integrated areas of these peaks were taken from the blanks and subtracted from the relevant signal in the related spiked sample.

Before sampling, a random selection of paper cups was analyzed using the same method to characterize any volatiles the inner coating may have contributed to the background. Benchtop profiles contained a series of small peaks in the C_9 – C_{14} range which was presumptively identified as aldehydes with S/N ratios below ten. Method blanks were also performed on the portable; however, the only visible peaks were siloxane fragments thought to be contributed by the CMV. Overall, volatile contribution by the paper cups did not significantly impact the extraction of ILRs during the course of experiments.

8.2.3.1 Dry Substrates

Matrix blank profiles from the benchtop GC-MS were used as a reference for profiles obtained on the G510. The majority of the portable chromatograms had less detail than the corresponding benchtop runs but still included several characteristic components. In a few instances, only an elevated baseline with two to three minor siloxane peaks was produced. In benchtop profiles, cardboard substrates produced several significant peaks presumptively identified as furaldehyde, 2-methoxyphenol, and other low-weight oxygenates. In the portable profiles, furaldehyde was consistently seen as the prominent peak with the other combustion products, including 2-methoxyphenol, at lower levels of intensity. The charred jean fabric produced several furan-containing prolyzates, phenols, and naphthalene. Furaldehyde was also the predominant peak in the portable jean fabric profiles. The plastic wrap profile displayed a pattern of medium-range cycloalkanes and alkenes on the benchtop (76), but this pattern was not reproduced on the portable instrument. The major ions for these background products were extracted from the matrix blanks to verify if they were present below the noise, but no discernible peaks were found. Given the lack of pyrolysis-generated analyte contribution from the G510 matrix samples, background subtraction from the spiked materials was not done before quantitation.

The combustion/pyrolysis products present in the blanks did not interfere with signals from the spiked debris samples. Even at the lowest spike level (1 µL), any signals present were attributed to gasoline. Extractions from all three materials resulted in six compounds that were consistently called by the method. These compounds include toluene, ethylbenzene, m-xylene, o-xylene, 4-ethyltoluene, and 1,2,4-trimethylbenzene. Mesitylene was undetectable until the 3 µL level, where it was consistently called for all materials with an average S/N of 11. Table 8 summarizes the average mass recovered and %RSD per compound and material. Overall, the lowest recoveries were from the cardboard matrix, followed by the plastic wrap and jean fabric. This trend is consistent at all three spike levels. Another trend across all levels is the low recoveries of ethylbenzene relative to the rest of the target analytes. This is likely due to a lack of resolution, as ethylbenzene coelutes as a shoulder peak with m-xylene. At lower concentrations, the deconvolution parameters tend to designate the entire peak as m-xylene, which necessitates reassignment of the targets and integrated areas in the level 2 software.

Compound	Cardboard		Plastic Wrap		Jean Fabric	
	Mass recovered (ng)	%RSD	Mass recovered (ng)	%RSD	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

Table 8: Mass recoveries (ng) and %RSD from simulated fire debris at the 1µL spike level using the Cup/CMV protocol and portable GC-MS

The precision of the measurements ranged between 16 – 47% at the 1 µL level, and slightly improved at 3 µL, ranging from 9 – 37%. Repeatability was best at the highest spike level, with %RSD values between 2 – 20%. In its current form, the cup apparatus lacks a seal at the base which allows for some amount of ambient air dilution during the extraction process. Additionally, some analyte vapor has a chance to escape, disrupting equilibrium concentrations. This was accounted for as best as possible by placing something heavy on top of the cup or pressing down by hand to better insulate the headspace during equilibration and sampling.

Compound	Cardboard		Plastic Wrap		Jean Fabric	
	Mass recovered (ng)	%RSD	Mass recovered (ng)	%RSD	Mass recovered (ng)	%RSD
Toluene	28±4	15	23±3	12	29±2	6
Octane	6±1	10	5±1	17	6±1	9
Ethylbenzene	12±1	8	10±1	13	13±1	10
m-Xylene	30±2	7	26±3	12	32±3	9
o-Xylene	13±1	9	10±1	12	13±1	10
Nonane	2±0.1	6	2±0.1	7	2±0.1	6
4-Ethyltoluene	10±2	22	6±1	15	9±1	9
Mesitylene	9±1	16	6±1	17	7±1	9
1,2,4 - TMB	22±4	17	15±3	20	16±2	10
1,2,4,5-TMB	2±0.4	23	1±1	38	1±0.1	13
Naphthalene	3±1	30	2±1	36	2±2	90

Table 9: Mass recoveries (ng) and %RSD from simulated fire debris at the 1µL spike level using the Cup/CMV protocol and benchtop GC-MS

Replicate experiments on the benchtop demonstrated overall higher mass recoveries and extraction of a greater range of analytes relative to the G510 (Table 9). The additional compounds detected with the benchtop analysis include octane, nonane, 1,2,4,5-TMB, & naphthalene. Figure 24 shows the chromatogram obtained for the jean fabric sampling at the 1 µL spike volume. Here, the characteristic gasoline pattern can be discerned in the TIC even in the presence of matrix background (middle row), and clearly extracted by the SIM for easier characterization (bottom row). 1-methylnaphthalene was also detected at the 1 µL level but the signal was too low to be accurately quantitated. The variation between recovered mass from each material was smaller than that of portable recoveries (between 1 – 3 ng), which is also reflected in the narrower %RSD ranges. The larger difference in portable recoveries and higher %RSD suggests that in addition to the cup sampling limitation, the software's integration capabilities are impacted at lower concentrations and by the instrument's high chromatogram baseline.

