Forensic Chemistry 27 (2022) 100397

Contents lists available at ScienceDirect

Forensic Chemistry

journal homepage: www.sciencedirect.com/journal/forensic-chemistry

# Evaluation of capillary microextraction of volatiles (CMV) coupled to a person-portable gas chromatograph mass spectrometer (GC–MS) for the analysis of gasoline residues

Michelle N. Torres, José R. Almirall *

*Department of Chemistry and Biochemistry, and Center for Advanced Research in Forensic Science, Florida International University, Miami FL 33199, USA*

ARTICLE INFO

*Keywords:*
Capillary Microextraction of Volatiles (CMV)
Gas-chromatography-mass spectrometry (GC–MS)
Fire Debris Analysis
Ignitable liquid residues (ILRs)
Dynamic headspace extraction

ABSTRACT

A novel dynamic headspace extraction device, the capillary microextraction of volatiles (CMV) was coupled to a person-portable GC–MS for the analysis of ignitable liquid residues (ILR) sampled from simulated fire debris. A benchtop GC–MS was used as a benchmark for the performance of the portable GC–MS. The use of a paper cup in conjunction with the CMV for in-field sampling of the VOCs associated with ILRs is presented for the first time. A five-minute sampling/extraction protocol was sufficient to recover six (6) analytes: toluene, ethylbenzene, m-xylene, o-xylene, 4-ethyltoluene, and 1,2,4-trimethylbenzene from a 0.01 μL spike of gasoline, with typical mass recoveries of 4–24 ng. Extractions from water-logged debris resulted in reliable detection of the same six compounds but up to 62% less was retained relative to dry debris. Recoveries for detected analytes ranged between 1 and 5% at several solution spike volumes suggesting proportional retention by the CMV. The CMV also demonstrated greater extraction capabilities than the portable GC–MS air sampling wand. Out of a 20-component mixture, 17 compounds were detected compared to the wand's 13, with the majority of these at higher overall intensities for CMV. 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 such as activated charcoal strips and SPME fibers.

## 1. Introduction

Person-portable gas chromatograph-mass spectrometry instrumentation has been increasingly sought after as a versatile tool to address in-field analysis needs. First responders, environmental surveyors, and military personnel have benefited from the rapid sampling capabilities and immediate identification of potentially hazardous chemicals. Recent reports have been devoted to the application of portable GC–MS to the analysis of ignitable liquid residues (ILR) in the field [1–4]. The implementation of portable GC–MS for fire scene investigation can provide several advantages over traditional evidence collection at the scene followed by laboratory examination. In addition to the quick feedback, the risk of analyte loss from sampling, packaging and transport is reduced [5,6]. 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.

While on-site instrumentation (e.g., high-quality battery powered GC–MS units) have improved, the extraction methods have not evolved in-step with field instrumentation capabilities. In the case of fire scene investigation, one common and standard practice employs headspace adsorption onto an activated charcoal strip (ACS) using ASTM E1412-19 [7]. This method is amenable to the laboratory setting but is not practical for field use. The time and resources needed for sample preparation - particularly the necessity to heat the container of the debris for several hours followed by solvent desorption of the strip– make it impractical to use in combination with a rapid field-analysis methodology [8]. Solid phase microextraction (SPME) is considerably more amenable to field sampling; however, as a sampling device the fibers are very fragile and easy to contaminate. Additionally, SPME is a static technique based on equilibrium sampling which may require headspace exposure over a long period of time (minutes to hours, depending on the analytes). A standard laboratory-based practice for extraction of ILRs from fire debris samples by passive concentration using SPME is also in use around the world primarily in Canada and Australia using ASTM E2154-15a [9].

