

# Characterization of a Headspace Sampling Method with a Five Component Diesel Fuel Surrogate<sup>§</sup>

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## ABSTRACT

PLOT-cryoadsorption concentrates headspace vapors by sweeping them through porous layer open tubular (PLOT) capillaries chilled to 0 °C to promote adsorption onto an alumina layer. Compared to passive headspace concentration employing activated charcoal strips (ACSs) as adsorbents, PLOT-cryoadsorption has several potential advantages for extracting ignitable liquid (IL) residue from fire debris evidence. Capillary vapor traps can be monitored for breakthrough to avoid problematic displacement that occurs when an adsorbent becomes saturated. Capillaries can also be eluted with acetone to avoid highly toxic carbon disulfide. Future adoption of PLOT-cryoadsorption for fire debris analysis requires investigation of sampling parameters including collection volume, flow rate, and temperature. Here we employ a simple five-component surrogate for diesel fuel (that is, a simulated or artificial diesel fuel) to study the effect of flow rate and sample temperature on the composition and spatial distribution of the collected headspace. Flow rates at or below 1.5 scc (standard cubic centimeters)/min yielded the most repeatable results. Across the range 60 °C to 120 °C, we found that high sample temperatures allowed for the collection of more total analyte and shifted its composition towards lower-volatility components. Consistent with chromatographic theory, higher-volatility components traveled furthest along the

length of the capillary and were more prone to breakthrough. We conclude that the surrogate mixture allowed for effective, quantitative comparisons between sampling conditions that could be translated to real diesel fuel.

### **Abbreviations:**

PLOT: porous layer open tubular; ACS: activated carbon strip

## **1. INTRODUCTION**

Arson remains a challenging crime to investigate because most of the physical evidence is destroyed by the fire and by fire-fighting efforts. National arson rates are unknown due to irregular reporting, but 45 % of reported arson offenses involved structures (2017 data) [1]. For structural fires, fire investigations often involve the collection of solid debris for subsequent laboratory analysis to extract and identify ignitable liquid (IL), which can indicate arson. The Ignitable Liquids Reference Collection Database provides chromatographic data and classification according to ASTM Standard Test Method E1618 for neat, weathered, and biologically degraded ILs [2, 3]. There have also been efforts to infer the specific source of neat and weathered gasolines [4].

Analyzing fire debris for IL residue requires extracting and concentrating IL compounds from debris into a form suitable for analytical instruments. ASTM Standard Practice E1412 describes the use of activated charcoal strips (ACSs) for passive headspace concentration and was originally approved in 1991; the method is well established in current forensic practice and is commonly used by forensic laboratories in the United States. The typical procedure is to sample headspace vapors by suspending an ACS above the fire debris in a steel can for 16 h to 24 h at 60 °C to 80 °C. Analytes are then desorbed from the ACS with solvent and analyzed by gas chromatography with mass spectrometry (GC-MS). The effects of time, temperature, and strip size on the recovery of IL compounds have been investigated over more than 20 years [5, 6]. If the results suggest displacement has occurred, the fire debris headspace may be re-sampled under different conditions, for example, for a shorter time and/or at a lower temperature. Displacement refers to the substitution of high-volatility compounds with low-volatility compounds at adsorbent sites. This process is driven by equilibration of each compound between the adsorbent and the headspace and occurs when the ACS becomes saturated due to high IL concentration (not easily

controlled, depends on the debris) and/or small adsorbent capacity (controlled, depends on the analyst) [7].

ACSs have a high affinity for hydrocarbons, which makes them effective adsorbents but demands a strong elution solvent. Carbon disulfide is usually the solvent employed, because its extreme affinity for carbon allows it to effectively displace IL compounds. The significant drawback of carbon disulfide is its high toxicity and flammability. Small exposures to carbon disulfide can cause cardiovascular, neurological, and reproductive toxicity. Accelerated solvent extraction with acetone is a proposed alternative to carbon disulfide for volatile organic compounds captured during air quality measurements in occupational environments; however, this approach has not been applied to less volatile target compounds found in ILs such as gasoline or diesel fuel [8]. Other solvents have been evaluated for their ability to desorb target compounds found in gasoline and diesel fuel towards the goal of improving laboratory safety [9]. ASTM Standard Practice E1412 permits diethyl ether and pentane as alternatives to carbon disulfide; however, both solvents are less effective at desorbing gasoline and diesel fuel compounds than carbon disulfide and are not commonly employed by forensic laboratories [5, 10, 11]. Dichloromethane has been proposed as a safer alternative to carbon disulfide, despite both its carcinogenicity and inferior desorption of target compounds from gasoline and diesel fuel [11].