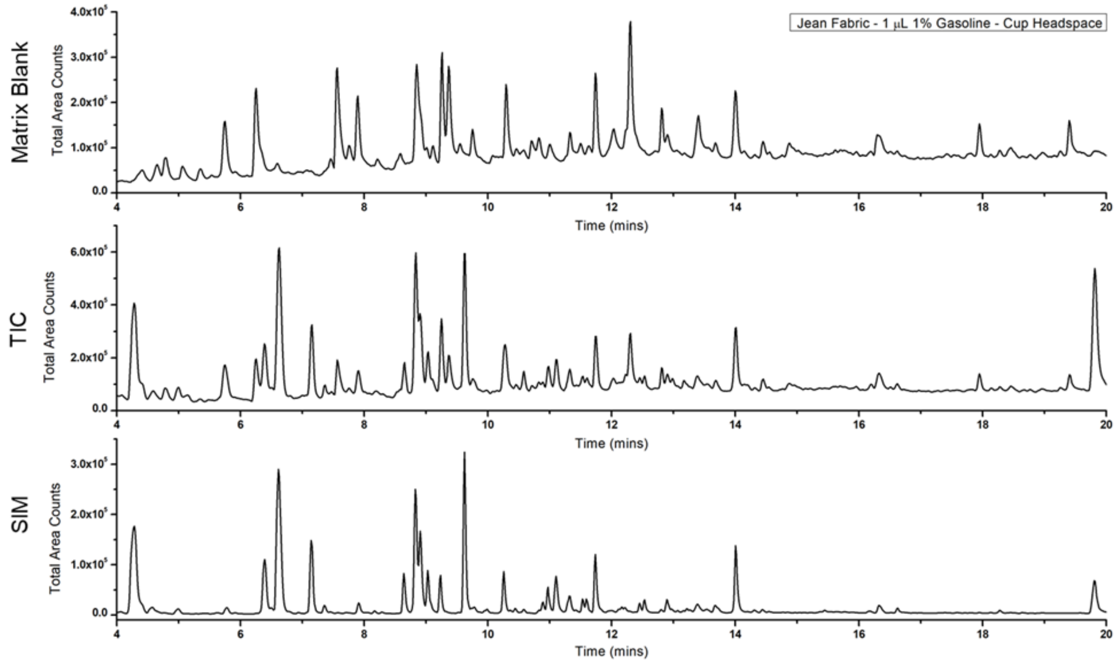


Figure 24: Chromatogram stack of a CMV/Cup sampling 1 µL of 1% gasoline solution from charred jean fabric (dry) on the benchtop GC-MS

8.2.3.2 Wet Substrates

Consideration was also given to the effect of moisture on ILR recoveries from debris. In many cases, the evidence collected from fire scenes is still wet from fire-fighting measures taken to combat the blaze. Drying out the material before packaging is avoided to prevent weathering of any potential residues. The presence of moisture, however, can reduce the extraction efficiency of mediums such as PDMS-based adsorption phases. High humidity within the headspace can lead to competitive adsorption of water molecules, reducing the availability of active sites for analytes (77,78). A recovery experiment using the CMV – a PDMS-based adsorption device – was performed using wet and dry simulated debris. The simulated debris material used was jean fabric. The dry replicates were prepared following the experimental design in section 8.2.3 and sampled using the protocol in section 5.3.3 For the wet debris, any existing flame after the two-minute burn time was extinguished using tap water delivered from a squeeze bottle. Enough water was dispensed to douse the flames and to completely saturate the fabric. The saturated debris was left to sit out uncovered at ambient temperature for the same amount of time as the dry replicates. In the second sampling stage, the fiberglass filter was allowed to touch the debris, becoming saturated prior to spiking.