The purpose of this study is to address a gap in the literature by evaluating the coupling of a dynamic sampling device with enhanced

* Corresponding author.
*E-mail addresses:* mtorr067@fiu.edu (M.N. Torres), almirall@fiu.edu (J.R. Almirall).

https://doi.org/10.1016/j.forc.2021.100397
Received 1 November 2021; Received in revised form 21 December 2021; Accepted 23 December 2021
Available online 28 December 2021

extraction efficiency compared to SPME, to a portable GC–MS for its applicability to fire debris analysis at ambient temperatures. Presented here is a laboratory-based evaluation of the Griffin G510 GC–MS (specifications found in [10]), manufactured by FLIR Systems. It is a low thermal mass (LTM) gas chromatograph-mass spectrometer with a linear quadrupole mass filter. It has several sample introduction options, including a detachable PSI (Prepless Sample Introduction)-Probe for direct insertion of solids, liquids, and trace residues. The use of the PSI-probe allows for the direct introduction of the capillary microextraction of volatiles (CMV) device [11] – a dynamic headspace extractor previously applied to ILR analysis and other forensic applications within the past decade [2,11–16]. Also presented here as proof of concept is the use of a paper drinking cup as part of a field-based headspace extraction technique. Originally paired with SPME fibers [17]; the cup's purpose is to facilitate increased recoveries of volatiles faster, compared to open-air sampling. A 5-minute sampling/extraction protocol at ambient temperatures (~25 $^0$C) has been developed and optimized for the pairing of a cup with the CMV device and presented here for the first time.

## 2. Materials and methods

### 2.1. 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 at ambient temperatures.

### 2.2. Instrumentation

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 × 0.18 mm × 0.18 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 min. The MS source was set to 200 °C. Data acquisition occurred in Full Scan mode, over the range of 45–400 *m/z*.

An Agilent Technologies 7890A gas chromatograph coupled to a 5975C inert mass spectrometer with a triple-axis detector was utilized for all benchtop experiments. The gas chromatograph was equipped with an Agilent Technologies Thermal Separation Probe (TSP) for the insertion of CMVs into the inlet for thermal desorption. A DB-5 ms Ultra Inert (28.9 m × 0.25 mm × 0.25 μm) was used as the analytical column. The oven was programmed at 35 °C with a 2 min hold, followed by a 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 min. The inlet temperature was set to 250 °C and run in split injection mode set at a 50:1 ratio. Helium was used as the carrier gas, set at a flow rate of 1.2 L min$^{-1}$. The MS quadrupole and ion source temperatures were set to 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. Monitored ions for analytes of interest on both instruments are summarized in Table 1. Compound identification was determined from a comparison of retention times and mass spectra obtained from the injection of standard solutions. Quantitation was performed on data collected from the selected ion mode.

### 2.3. Methods

#### 2.3.1. Solution preparation

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$^{-1}$.

#### 2.3.2. Cup headspace 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 (Fig. 1). The cup was left over the debris undisturbed for two minutes at ambient temperature (~25 $^0$C) 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.

## 3. Results and discussion

### 3.1. 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 1) before

**Table 1**
Limits of Detection and Retention times (G510) for selected analytes. LOD concentrations are given in ng $\mu L^{-1}$.

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

**Fig. 1.** Photograph depiction of the CMV/Cup apparatus with debris placed on the glass platform (left) and the CMV sampling using the hand-held vacuum pump (right).

they were added to the list of calibration files.

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 1 summarizes the limits of detection for the compound sub-library, determined using two different approaches. The portable LODs (generated by the method) are 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 $\mu L^{-1}$ 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.

### 3.2. 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 were 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 and 30 ng $\mu L^{-1}$ and between 22 and 41 ng $\mu L^{-1}$ for the aliphatics.

### 3.3. Simulated debris sampling with CMV/Cup protocol

Simulated debris experiments were carried out using the CMV/Cup protocol outlined in Section 2.3.2. 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 g of material fit into a 150 mL porcelain crucible. The material was then ignited by direct contact with a propane torch flame for 15 s and allowed to burn and/or smolder for an additional minute and 45 s. Following the two-minute burn time, a metal lid was used to suffocate any existing flames for 30 s. 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 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 were 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 were presumptively identified as aldehydes with signal-to-noise (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.

### 3.3.1. 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 pyrolysates, 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 [18], 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 prior to 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 2 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.

The precision of the measurements ranged between 16 and 47% at the 1 μL level, and slightly improved at 3 μL, ranging from 9 to 37%. Repeatability was best at the highest spike level, with %RSD values between 2 and 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.

