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TECHNICAL NOTE

Modifications to Capillary Microextraction of Volatiles (CMV) for the Extraction of Ignitable Liquid Residues (ILRs)

Introduction

Investigating suspected arson crimes can be challenging for forensic analysts and investigators. Fire can render much of any existing physical evidence unusable, obscuring signs that may point to the cause as accidental or otherwise. Most deliberately set fires are started with some type of ignitable liquid, such as gasoline, diesel fuel, lighter fluid, or commercial solvent. Analysts look for trace amounts of such fluids in fire debris from a suspected crime scene and, if present, try to characterize it. Flammable liquids are products refined from crude oil, resulting in chemically similar compounds, which can be used to point to a criminal act, namely arson. However, other chemicals, such as paraffins, naphthenes, aromatics, and certain oxygenated compounds, are commonly added in varying fractions depending on the individual material's intended use [1].

In order to analyze and identify compounds found at a crime scene, they must be isolated from the debris and other chemicals, a process called "extraction." Several types of extraction methods exist for analyzing ignitable liquid residues (ILRs) from fire debris. Solid-phase microextraction (SPME) and activated charcoal strips (ACS) are currently the preferred choices in forensic laboratories;

however, each technique has notable drawbacks, such as SPME's limited surface area. Sampling with a charcoal strip can take between 2 to 16 hours, followed by desorption using an organic solvent – typically very toxic carbon disulfide, as it performs the best. This report summarizes the development and implementation of a novel sampling device (capillary microextraction of volatiles [CMV]) invented in the Almirall research group at Florida International University [2] for ILR extraction as an alternative to current techniques. The versatility of the CMV device has the potential for field sampling applications when coupled with portable analytical systems, and it has been successful in the following studies: sampling volatile compounds generated by explosives [3], detecting marijuana plants [4], detecting volatile organic compounds (VOCs) released from amphetamines [5], analyzing breath samples [6], sampling organic gunshot residue (OGSR) VOCs [7, 8], and sampling BTEX (benzene, toluene, ethylbenzene, and the three xylene isomers) compounds in environmental studies [9]. This report is intended for forensic practitioners who want to better understand newly developed technologies and their use and application to forensic casework.

Extraction of ILRs

ILRs are trace amounts of unburned flammable liquids that could be used to start a fire. They are commonly left behind in debris at the scene of a fire and must be extracted from the debris to confirm their presence and determine their identity.

Most compounds that make up ILRs are considered volatile or semi-volatile. Their high vapor pressures allow them to readily vaporize in ambient conditions and, if confined in an enclosed space, collect in the headspace (the upper area, above the liquid) of a sampling container. It also makes these VOCs ideal for collection via the headspace sampling using passive or active extraction techniques. Most forensic laboratories conducting suspected arson investigations use passive techniques, which involve adsorption of the compounds onto ACS or a SPME fiber. Active sampling techniques, such as purge-and-trap systems, are more sensitive but less common due to the specialized equipment they require [10].

CMV

The CMV is a small, inexpensive headspace-sampling device developed in the Almirall research group as a result of National Institute of Justice (NIJ) support (2006-DN-BX-K027) to improve the detection of explosives residues. The design consists of a glass capillary tube, 2 centimeters (cm) long by 2 millimeters (mm) wide, that is open at both ends. The tube is designed to fit inside the injection port of a gas chromatograph (GC) that is filled with seven sorbent-coated glass filter strips stacked atop each other. The sorbent is vinyl-terminated polydimethylsiloxane (vt-PDMS) that has been physically incorporated into a polymer lattice using sol-gel synthesis. The CMV acts as an active headspace sampling device; connection to a vacuum pump allows for continuous airflow through the tube and subsequent adsorption of compounds. Analyte desorption occurs via a thermal separation probe after placing the CMV directly into a GC's injection port. Previous applications have reported enhanced sensitivity and extraction capabilities for multiple classes of volatile and semi-volatile organic compounds when using CMV compared to more traditional sampling techniques like SPME [3].