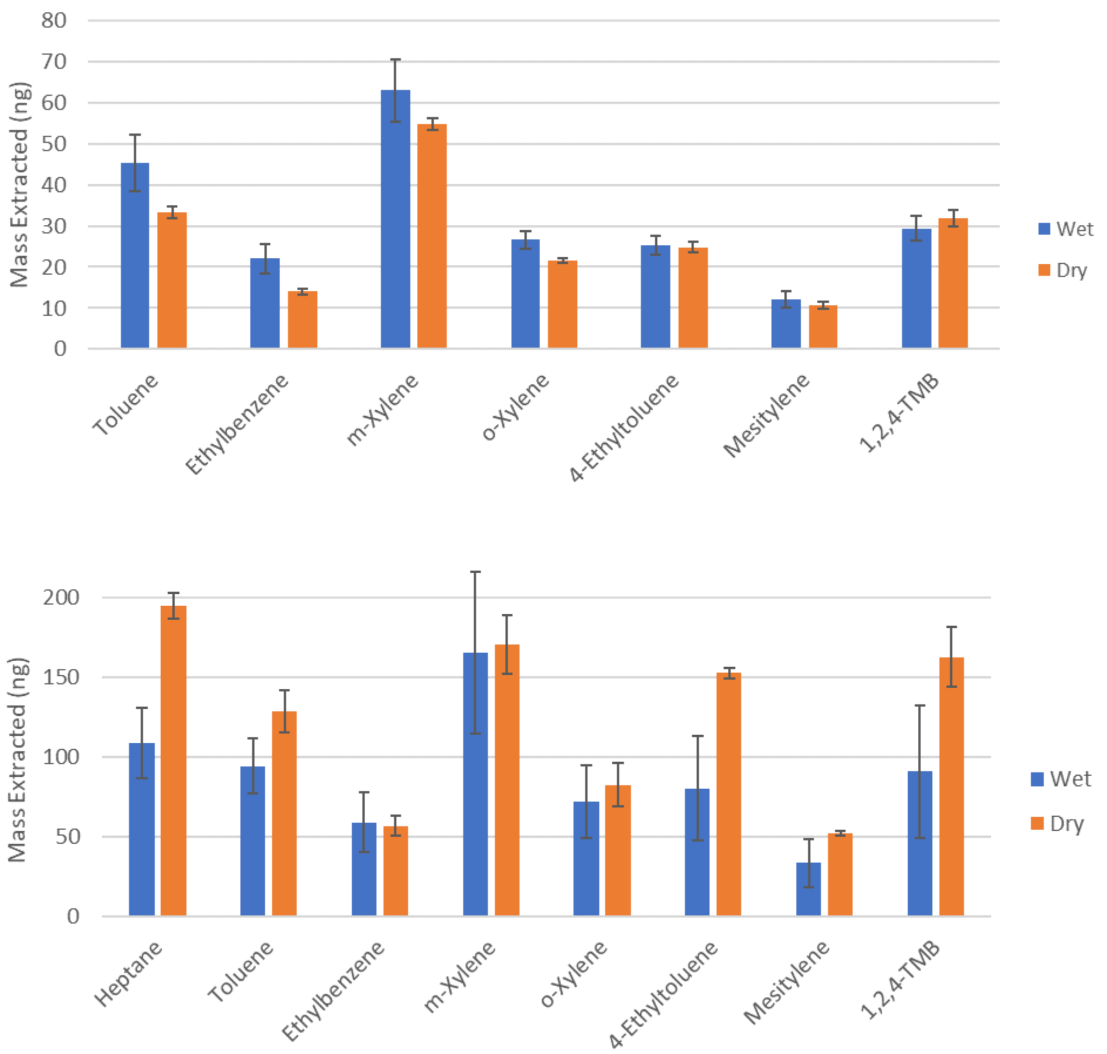


Figure 25: Average (n=3) extracted masses of ILR analytes from 1 µL (a, top) and 3 µL (b, bottom) spikes of 1% gasoline. Analytes sampled from wet and dry charred jean fabric using the CMV/Cup protocol and analyzed on the G510

The presence of moisture in the cup chamber did appear to inhibit recoveries from the spiked debris. At the lowest spike volume, average mass recoveries were greater from the wet samples, but the mass uncertainty and %RSD was also greater relative to the dry samples. For toluene, extractions from the wet debris averaged 45±7 ng, while from dry debris averaged 33±1 ng. The %RSDs were 15 and 7%, respectively.

m-Xylene also had a large uncertainty margin, where 63±8 ng was extracted from wet versus 55±1 ng from dry. Overall, precision between 8 – 17% and 4 – 15% was determined for the wet and dry jean fabric replicates (Figure 25a). The difference in recoveries grew larger at the higher spike volumes. At 3 µL, percent differences in average mass extractions from the dry material were as much as 62% greater. Mass uncertainty also significantly increased for the wet samples. For m-Xylene, dry extraction averaged 171±18 ng, compared to 165±51 ng from wet. Uncertainty and precision at the 3 µL spike volume ranged from 15-51 ng (18-46%) and 2-19 ng (7-29%) for wet and dry replicates, respectively (Figure 25b). The dry recoveries calculated from the 5 µL volume were outside the linear working range and thus were not considered here.

8.2.3.3 Recoveries relative to ASTM Detection Limits

The detection limits of activated charcoal strips and SPME fibers from their respective ASTM methods (ASTM E1412-19 and ASTM E2154-15a) are stated as at least 0.1 µL of neat gasoline from a sample. This detection limit was used as a benchmark to evaluate the extraction capabilities of the CMV. Triplicate measurements of a 0.1 µL gasoline spike (Marathon brand) were taken using the CMV/Cup protocol and analyzed on the G510 and Agilent benchtop. Mass recoveries were based on the individual system calibration curves for all detected gasoline compound targets. These recovered amounts were used as absolute amounts relative to what was extracted from the dry and wet substrate experiments (Sections 8.2.3.1 and 8.2.3.2). The lowest spike volume

(1 µL of a 1% solution) is equivalent to a 0.01 µL amount of neat gasoline (Figure 26). Tables 10 and 11 summarize the average percent recoveries of the targets detected on both instruments from all three debris materials. Interestingly, percent differences only range between 1 – 5 % at the higher spike levels on the G510 and at a greater range of 6 – 20% on the benchtop. This suggests that the ratio of targets within a sample is proportionally extracted, even at trace concentrations. Relative percent recoveries from the wet/dry jean fabric experiment exhibited the same trend. This suggests that while the presence of moisture inhibited overall recoveries, it did not preferentially inhibit certain analytes.