Replicate experiments on the benchtop demonstrated overall higher mass recoveries and extraction of a greater range of analytes relative to the G510 (Table 3). The additional compounds detected with the benchtop analysis include octane, nonane, 1,2,4,5-TMB, & naphthalene. Fig. 2 shows the chromatogram obtained for the jean fabric sampling at the 1 μL spike volume. Here, the targeted aromatic 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 and 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.

### 3.3.2. 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 prior to 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 [19,20]. 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 3.3 and sampled using the protocol in section 2.3.2 For

**Table 2**
Mass recoveries (ng) and %RSD from simulated fire debris at the 1 μL spike level using the Cup/CMV protocol and portable GC–MS.

| 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 3**
Mass recoveries (ng) and %RSD from simulated fire debris at the 1 μL spike level using the Cup/CMV protocol and benchtop GC–MS.

| 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 |

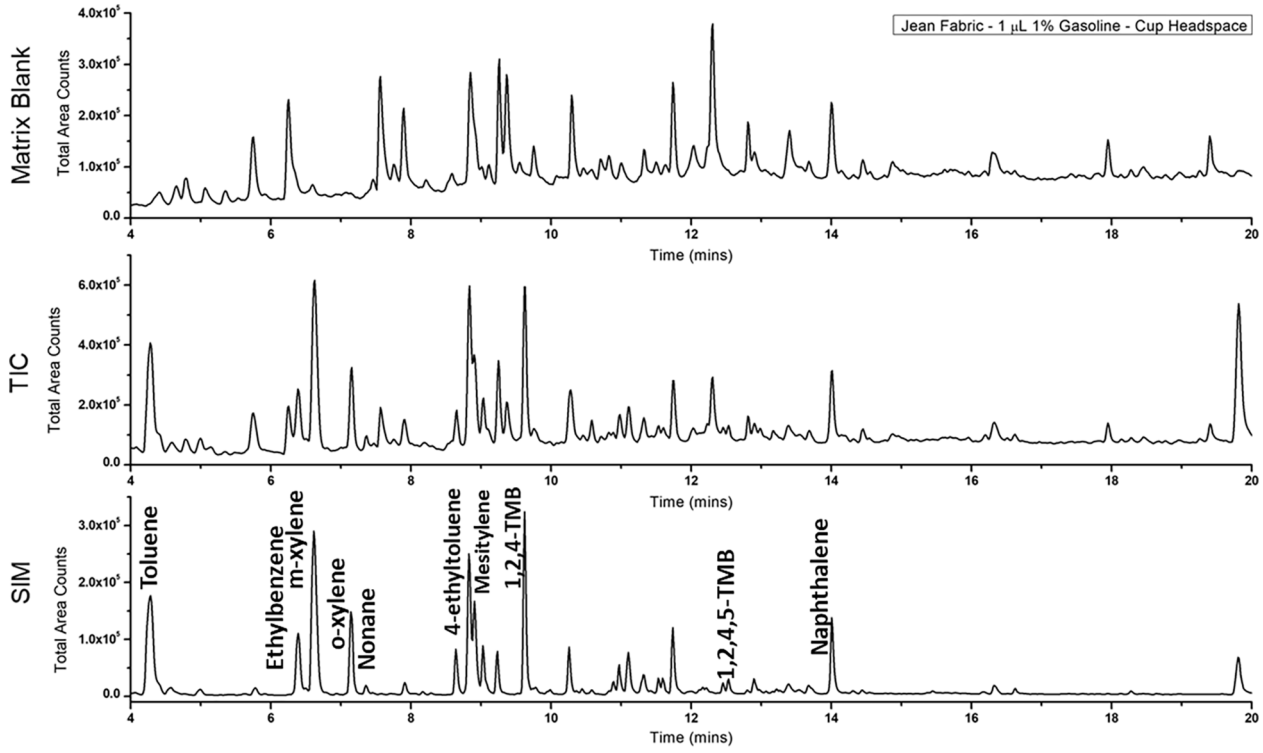


**Fig. 2.** Chromatogram stack of a CMV/Cup sampling 1 μL of 1% gasoline solution from charred jean fabric (dry) on the benchtop GC–MS.