This technical note presents findings from the evaluation of modified existing vt-PDMS sorbent chemistries that were developed to improve CMV extraction capabilities without the need for temperature manipulation at collection (e.g., cryofocusing). Phenyl groups were incorporated into the sol-gel backbone to increase the affinity between the sorbent phase and volatile aromatic compounds. Evaluation of the new phenyl-modified sorbent phase (CMV A) was done through comparison to original methyl-based phase (CMV B) while performing simulated open-air sampling. Compounds from the aromatic group of compounds known as BTEX—which are highly prevalent in gasoline—were used for the evaluation [9]. Additionally, the two sorbent types were used in conjunction to optimize sampling of ILRs from an enclosed system for this evaluation effort.

Additional extraction improvements were evaluated via incorporation of the two sorbent phases into a single CMV device. A 50-50 combination of phenyl- and methyl-sorbent strips was evaluated against devices containing strips of a singular phase for the sampling of ILR compounds. Finally, work has progressed into developing other modified phases for combined use in the CMV, akin to multiphase SPME fibers for comprehensive extractions.

Instrumentation

An Agilent Technologies 7890A GC coupled to a 5975C inert mass spectrometer with triple-axis detector was utilized for all evaluations. The GC was equipped with an Agilent Technologies Thermal Separation Probe for the direct insertion of a CMV into the inlet for thermal desorption. A DB-5ms Ultra Inert (30 m x 0.25 mm x 0.25 µm) was used as the analytical column. The inlet temperature was set to 250°C, 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 liters (L)/minute.

Evaluation of BTEX recoveries: The oven was programmed with the following temperature profile: 35°C with a 1-minute hold, ramp up to 120°C at 15°C/minute, and then to 280°C at 50°C/minute with a 2-minute hold (total run time 11.90 minutes).

Open-air system (vapor source): The injector port of a Varian (Palo Alto, California) CP 3800 GC was used to generate analyte vapor of known concentration. The source parameters were reported previously[9].

Analysis of ILRs by CMV extraction: The oven was programmed with the following temperature profile: 35°C with a 2-minute hold, ramp up to 200°C at 7°C/minute, and then to 275°C at 15°C/minute (total run time of 30.57 minutes).

Open-Air System Extraction

To achieve a quantitative measure of each phase's trapping efficiency, known amounts of BTEX vapors were actively sampled using the simulated open-air system. Three sets of evaluations were conducted to assess the effects of concentration and sample volume on analyte retention. **Figure 1** shows the average recoveries (n = 3), as percent recovery observed when using CMV A and CMV B from sampling 100 nanograms (ng) of BTEX at a flow rate of 0.2 L/minute. The other two experimental designs involved sampling 1,000 ng of BTEX at the optimized rate of 0.2 L/minute and at a vigorous rate of 0.5 L/minute. All three evaluations showed that the phenyl-modified phase had a much greater affinity and fewer instances of breakthrough (the loss of originally retained analyte) for all BTEX compounds.

As shown in **Figure 1**, the average percent recovery when using CMV A for the less volatile compounds (ethylbenzene and the xylene isomers) ranged between 29% and 72%. For toluene recovery ranged between 7% and 50%, and for benzene it was between 3% and 22%. Breakthrough was more apparent at the larger air volumes for both phases, but its effects were more significant for CMV B. Using CMV B, complete loss of benzene occurred after 1 L air volume and then loss of toluene and ethylbenzene at 4 L. The maximum percent recovery by CMV B for any one BTEX compound did not exceed 58%. The precision of each evaluation was determined by the reported percent relative standard deviation (%RSD). The less volatile compounds were considered separately from benzene and toluene; the precision for both CMVs were found as 0.3%–16% and the lighter compounds were 3%–44%. The larger %RSD values were seen with CMV B at the higher mass loadings and increased air volume. In comparison, typical recoveries when using static headspace sampling with SPME is expected to be 2%–5% for most BTEX compounds.