Compound	**Solution spike volume**		
	1 µL	**3 µL**	**5 µL**
Toluene	2	7	13
Ethylbenzene	2	6	14
m-Xylene	2	8	18
o-Xylene	2	7	15
4-Ethyltoluene	2	6	15
Mesitylene	-	6	13
1,2,4 - TMB	2	6	16

Table 10: Average recovery (as % recovery) of gasoline ILRs from simulated fire debris relative to 0.1 µL of neat gasoline - portable analysis

Compound	Solution spike volume		
	1 µL	3 µL	5 µL
Toluene	14	43	74
Octane	16	50	89
Ethylbenzene	14	52	81
m-Xylene	14	53	80
o-Xylene	13	52	79
Nonane	14	53	90
4-Ethyltoluene	19	63	93
Mesitylene	16	60	93
1,2,4 - TMB	15	60	95
1,2,4,5-TMB	14	49	85
Naphthalene	13	42	66

Table 11: Average recovery (as % recovery) of gasoline ILRs from simulated fire debris relative to 0.1 µL of neat gasoline – benchtop analysis

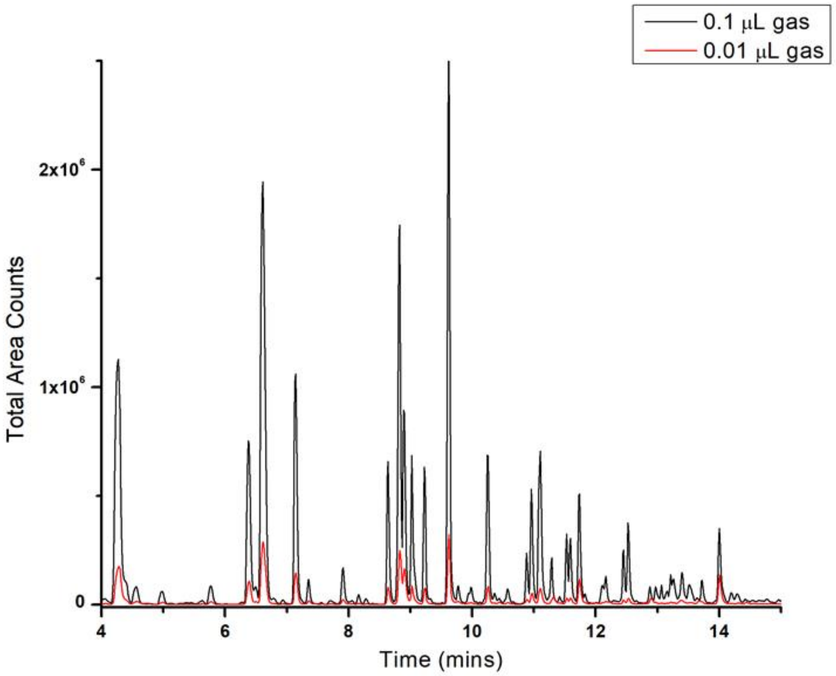


Figure 26: Chromatographic overlay of 0.01 (red) and 0.1 (black) µL of neat gasoline, sampled using CMV/Cup protocol, analyzed on benchtop GC-MS (SIM mode)

8.2.4 Heated Air Sampling Probe Performance Evaluation

The G510 portable unit is equipped with an air sampling wand that can be operated in two modes: survey and air confirm. In survey mode, the sampled vapor bypasses the GC column and goes through to the mass spectrometer via membrane introduction (MIMS). In air confirm mode the sampled vapors are first preconcentrated on the internal adsorbent trap (the dual-bed), then desorbed onto the column for separation and analysis (79,80). For this study, preliminary evaluations were conducted using the sampling wand in air confirm mode.

To compare the wand's performance to the CMV, several method parameters were kept consistent with the established CMV/Cup protocol. The oven program and fire debris sub-library were copied for use with the air wand. The only parameters that changed were related to the wand's operation. To match the inlet temperature used with the CMV, the desorption temperature for the trap was set at 250 °C. Headspace sampling was carried out using the 9 oz paper cup, and the equilibrium time was kept at two minutes. The extraction time (indicated as trap time in the method) was evaluated at two levels: one minute for 'fast' extraction and then at three minutes to match the optimized time for the CMV. A 1 µL spike of a 1% '20-mix' standard solution was sampled in triplicate by the wand at both time intervals and by the CMV. Figure 27 demonstrates the suite of compounds extracted by both devices as a function of the quant ion intensities. A longer sampling time of three minutes was beneficial for higher recoveries of all 13 compounds extracted by the air wand, with percent increases ranging from 33 – 99%. The greatest improvements in recovery (60 – 99%) were seen with the n-alkane series. Extractions with the CMV/Cup protocol exceeded the capacity of the wand at both time intervals apart from the first two compounds of the series. Recoveries of octane through nonane saw smaller increases within a 9 – 30% range relative to the wand sampling at three minutes, while the remaining compounds saw larger recoveries between 58 – 158%. The diminished extractions of heptane and toluene are thought to be the result of breakthrough or displacement on the adsorption phase by the larger analytes. Additionally, the CMV extracted a total of 17 compounds from the 20-mix standard solution. This includes the 13 extracted by the wand in addition to naphthalene, dodecane, tridecane, and 1-methylnaphthalene. The remaining three compounds in the standard mix (tetradecane, pentadecane, & hexadecane) were not detected in any replicate measurement.