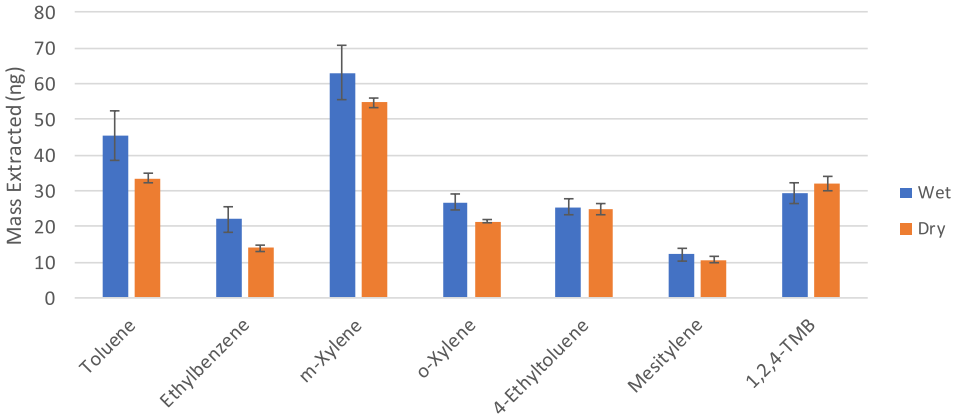


**Fig. 3a.** Average (n = 3) extracted masses of ILR analytes from 1 μL spikes of 1% gasoline. Analytes sampled from wet and dry charred jean fabric using the CMV/Cup protocol and analyzed on the G510.

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.

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 were 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 and 17% and 4–15% was determined for the wet and dry jean fabric replicates (Fig. 3a). 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 to 51 ng (18–46%) and 2–19 ng (7–29%) for wet and dry replicates, respectively (Fig. 3b). The dry recoveries calculated from the 5 μL volume were outside the linear working range and thus were not considered here.

### 3.3.3. *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 compound targets. These recovered amounts were used as absolute amounts relative to what was extracted from the dry and wet substrate experiments (Sections 3.3.1 and 3.3.2). The lowest spike volume (1 μL of a 1% solution) is equivalent to a 0.01 μL amount of neat gasoline (Fig. 4). Tables 4 and 5 summarize the average percent recoveries of the targets detected on both instruments from all three debris materials. Interestingly, percent differences only range between 1 and 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.

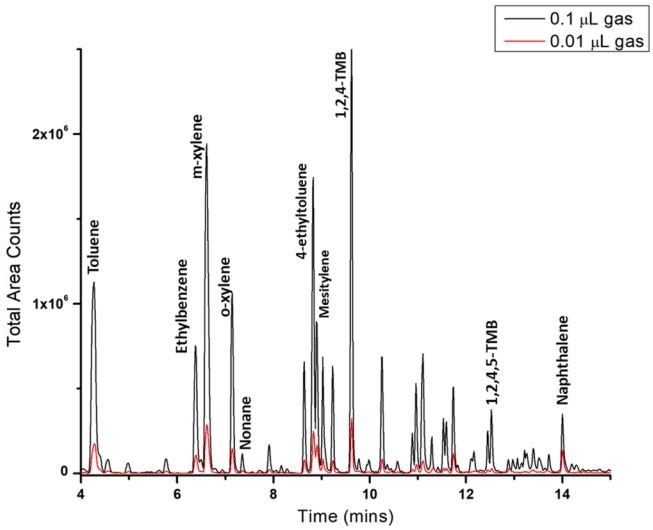


**Fig. 4.** Chromatographic overlay of 0.01 (red) and 0.1 (black) μL of neat gasoline, sampled using CMV/Cup protocol, analyzed on benchtop GC–MS (SIM mode). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

**Table 4**
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 | 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 |