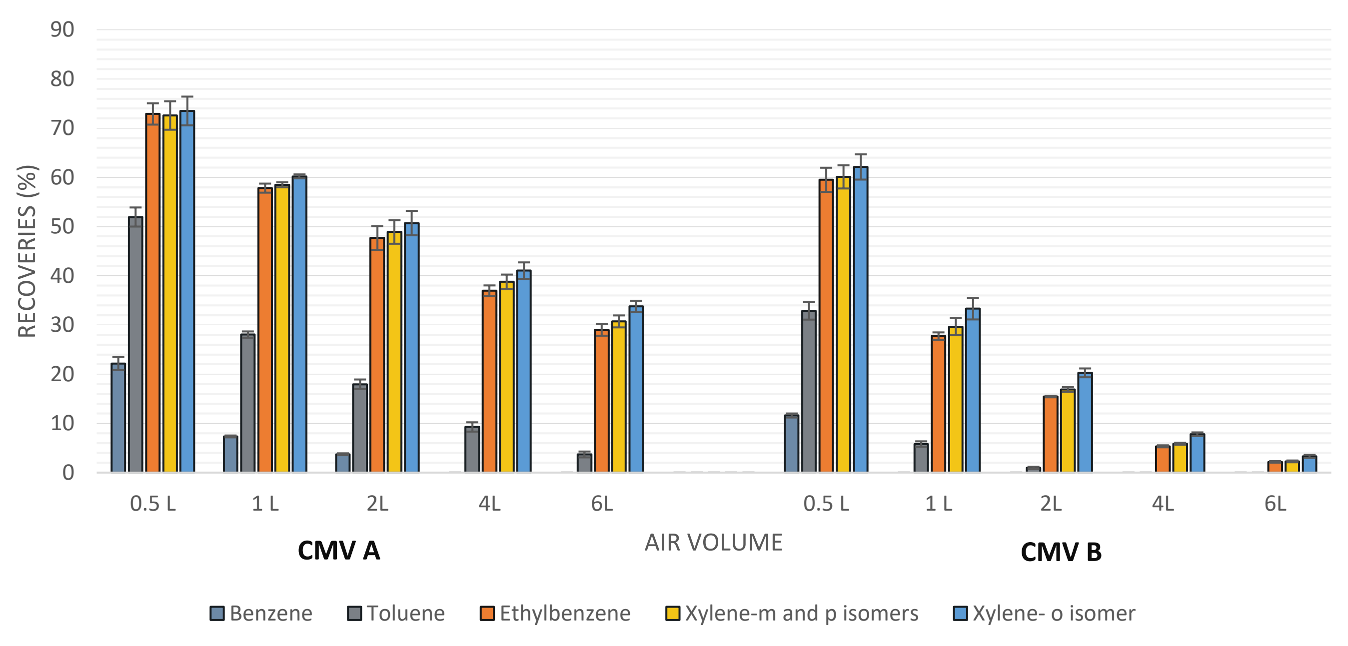

Figure 1: Trapping efficiency measured as average percent recoveries of 100 ng BTEX (n = 3) by CMVs A and B at a vacuum flow rate of 0.2 L/minute. X1 represents the m- and p- isomers of xylene, and X2 is the o- isomer of xylene.

Sampling Optimization for ILRs

Optimization of a sampling protocol was carried out with both CMV phases for the extraction of ILRs. Prior to sampling different neat ignitable liquids, a representative cocktail of ten compounds found in ILRs was created. This included toluene, eicosane and other aromatic-, naphthenic-, and aliphatic-type molecules (see **Figure 3** for complete list). The sampling vessel chosen for the protocol was a 1 L stainless steel paint can, as paint cans are commonly used in the field for storing and transporting fire debris from a scene. Recommendations for each tested parameter were taken from ASTM methods 1388, 1413, and 1618 [11, 12, 13].