There have been efforts to develop passive headspace concentration methods that avoid carbon disulfide in favor of thermal desorption [12]. Solid-phase microextraction (SPME) utilizes fibers coated with an adsorbent phase, often polydimethylsiloxane, that are thermally desorbed directly into a gas chromatograph for analysis [13]. ASTM Standard Practice E2154 describes SPME passive headspace concentration as suitable for screening fire debris samples and was originally approved in 2001 [14]. SPME fibers are more prone to displacement than ACSs due to the lower number of adsorption sites, and SPME fibers may preferentially collect aliphatic or aromatic compounds depending on the adsorbent phase and temperature [15, 16] because of competitive adsorption. The relative concentration of a compound equilibrated between two phases is described by its partition coefficient, but even if this value can be predicted at the sample temperature [17], relating adsorbent concentration to vapor concentration is impractical for complex mixtures. Headspace sorptive extraction (HSSE) is similar in concept but utilizes polydimethylsiloxane stir bars to provide approximately 100x the adsorbent volume [18]. The method appears promising and should be less prone to displacement, but it requires additional

validation. Common among these passive concentration methods is the issue of competitive adsorption or displacement. Capillary microextraction of volatiles (CMV), utilizing glass fiber filters modified with a sol-gel adsorbent phase [19], was recently employed to extract IL compounds from simulated fire debris [20]. CMV fibers are like SPME fibers in that both can be thermally desorbed; however, CMV filters are robust and can be used for dynamic headspace concentration.

Displacement is less of a concern for dynamic headspace concentration methods because they can be monitored for breakthrough. PLOT (porous layer open tubular)-cryoadsorption (PLOT-cryo) was developed at NIST in 2008 to concentrate vapors from low-volatility explosives and identify compounds in the headspace of these materials [21, 22]. This headspace concentration method sweeps headspace vapor through a capillary vapor “trap” coated with a porous alumina adsorbent layer that is cooled to promote adsorption. Breakthrough may be a sign that the adsorbent is becoming saturated (leading to displacement), but it can also indicate that the flow rate is too high to permit adsorption of all compounds onto the porous alumina. In either scenario, breakthrough can be detected by bubbling the vapor exiting the capillary through a vial of solvent and subsequently analyzing this solvent for the presence of analytes. Capillaries are easily eluted with solvent and the eluate can be analyzed by GC-MS or other analytical techniques. Over the last decade, PLOT-cryo has been applied to detection of grave soil, poultry spoilage, and natural gas contaminants, among other applications [23-25]. The portable PLOT-cryo instrument developed in 2014 was first applied to detect diesel fuel spiked on glass beads (with a detection limit below 1 ppm) and more recently used to detect explosives- and decomposition-related compounds inside a simulated shipping container [26-28].

In a preliminary investigation of its application to fire debris, PLOT-cryo was shown to extract representative IL compounds from gasoline and diesel fuel from laboratory-generated fire debris [29]. Several advantages stood out from that work. Unlike passive headspace concentration methods in which the distribution of compounds recovered may not represent the distribution of compounds in the headspace vapor due to competitive adsorption or displacement, headspace flow through a capillary vapor trap cooled to sub-ambient temperatures promoted adsorption of all IL compounds by the alumina adsorbent. Because alumina is a weaker adsorbent than carbon, capillaries could be completely eluted with acetone, which is a respiratory irritant, but still a much safer solvent than carbon disulfide. Solvent flow through the capillary also promotes complete

desorption compared to equilibrium desorption with the same solvent. Alumina's ability to be reused is another advantage, while carbon is considered disposable because of the difficulty of verifying complete sample removal. In our 2014 paper, PLOT-cryo was directly compared to the ACS method and found to collect a larger number of compounds on the low-volatility end of each fuel; however, we must note that due to safety concerns, the student researcher eluted ACSs with acetone instead of carbon disulfide. This choice surely had a negative impact on ACS performance, and additional head-to-head experiments are needed before any definitive conclusion can be made.