### 3.4. *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,

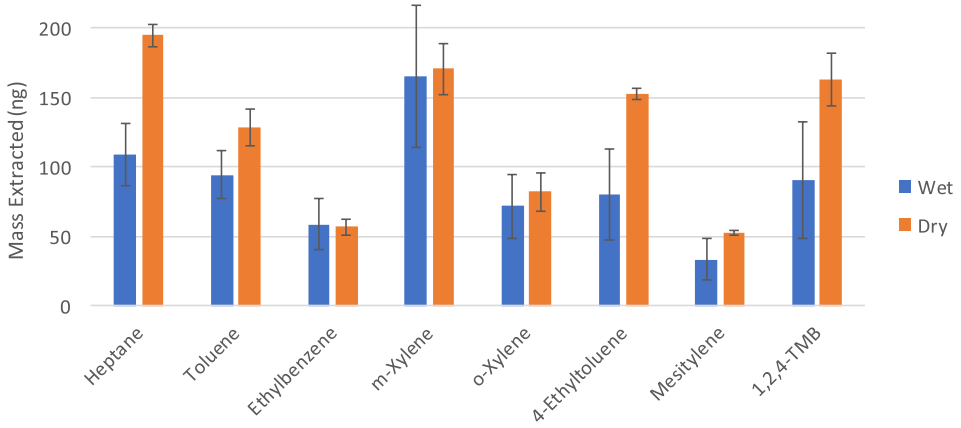


**Fig. 3b.** Average (n = 3) extracted masses of ILR analytes from 3 μL spikes of 1% gasoline. Analytes sampled from wet and dry charred jean fabric using the CMV/Cup protocol and analyzed on the G510.

**Table 5**
Average recovery (as % recovery) of gasoline ILRs from simulated fire debris relative to 0.1 μL of neat gasoline – benchtop 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 |

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. 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 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. Fig. 5 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 to 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 and 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.

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 3.3. 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 6 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 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 (Fig. 6). At samplings of 0.05 μL of gasoline, this average drops to 15%.

## 4. Conclusions

The potential of the CMV's use in conjunction with a paper drinking cup for enhanced extraction of ignitable liquid residues from fire debris has been demonstrated. Fast results were achieved with an overall 21-minute analytical method, including a five-minute ambient

**Table 6**
Average recovery (as ratios of wand to CMV) for replicate samplings of 1% gasoline at varied volumes using Cup headspace sampling.

| Compound | Solution spike volume | | |
|---|---|---|---|
| | 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 |

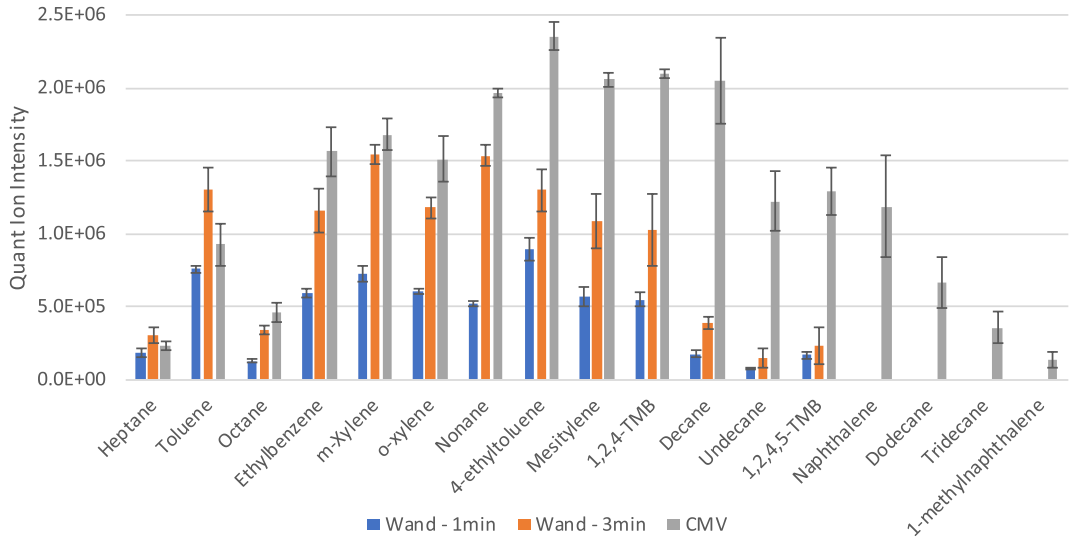


**Fig. 5.** Average (n = 3) quant ion intensities for analytes recovered from 1 μL spikes of 1% 20-mix, pairing the cup protocol with the CMV and the air wand.