Sampling parameters chosen for this evaluation were the pumping flow rate, sample equilibration time, and temperature of the can heating mantle (**Figure 2**), as well as GC inlet temperature due to its effects on desorption and recovery of analytes. To optimize the sampling parameters, 1 µL of the ten-compound mixture was deposited directly onto the bottom of a 1 L can. The can's lid was pre-punctured with two holes—one directly in the center and one off-center—sealed with rubber septa. The can was immediately covered and hammered shut to minimize volatile loss, then placed in a heating mantle. To sample the headspace, a 16-gauge hypodermic needle was used to pierce through the center septum. A short length of PFA tubing was then used to connect the needle to the CMV. The other end of the CMV is connected by tubing to a flowmeter and a Bailey Nurture III vacuum pump. Seals around the CMV were air-tight to prevent analyte loss while sampling. A second hypodermic needle with open-ended tubing was used to pierce the off-center septum to allow ambient air in and preventing a vacuum inside the can (see **Figure 2**).

Due to the diversity of compound volatilities—and more generally in ignitable liquids—in the mixture, 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 10-minute equilibration time made significant differences in aromatic recovery compared to 5 minutes. The alkane series undecane (C_{11}) through pentadecane (C_{15}) saw increased recoveries at 10 minutes compared to 20 minutes. Comparison between flow rates of

0.2 L/minute and 0.5 L/minute showed that the lower flow rate produced the best recoveries, in agreement with the evaluation that looked at BTEX alone. 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 recovery of toluene from the sample mixture. This is thought to be the result of breakthrough. The higher flow rate either caused an insufficient amount of contact time between the compound and the phase to allow adsorption, or it was so strong it carried off adsorbed analyte.