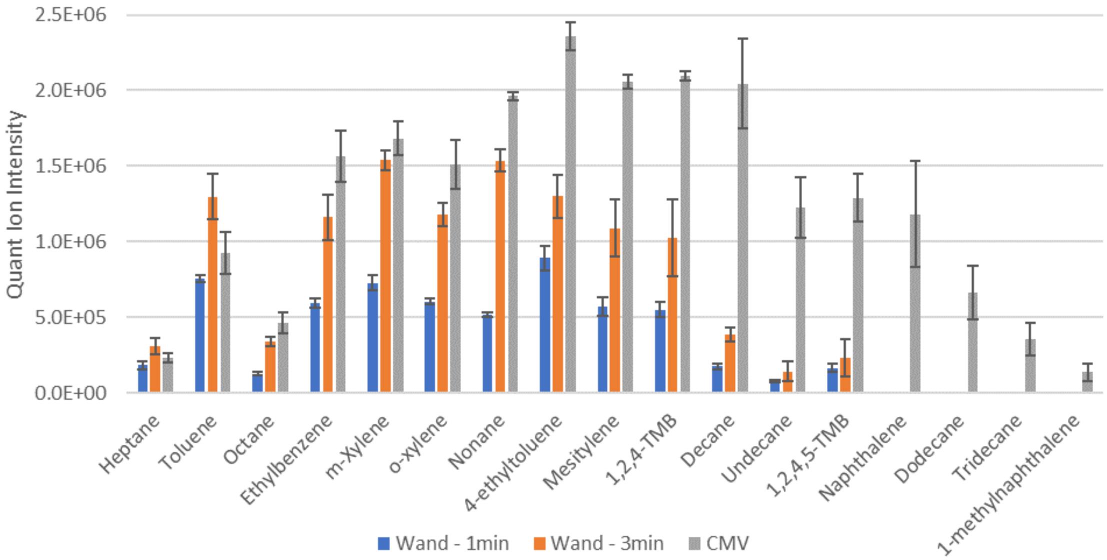


Figure 27: Average (n = 3) quant ion intensities for analytes recovered from 1 µL spikes of 1% 20-mix, pairing the cup protocol with the CMV and the air wand

Air wand comparisons were also conducted on a set of simulated debris. Jean fabric was used in this evaluation and prepared in triplicate according to the experimental design in section 8.2.3. The wand and method parameters were kept consistent from the previous experiment; the optimal trap time of three minutes was incorporated for these measurements. Table 12 demonstrates the average relative recovery ratios of the wand to the CMV. As seen with the trap time evaluation, the CMV recoveries exceeded those of the wand for all monitored gasoline analytes at all spike volumes. Toluene was most abundant at all levels, followed by m-Xylene. Trap capacity is thought to be the wand's greatest limiting factor. While it is sensitive enough to extract a suite of components from as little as 0.03 µL of gasoline, the average recovery is only around 30% as effective as the CMV (Figure 28). At samplings of 0.05 µL of gasoline, this average drops to 15%.

	Solution spike volume		
Compound	**1 µL**	**3 µL**	**5 µL**
Toluene	0.70	0.67	0.36
Ethylbenzene	-	0.27	0.11
m-Xylene	0.18	0.37	0.16
o-Xylene	-	0.27	0.13
4-ethyltoluene	-	0.11	0.09
Mesitylene	-	0.14	0.11
1,2,4-TMB	-	0.12	0.09

Table 12: Average recovery (as ratios of wand to CMV) for replicate samplings of 1% gasoline at varied volumes using Cup headspace sampling