PLOT-cryo shares features with ASTM Standard Practices E3189-19 and E1413-19 for static and dynamic headspace concentration of IL residues onto adsorbent tubes [30, 31]. In the 2014 fire debris work, we used a flow rate of 1.3 mL/min, which is close to, but still less than, the recommendation for static headspace concentration: 2 mL/min to 80 mL/min. Since then, however, we have employed carrier gas flow rates of up to 10 mL/min in other work with pure compounds and rates up to 100 mL/min using the portable instrument. On the other hand, the collection volume may be greater than 10 % of the headspace volume (guidance that separates static from dynamic headspace concentration), although this depends on the sample container. In the 2014 paper, we used a 2 mL sample vial and collected approximately 40 mL of headspace. This collection volume represents a small fraction of the volume of a quart (< 5 %) or gallon-sized steel can (~ 1 %), which are commonly used to collect fire debris. However, this calculation does not account for the volume occupied by the debris, which typically occupies one-quarter to one-half of the can volume. PLOT-cryo therefore falls somewhere between the ASTM definitions for static and dynamic headspace concentration regarding flow rate and collection volume. Regarding temperature, samples in the 2014 paper were heated to 175 °C, which is higher than recommended in any ASTM standard for headspace concentration of IL residues. Although high sample temperatures generate rapid results, temperatures above 90 °C are unsafe for moist samples because the pressure exerted by water vapor can cause sample containers to violently fail. PLOT-cryo also utilizes a chilled adsorbent to enhance trapping, which is not recommended in any ASTM standard and is a key feature of the PLOT-cryo method.

Our primary goal here is to determine to what extent the PLOT-cryo method might be optimized with a surrogate mixture or “artificial” diesel fuel by examining the influence of flow rate and temperature on the composition and spatial distribution of the collected headspace compounds. Surrogate or artificial mixtures have been used in the past primarily for engine testing

and have been designed to approximate kinetics, combustion, and certain thermophysical characteristics important in that application, such as volatility, viscosity, and energy content [32, 33]. In a recent application to forensic science, researchers used a seven-component artificial gasoline mixture to study the temperature dependence of IL weathering behavior [34, 35]. To investigate variables contributing to distortion of the collected headspace compounds related to ACS saturation, Williams et al. employed a simple hydrocarbon mixture [7]. The mixture was composed of five hydrocarbons selected for their relative volatilities and was an effective choice for the questions being investigated, but it was not intended to be a surrogate (i.e., it did not represent the thermophysical properties of any fuel). We propose that by selecting a thermodynamically representative surrogate mixture we will not only simplify the analysis of trends, but the method development will also be transferable to the more complex target fuel.

To investigate the fitness of surrogate mixtures for this purpose, we first selected a five-component diesel surrogate comprised of compounds with a range of volatilities (described in the next section). While varying the flow rate (0.5 scc/min – 2.5 scc/min) and sample temperature (60 °C – 120 °C), we examined PLOT-cryo collections from neat diesel surrogate and neat diesel fuel to compare the total quantity of collected headspace as well as trends in the volatility and hydrocarbon class. Our findings indicate that the surrogate was a useful tool for predicting the effects of variable sampling parameters on the diesel fuel collections, but it had limitations associated with its simplicity.

## 2. MATERIAL AND METHODS

**2.1. Materials.** Table 1 shows the composition of the diesel surrogate. It contains *n*-octadecane (OD) to represent alkanes, 2,2,4,4,6,8,8-heptamethylnonane (HMN) to represent isoalkanes, 1,2,3,4-tetrahydronaphthalene or tetralin (THN) to represent naphthoaromatics, 1,2,4-trimethylbenzene (TMB) to represent alkylbenzenes, and 1-methyl naphthalene (MN) to represent polynuclear aromatics [33]. We chose this five-component surrogate because its distillation curve has the lowest average difference from the target fuel [36]. Low-volatility compounds are more difficult to collect by headspace methods because they require higher sample temperatures or longer sampling times, which increase the likelihood of displacement. They are often necessary, however, to identify ILs like diesel fuel, especially because ILs undergo weathering at high

temperatures during fires, which preferentially leaves behind less-volatile compounds [37]. OD enabled us to evaluate the effect of experimental parameters on low-volatility compounds, but we note that the surrogate is more volatile than the target fuel, especially at distillate volume fractions of 80 % or greater [33]. The five components of the diesel surrogate and the acetone used as solvent were evaluated for purity and used as received. The diesel surrogate was prepared on a mass basis. The diesel fuel was a commercial, red-dyed, unoxxygenated diesel fuel, which was stored at room temperature in a steel fuel can.