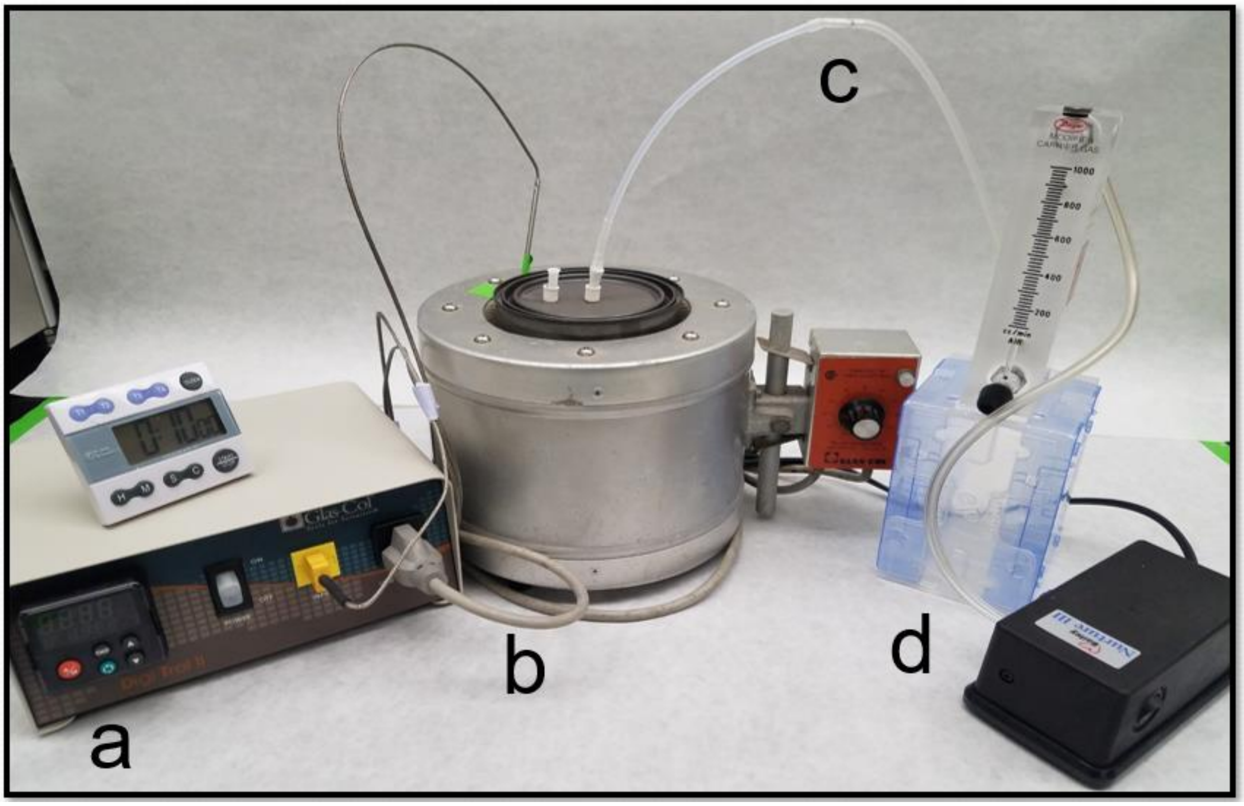

Figure 2: Image of the active headspace sampling apparatus: (a) temperature modulator, (b) heating mantle, (c) PFA tubing with housed CMV, (d) Nurture III vacuum pump with Dwyer mL/minute flowmeter

The GC inlet temperature was expected to be an important factor because too low of a temperature would result in inadequate desorption and ultimately sensitivity. Likewise, thermal decomposition at higher temperatures is important to avoid, considering that classification of ILRs partly depends on the appearance of the chromatographic profile. **Figure 3** shows the recoveries at three different inlet temperatures for CMV A. Sampling was done by directly adding 1 µL of a 30 µg/mL of a 10-analyte solution onto one end of the CMV followed by immediate introduction into the inlet. Despite the expectation that higher inlet temperatures would favor the lower volatility compounds, decreases in the recoveries were seen across the entire series for CMVs A and B at 270°C and 290°C compared to 250˚C. It is likely that some degree of thermal degradation occurred, lowering the recoveries. Limitation of the 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 29%–85% for CMV A, relative to 270˚C.

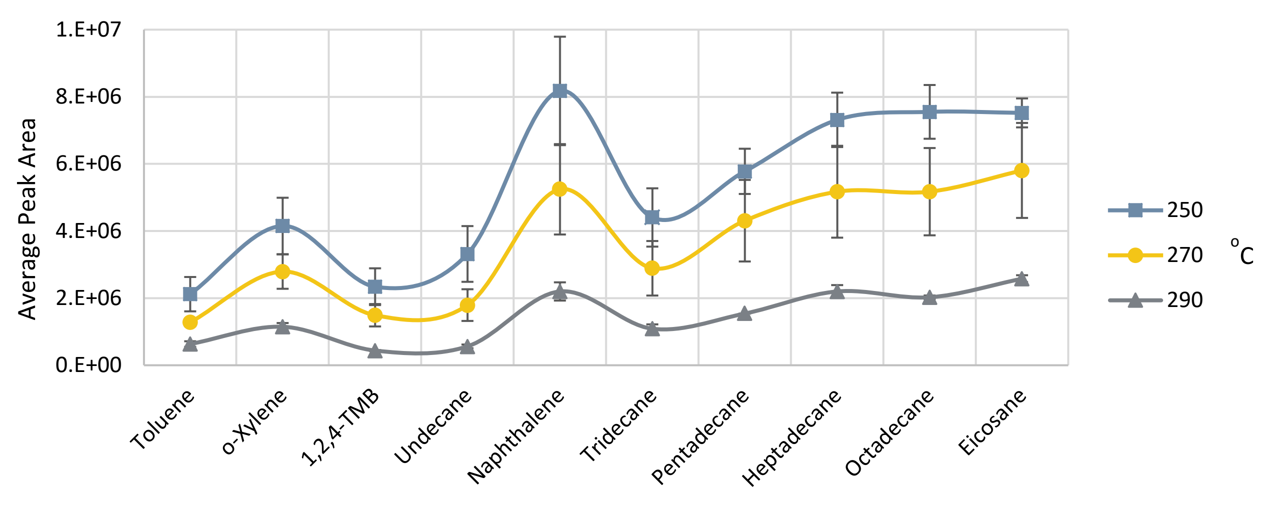

Figure 3: Averaged peak areas (n = 3) from 1 µL direct spikes of 30 µg/mL “10-mix” onto CMV A to determine the optimal desorption temperature