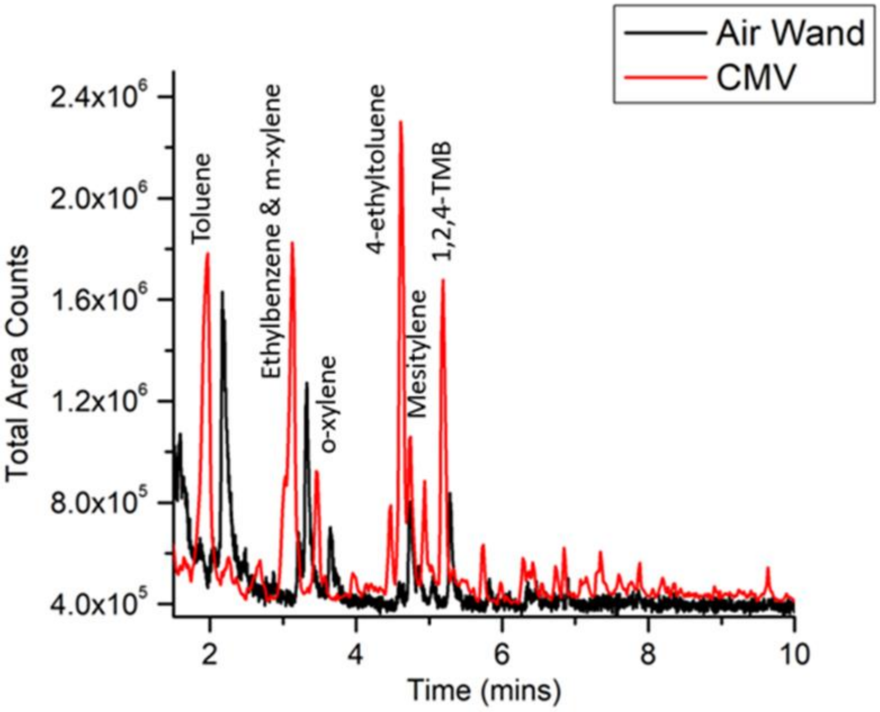


Figure 28: Chromatographic overlay of a 3 µL spike sampling of a 1% gasoline dilution with the air wand (black) and CMV (red) using the cup protocol

9. FIELD TESTING

The optimized cup protocol and a 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 where several small-scale burns were 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 before 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.

Figure 29: Photographs of the farmhouse exterior (top), back room post-burn (middle), and front room mattress, post-burn (bottom)

Random samplings of both mattresses produced high variation in the intensities of detected compounds. In all samples taken from the first (back) room's mattress, background interference was minimal concerning the number of compounds present. 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 (Figure 30). Nine gasoline markers were detected in similar amounts from both areas, with peak intensities reaching between 0.6 – 1.3 M counts. The nine compounds are the same nine consistently detected in the protocol optimization experiments (Section 8.2.1). In contrast, headspace sampling of the mattress in the second (front) room produced significantly overloaded chromatographic profiles. Recoveries were heavily skewed in favor of the lightest aromatics (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 (16), up to and including 1- and 2-methylnaphthalene. The time window of substrate exposure to ambient conditions post-fire extinction is thought to be the cause of the detection sensitivity variability. In the instance of the back room's mattress, the gasoline deposition, room ignition, and extinction happened within a twenty-minute window in the early afternoon the day prior. At the time of sampling, the window of substrate exposure to ambient conditions was approximately 18 hours. In contrast, the front room mattress only had an approximately 30-minute exposure window before the sampling/extraction. Not enough time had passed for the residues to weather down to a concentration amenable to the sampling capacity of the CMV, leading to overloading.

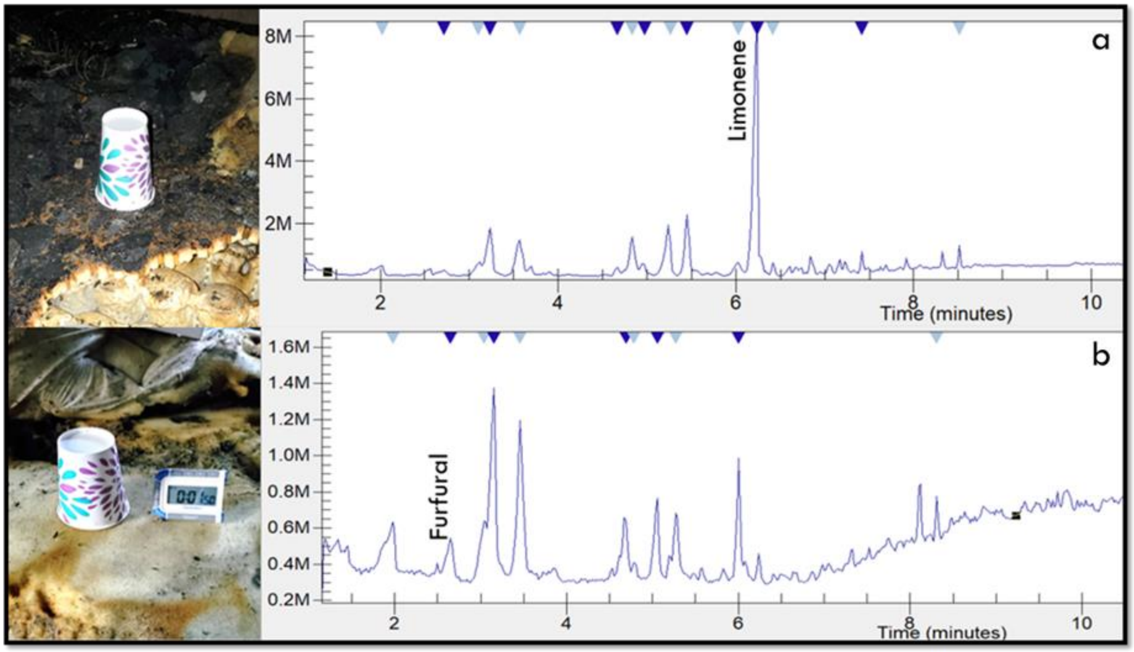


Figure 30: G510 Chromatograms from (a) charred mattress top and (b) exposed mattress foam from the first (back) room mattress

The sampling protocol for known volume spikes in both rooms incorporated a 5-minute delay before the 2-minute 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 31a and 31b). All analytes of interest were identified based on their retention times and mass spectra.