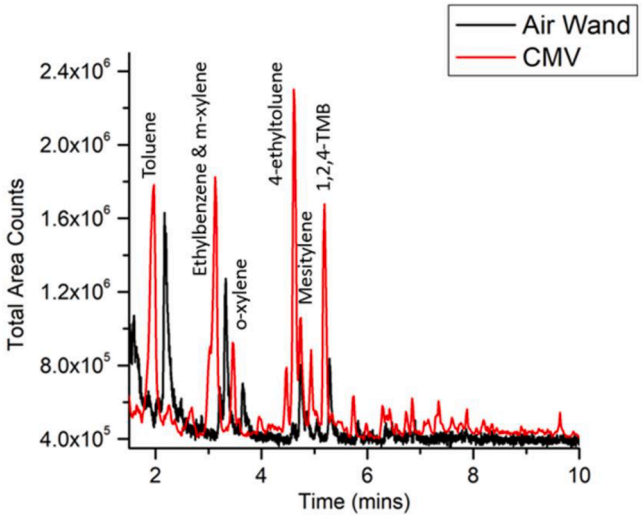


**Fig. 6.** Chromatographic overlay of a 3 μL spike sampling of a 1% gasoline dilution with the air wand (black) and CMV (red) using the cup protocol.

temperature extraction and a 16-minute chromatographic method on the G510 portable GC–MS. Consistent detection and quantitation of six ILR-related components on the portable GC–MS and up to 11 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 from the combustion/pyrolysis products from any of the charred debris materials investigated. The CMV was also shown to be highly sensitive; recoveries of several targeted analytes were possible from up to 10x less 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 indicates 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 comparative amounts recovered from a 0.1 μL spike of 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.

Limitations of the current cup protocol are its lack of an airtight seal and the incorporation of a heat source to increase volatilization of heavier analytes from debris. Future work aims to develop a field-amenable sampling accessory based on the cup enclosure that incorporates these features, thereby increasing the detectable range and recovery of many ignitable liquid residues. Expansions on this study would include assessing the CMV's extraction efficiency of known quantities of gasoline from other debris types, primarily those known to produce several of the aromatics targeted here as pyrolysis products. Emphasis would be placed on a chemometric approach to conclusive identification, including assessing peak ratios and characteristic peak patterns. Finally, studies would include the implementation of the CMV/Cup protocol and a portable GC–MS unit like the G510 in real-world controlled-burn field exercises for ILR extractions.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Acknowledgements

The authors would like to thank the Forensic Technology Center of Excellence (FTCoE) at the Research Triangle Institute (RTI), USA, for funding this work at Florida International University (FIU) through a sub-award to the National Institute of Justice FTCoE at RTI (2016-MU-BX- K110). This project was partially funded by the Center for Advanced Research in Forensic Science (CARFS), a National Science Foundation-funded Industry University Cooperative Research Center at FIU (Award # 1739805).