Preliminary Evaluation of a Multiphase CMV and Additional Sol-Gel Synthesis

Previous studies have shown that SPME fibers functionalized with multiple sorbents have improved extraction efficiencies for different ignitable liquids. This is in contrast to SPME fibers with a single sorbent, which tend to perform best for limited classes of compounds [14]. Considering the success of the phenyl-modified phase, a fourth experiment was done to compare compound recovery of pure CMV A and CMV B phases to an even mix of the two. This evaluation utilized the optimized sampling protocol, apart from the desorption temperature that was set at 230°C before reoptimization. Measurements were made sampling 300 ng of a mixture of seven compounds (**Figure 4**). To determine the amount recovered, calibration curves were built by directly depositing 1 µL of the mixture at concentrations ranging from 15–300 µg/mL, in triplicate.

Based on prior BTEX studies, it was expected that the A/B phase CMVs would have recoveries between what was possible for either single phase, but CMV B performed better than expected, even for compounds known to have greater affinity for CMV A. The inlet temperature may have 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. This may also have been due to the omission of the three largest compounds in the ten-compound mixture, which were excluded from this solution due to heavy background interference, preventing accurate quantitation. Their absence may have left more surface area available for greater amounts of the smaller molecules to adsorb, increasing the recoveries despite weaker affinity. Future work includes a revaluation of the 50-50 combination using the ten-compound mixture and actual ignitable liquid samples, in addition to trying varying ratios of A to B within a device.