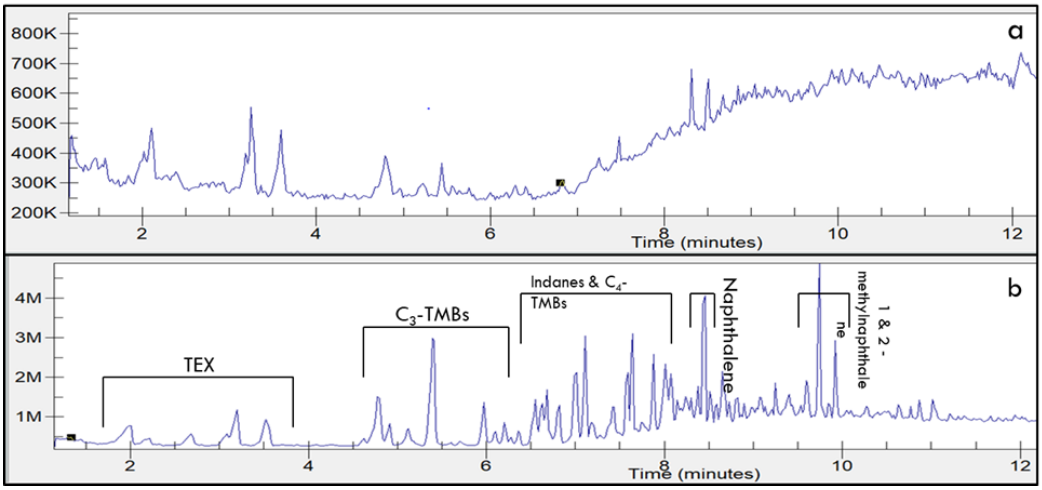


Figure 31: G510 chromatograms of (a) front room carpet blank and (b) 10 µL spike of 87-grade gasoline onto front room carpet with labeled analytes of interest

The G510 used in all laboratory experiments was down for maintenance, thus a different unit was sent by the company to use at the burn site. Calibration standards could not be run due to the limited timeframe, so only qualitative data was gathered. Movement around both rooms at the fire scene was not hampered by transporting the unit or the sampling kit around. The GC-MS itself is light enough to be hand-carried by a single person without difficulty. It is also compact enough to keep alongside the analyst within a small scene without getting in the way. Unfortunately, its operational time on battery power was limited. Within two hours of continuous use, both batteries had drained down to 20%. The unit had to be relocated outside the structure and connected to an external power supply, where it stayed for the remainder of the day. Despite the relocation, instrument up-time went uninterrupted. A single 13 L helium cartridge was more than sufficient for a full day of operation.

10. CONCLUSIONS AND FUTURE DIRECTIONS

10.1 Conclusions

The improvements and successful application of the Capillary Microextractor of Volatiles (CMV) device to the analysis of ignitable liquid residues have been demonstrated.

10.1.1 CMV Modifications

The original PDMS phase was modified to improve upon the affinity for aromatic compounds. Substitution of the trimethoxysilane precursor within the sol-gel resulted in a new, phenyl-incorporated absorption phase which demonstrated up to 8-fold higher recoveries of aromatic, BTEX compounds. Improvements in phase retention over the original methyl-phase were also demonstrated through generated open-air vapor-source experiments. The phenyl-modified phase consistently had higher retention of all BTEX compounds over the methyl phase at different airflow rates and mass loadings. A hybrid CMV device was assembled using a combination of the two validated phases for improved retention of broad ranges of compounds at once.

The precursor-substitution approach was applied to the development of four additional phases, to make the CMV device customizable for more sampling applications. Two of the four sol-gel sorbents were carried through the PSPME coating stage and assembled into CMV devices. Direct standard spiking evaluations of the devices showed adequate desorption, suggesting the phases were functional. The other two phases remain in the synthesis stage, as incompatibility with other components in the original formulation prevented full gelation. Nevertheless, the assortment of phases and the potential to further modify the sol-gel chemistry are major advantages to CMV usage.

10.1.2 Fire Debris Applications and Technique Comparisons

A laboratory sampling protocol for fire debris was adapted for use with the CMV. The sampling parameters and choice of apparatus were optimized based on recommendations from several ASTM standard sampling practices. A 20-minute sampling protocol from a 1 L metal paint can was developed using a moderately low flow rate (0.2 L min^{-1}), capable of detecting a suite of 10 compounds with a broad range of volatilities (toluene – eicosane).

The laboratory protocol was utilized in the comparison experiments to activated charcoal strips and solid-phase microextraction. In accordance with their own ASTM practices, different classes of ignitable liquids were analyzed by each technique. Signal intensities obtained by the CMV from four different ignitable liquid classes were slightly higher than those of SPME and at least one to two orders of magnitude higher compared to charcoal strips. The CMV also had greater responses to highly volatile gasoline components, performing up to 23x and 1000x better than SPME and ACS, respectively. Finally, the overall sampling time was fastest with CMV, at twenty minutes.