## References

[1] A. Visotin, C. Lennard, Preliminary evaluation of a next-generation portable gas chromatograph mass spectrometer (GC-MS) for the on-site analysis of ignitable liquid residues, Aust. J. Forensic Sci. 48 (2) (2016) 203–221, https://doi.org/10.1080/00450618.2015.1045554.
[2] M.N. Torres, N.B. Valdes, J.R. Almirall, 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. 19 (2020) 100240, https://doi.org/10.1016/j.forc.2020.100240.
[3] R. Lam, C. Lennard, G. Kingsland, P. Johnstone, A. Symons, L. Wythes, J. Fewtrell, D. O'Brien, V. Spikmans, Person-portable equipment in environmental forensic investigations: application to fire scenes, Aust. J. Forensic Sci. 50 (2018) 672–681, https://doi.org/10.1080/00450618.2018.1424242.
[4] W.R. de Araujo, T.M.G. Cardoso, R.G. da Rocha, M.H.P. Santana, R.A.A. Muñoz, E. M. Richter, T.R.L.C. Paixão, W.K.T. Coltro, Portable analytical platforms for forensic chemistry: A review, Anal. Chim. Acta. 1034 (2018) 1–21, https://doi.org/10.1016/j.aca.2018.06.014.
[5] P.E. Leary, G.S. Dobson, J.A. Reffner, Development and Applications of Portable Gas Chromatography-Mass Spectrometry for Emergency Responders, the Military, and Law-Enforcement Organizations, Appl. Spectrosc. 70 (5) (2016) 888–896, https://doi.org/10.1177/0003702816638294.
[6] V. Spikmans, The evolution of environmental forensics: From laboratory to field analysis, Wiley Interdiscip. Rev. Forensic Sci. 1 (3) (2019), https://doi.org/10.1002/wfs2.1334.
[7] ASTM International, Standard Practice for Separation of Ignitable Liquid Residues from Fire Debris Samples by Dynamic Headspace Concentration, 2019. https://doi.org/10.1520/E1412-19.Copyright.
[8] R. Lam, C. Lennard, G. Kingsland, P. Johnstone, A. Symons, L. Wythes, J. Fewtrell, D. O'Brien, V. Spikmans, Rapid on-site identification of hazardous organic compounds at fire scenes using person-portable gas chromatography-mass spectrometry (GC-MS)—part 1: air sampling and analysis, Foren. Sci. Res. 5 (2020) 150–164, https://doi.org/10.1080/20961790.2019.1662648.
[9] ASTM International, Standard Practice for Separation of Ignitable Liquid Residues from Fire Debris Samples by Solvent Extraction, ASTM E1386 - 15. (2015). https://doi.org/10.1520/E1413-13.Copyright.
[10] FLIR Systems, Griffin G510 - Data Sheet, (2020).
[11] W. Fan, J. Almirall, High-efficiency headspace sampling of volatile organic compounds in explosives using capillary microextraction of volatiles (CMV) coupled to gas chromatography-mass spectrometry (GC-MS) Microextraction Techniques, Anal. Bioanal. Chem. 406 (8) (2014) 2189–2195, https://doi.org/10.1007/s00216-013-7410-3.
[12] S. Gura, A. Tarifa, J. Mulloor, M.N. Torres, J.R. Almirall, Capillary microextraction of volatiles device for enhanced BTEX vapors sampling based on a phenyl modified PDMS sol-gel adsorption phase, Anal. Chim. Acta. 1014 (2018) 27–40, https://doi.org/10.1016/j.aca.2018.01.043.
[13] M.V. Nair, G.M. Miskelly, Capillary microextraction: A new method for sampling methamphetamine vapour, Forensic Sci. Int. 268 (2016) 131–138, https://doi.org/10.1016/j.forsciint.2016.09.020.
[14] M.V. Nair, G.M. Miskelly, Determination of airborne methamphetamine via capillary microextraction of volatiles (CMV) with on-sorbent derivatisation using o-pentafluorobenzyl chloroformate, Forensic Chem. 14 (2019) 100161, https://doi.org/10.1016/j.forc.2019.100161.
[15] R. Williamson, S. Gura, A. Tarifa, J.R. Almirall, The coupling of capillary microextraction of volatiles (CMV) dynamic air sampling device with DART-MS analysis for the detection of gunshot residues, Forensic Chem. 8 (2018) 49–56, https://doi.org/10.1016/j.forc.2018.01.005.
[16] A. Tarifa, J.R. Almirall, Fast detection and characterization of organic and inorganic gunshot residues on the hands of suspects by CMV-GC-MS and LIBS, Sci. Justice. 55 (3) (2015) 168–175, https://doi.org/10.1016/j.scijus.2015.02.003.
[17] J.D. DeHaan, D. Byron, D. Matthew, R. Jones, R. Harper, Advancing Fire Scene Investigations with Field Portable Technologies, (2021).
[18] National Center for Forensic Science (NCFS), Plastic Wrap, (n.d.).
[19] J. Koziel, M. Jia, J. Pawliszyn, Air sampling with porous solid-phase microextraction fibers, Anal. Chem. 72 (21) (2000) 5178–5186, https://doi.org/10.1021/ac000518l.
[20] K.G. Furton, J.R. Almirall, M. Bi, J. Wang, L. Wu, Application of solid-phase microextraction to the recovery of explosives and ignitable liquid residues from forensic specimens, J. Chromatogr. A. 885 (1-2) (2000) 419–432, https://doi.org/10.1016/S0021-9673(00)00368-X.