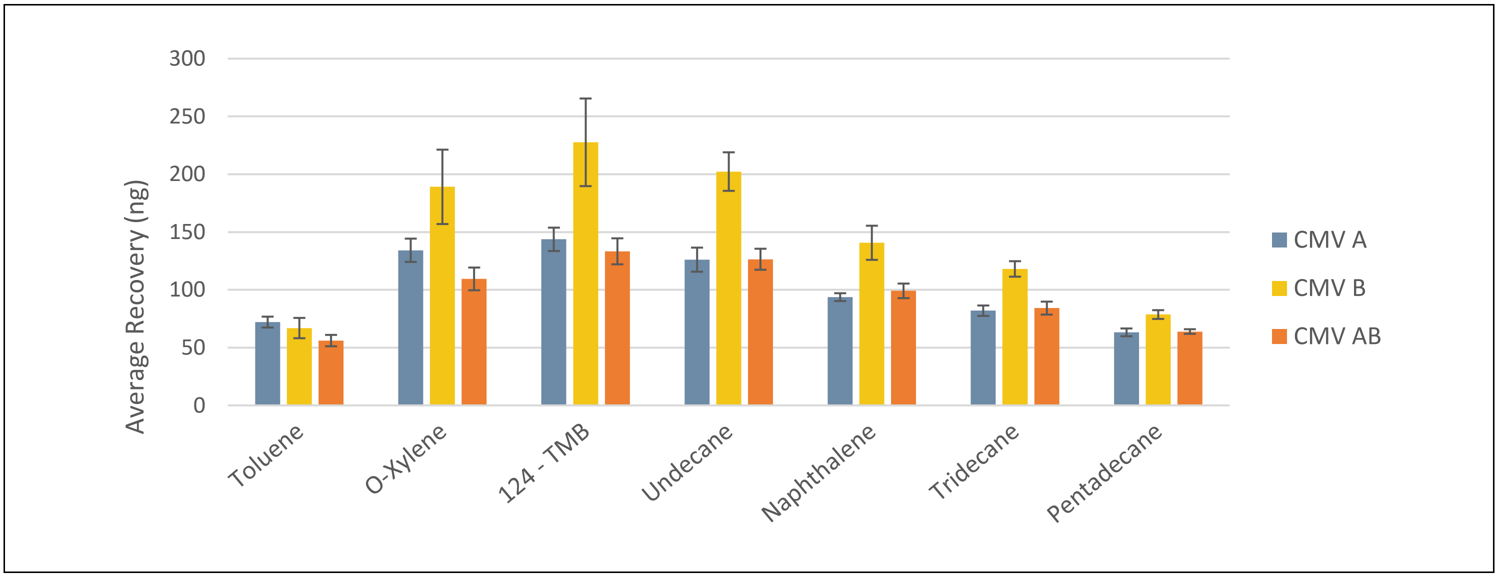

Figure 4: Average recoveries (ng) of a 300 ng “7-mix” solution by CMVs A, B, and A/B (n = 3) from a 1 L stainless steel paint can

Ongoing efforts have progressed towards synthesizing new sol-gel phases with varying functionalities for use in the CMV. The approach has been modeled after the phenyl phase synthesis, which involves substituting the functional moiety on the trimethoxysilane precursor. Currently, two additional phases have reached the prototype stage of development. In addition, NIJ is supporting research efforts for a full comparison of sampling techniques. CMVs C and F have undergone desorption comparisons with CMVs A and B, via triplicate measurements of 1 µL direct spikes of a 30 µg/mL “10-mix” solution. Of the two prototypes, CMV C—targeted towards highly hydrophobic compounds—shows the most promise as the strongest sorbent of the four phases. Apart from octadecane and eicosane, recoveries for CMV C were 5%–82% greater than CMV A. When compared directly to CMV B, recoveries across the entire compound series were 13%–303% higher, particularly for the aromatic compounds.

Conclusions

Previous forensic applications of CMV for the extraction and analysis of VOCs have shown it is a sensitive, versatile technique. Improvements to the device can increase its versatility, specifically in its ability to sample a range of compounds characteristic to ILRs. The continued development and combination of new phases should both improve comprehensive extractions regardless of the ignitable liquid and also achieve the sensitivity needed for recovery of sub-nanogram amounts of ILRs from fire debris.

Related FTCoE work

The Forensic Technology Center of Excellence (FTCoE) is conducting an evaluation of field-portable instrumentation for the sampling and analysis of ILRs from fire debris. Currently, the evaluation includes SPME and direct air sampling on a FLIR G510. The FTCoE is also examining the application of a CMV-sampling front end for this purpose.

Other FTCoE resources related to fire debris investigation include the archived webinar, “Fire Debris is Not Black Magic,” a primer on fire debris analysis for the crime laboratory manager [15]. The FTCoE has published a success story on NIJ-supported research (2008- DN-BX-K168):to develop objective methods to examine fire dynamics and patterns at investigation scenes [16]. Finally, the FTCoE published a technical note on the application of CMV to the collection of gunshot residue [17].

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References

[1] Martín-Alberca, C., Ortega-Ojeda, F. E., & García-Ruiz, C. (2016). Analytical tools for the analysis of fire debris. A review: 2008–2015. *Analytica Chimica Acta*, *928*, 1–19. doi:10.1016/j.aca.2016.04.056

[2] CMV Disclosure filed in February 2013—Capillary Microextraction of Volatiles, Patent No. US 9,267,866 B2 Awarded on Feb. 23, 2016.