10.1.3 Portable GC-MS Evaluations

The last aim of this project was geared towards the on-scene analysis aspect of fire investigation. This involved the dual evaluation of the CMV and portable GC-MS units for their utility in ignitable liquid detection. In this work, the TRIDION-9 and Griffin G510 units went through a laboratory-based evaluation with the CMV as the coupled extraction technique.

The versatility of the CMV allowed for successful coupling to the TRIDION-9 (T9) by incorporating the SPS-3 accessory. The use of the needle trap holder facilitated analyte transfer between the devices, enabling fast analysis (~3 mins) within 5 minutes of sampling with the CMV. The secondary transfer to the needle trap did not affect the final chromatographic profile, suggesting that affinity bias is not a disadvantage to this technique. The analytical performance of the T9 was also compared to a traditional benchtop GC-MS using CMV as the extraction technique. Both coupled techniques retained many key components of ignitable liquid formulations with sub-nanogram levels of detection. The CMV was also shown to be a fast (~ 5 min. sampling) and sensitive fieldable device through the open-air system followed by the 3-minute method on the T9.

The TRIDION-9 suffered from some significant limitations. Most notable was the 5-meter column. The entire analytical method benefited from a rapid 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 chemistry background would be at a disadvantage if they only had the reports generated by the software to rely on.

The Griffin G510 portable GC-MS was the second unit evaluated. Additionally, the use of a paper cup to facilitate in-field headspace sampling was adapted to the CMV. Fast results were achieved with an overall 21-minute analytical method, including a five-minute ambient temperature extraction and a 16-minute chromatographic method. Consistent detection and quantitation of six characteristic gasoline components on the portable GC-MS and up to 11 gasoline components on the benchtop GC-MS were possible using the CMV/Cup protocol. The analyses of the extracts were not significantly impacted by interferents associated with VOC contributions from the cup apparatus or the combustion/pyrolysis products from any of the charred debris materials investigated. The CMV also maintained high sensitivity; ILR recoveries of gasoline were possible from up to 10x less than the minimum detectable amount as per ASTM E1618-19 criteria for the ACS extraction technique, for example. Ambient temperature recoveries from debris at all spike volumes indicate that ILR components are equally extracted by the CMV/Cup protocol, mitigating issues of displacement/adsorption discrimination. The presence of moisture from water-logged debris did inhibit recoveries by as much as 62% relative to dry debris, but detection sensitivity was still well below the ASTM E1618-19 criteria (0.1 µL of neat gasoline), even at the lowest spike volume. Finally, the CMV was shown to have a greater extraction capacity than the G510's heated air sampling wand. Sampling conducted with the cup protocol resulted in a larger suite of detectable compounds from a standardized solution and was up to 70% more efficient at ILR extraction from simulated debris.

Lastly, the G510 and cup field protocol underwent a preliminary evaluation during a large-scale supervised structural burn. Highlights of that exercise include the demonstrated utility of the instrumentation and the extraction technique for successful gasoline residue screening on-scene. Several key gasoline components were presumptively identified from pre- and post-burn sample depositions, using mass spectral data and chromatogram profile matching. The fast-sampling protocol also made for high throughput analysis, as extractions could be done in quick succession and stored for a short duration. Logistically, the GC-MS and CMV sampling kit were easy to transport around the scene. It took up minimal space and was often left stationary while sampling occurred elsewhere.

The study also highlighted some shortcomings in the transition from laboratory to field. The upper limits of residue concentrations were not fully accounted for in the optimization of the protocol, leading to abrupt method changes to protect the equipment. The period between fire extinction and extraction is an important factor to consider, given the immense retention capacity of the CMV. Instrument up-time may also be limited if there is no available power source to supplement the battery power. Limitations of the cup protocol in its current form are its lack of an airtight seal around the base, allowing for disruption of equilibrium concentrations.

10.2 Future Directions

Several expansions are suggested for this body of work. The sol-gel modification work can be continued, starting with the four formulations experimented with here. The two prototype phases require further refinement and validation studies before they can be incorporated into devices for long-term use. The remaining formulations require greater changes to the reaction chemistry to result in proper gelation. There is also room to incorporate other functionalized precursors not considered in this study. Any successfully validated phase can be combined with several others in the CMV capillary for further customization, as seen herein with the methyl- and phenyl- sorbents.

Future work regarding the use of the CMV/NTD technique with the TRIDION-9 could aim to improve upon the SPS-3 desorption method to limit overloaded chromatograms and improve pattern recognition and instrumental sensitivity. Method parameters were kept at the manufacturer’s recommendations; future work should consider optimization of the maximum heating temperature, total desorption time, and helium flow rate. Other ignitable liquid formulations can also be examined using the combined technique.

Work to improve upon the limitations of the cup protocol could include the development of a field-amenable heating accessory, theoretically increasing the detectable range and recovery of many ignitable liquid residues. Further field-based work should be done on the protocol and the analytical method to account for more realistic residue amounts from a variety of substrates. The laboratory evaluation of the

G510 should also be expanded to other ignitable liquid classes to potentially build a comparison library of chromatogram profiles.

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PUBLICATIONS AND PRESENTATIONS

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