[3] Fan, W., & Almirall, J. (2013). High-efficiency headspace sampling of volatile organic compounds in explosives using capillary microextraction of volatiles (CMV) coupled to gas chromatography–mass spectrometry (GC-MS). *Analytical and Bioanalytical Chemistry*, *406*(8), 2189–2195. doi:10.1007/s00216-013-7410-3

[4] Wiebelhaus, N., Hamblin, D., Kreitals, N. M., & Almirall, J. R. (2016). Differentiation of marijuana headspace volatiles from other plants and hemp products using capillary microextraction of volatiles (CMV) coupled to gas-chromatography–mass spectrometry (GC–MS). *Forensic Chemistry*, *2*, 1–8. doi:10.1016/j.forc.2016.08.004

[5] Nair, M., & Miskelly, G. (2016). Capillary microextraction: A new method for sampling methamphetamine vapour. *Forensic Science International*, *268*, 131–138. doi:10.1016/j.forsciint.2016.09.020

[6] Hamblin, D., & Almirall, J. (2017). Analysis of exhaled breath from cigarette smokers using CMV-GC/MS. *Forensic Chemistry*, *4*, 67–74. doi:10.1016/j.forc.2017.02.008

[7] Almirall, J., & Grabenauer, M. (2017). Detection of organic gunshot residue using capillary microextraction of volatiles with cryofocusing. Technical Note in Forensic Technology Center of Excellence, Department of Justice, National Institute of Justice, Office of Investigative and Forensic Sciences. https://rti.connectsolutions.com/p83f1jprwtn/

[8] Tarifa, A., Kreitals, N. M., Mulloor, J., Gura, S., & Almirall, J. R. (2017). Cryofocusing capillary microextraction of volatiles (Cryo-CMV) as a novel headspace extraction device for the analysis of volatile organic compounds and smokeless powders. *Forensic Chemistry*, *3*, 81–89. doi:10.1016/j.forc.2017.02.007

[9] Gura, S., Tarifa, A., Mulloor, J., Torres, M. N., & Almirall, J. R. (2018). Capillary microextraction of volatiles device for enhanced BTEX vapors sampling based on a phenyl modified PDMS sol-gel adsorption phase. *Analytica Chimica Acta*, *1014*, 27–40. doi:10.1016/j.aca.2018.01.043

[10] Stauffer, E., Dolan, J. A., Newman, R., & Sandercock, P. M. (2008). *Fire debris analysis*. Amsterdam: Academic Press. doi:10.1016/B978-0-12-663971-1.X5001-5

[11] ASTM International. (2014). Standard Test Methods for Ignitable Residues in Extracts from Fire Debris Samples by Gas Chromatography-Mass Spectrometry. ASTM International, West Conshohocken, PA. https://www.astm.org/Standards/E1618.htm

[12] ASTM International. (2017). Standard Practice for Static Headspace Sampling of Vapors from Fire Debris Samples. ASTM International, West Conshohocken, PA. https://www.astm.org/Standards/E1388.htm

[13] ASTM International. (2019). Standard Practice for Separation of Ignitable Liquid Residues from Fire Debris Samples by Dynamic Headspace Concentration onto an Adsorbent Tube. West Conshohocken, PA. https://www.astm.org/Standards/E1413.htm

[14] Fettig, I., Krüger, S., Deubel, J. H., Werrel, M., Raspe, T., & Piechotta, C. (2013). Evaluation of a Headspace Solid-Phase Microextraction Method for the Analysis of Ignitable Liquids in Fire Debris. *Journal of Forensic Sciences*, *59*(3), 743–749. doi:10.1111/1556-4029.12342

[15] Forensic Technology Center of Excellence. (2019). Fire Debris Analysis is Not Black Magic! National Institute of Justice, Forensic Technology Center of Excellence, https://forensiccoe.org/webinar/ascld-train-directors-2019-fire-debris-csi/

[16] Forensic Technology Center of Excellence. (2018). *Success Story: NIJ and Jensen Hughes: Advancing the Forensic Analysis of Ignitable Liquid Fuel Fires.* National Institute of Justice, Forensic Technology Center of Excellence, https://forensiccoe.org/private/5d93694918913

[17] Forensic Technology Center of Excellence. (2017). TECHNICAL NOTE Detection of Organic Gunshot Residue Using Capillary Microextraction of Volatiles with Cyrofocusing. National Institute of Justice, Forensic Technology Center of Excellence, https://forensiccoe.org/private/5dc46f280c7be

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