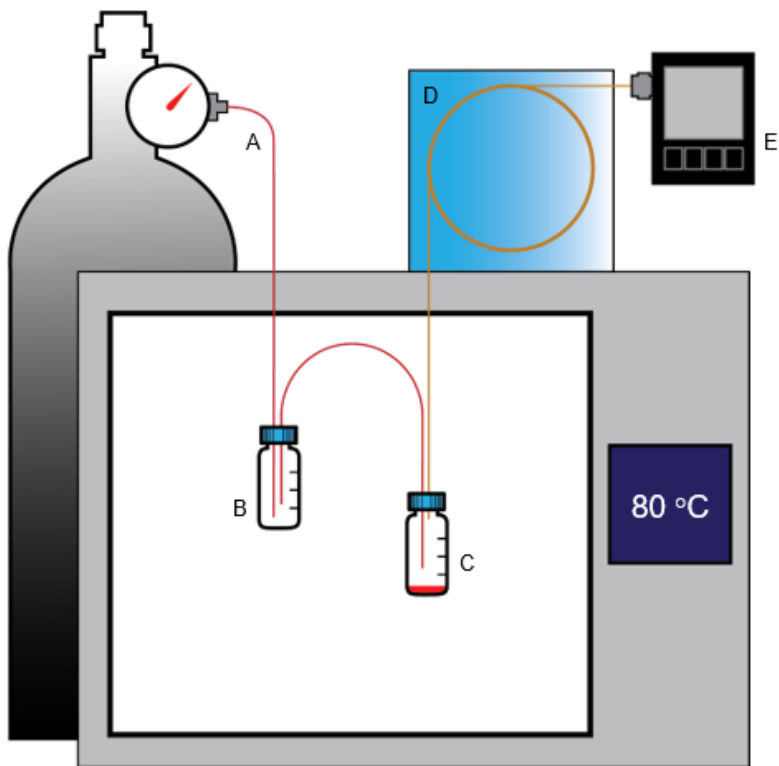
**Table 1. Composition of diesel surrogate [33]**

Compound	Molecular Weight [g/mol]	Boiling Point [°C]	Mole %	Mass %
1,2,4-trimethylbenzene (TMB)	120.2	169	12.5	8.1
1,2,3,4-tetrahydronaphthalene (tetralin) (THN)	132.2	208	20.9	14.7
2,2,4,4,6,8,8-heptamethylnonane (HMN)	226.4	240	27.0	32.8
1-methylnaphthalene (MN)	142.2	244	16.1	12.3
<i>n</i> -octadecane (OD)	254.5	316	23.5	32.1

Sources: 1,2,4-trimethylbenzene [38]; 1,2,3,4-tetrahydronaphthalene (tetralin) [39]; 2,2,4,4,6,8,8-heptamethylnonane [40]; 1-methylnaphthalene [41]; *n*-octadecane [41]

**2.2. Headspace collection.** PLOT-cryo is based on the principles of purge-and-trap headspace collection. Figure 1 shows the complete system, which repurposes a GC oven to provide temperature and flow control. For the experiments presented here, samples were sealed in 2 mL crimp-capped autosampler vials, but larger sample containers can be used. The helium carrier gas is introduced to the oven via the GC inlet and passes through a clean transfer vial before entering the vial containing the sample and flowing upward through the capillary vapor trap. The alumina-coated PLOT capillaries had a diameter of 530  $\mu\text{m}$  and were 95 cm to 100 cm in length. The portion of the capillary that did not descend into the oven was maintained at approximately 0 °C (ranging from -2 °C to 2 °C) with a cryostat installed on top of the oven. The flow rate was controlled by setting the inlet pressure and monitored with a mass flow meter equipped with a totalizer. Manufacturer stated uncertainty in the flow rate measurement is  $\pm 0.01$  scc/min; however, flow rates drifted up to  $\pm 0.1$  scc/min during individual experiments due to the limitations of the electronic pressure controller (EPC) of the GC inlet. Uncertainty for a 40 scc collection volume is 2 % or less. Following each experiment, the capillary was removed for solvent elution at room

temperature. Capillaries were eluted with two sequential 1 mL aliquots of acetone. The first rinse contains the sample, and the second rinse confirms that the captured sample was completely removed, leaving a clean capillary ready for reuse. Smaller volumes of solvent have been sufficient for complete desorption in other work [42].



**Figure 1. PLOT-cryoadsorption.** The carrier gas flows through uncoated fused silica capillary (A) into a clean, empty transfer vial (B), then into the sample vial (C) where the carrier gas mixes with headspace vapor. The carrier gas plus headspace vapor flow upward through the PLOT capillary vapor trap, which is coiled inside the cryostat (D) maintained at 0 °C. The flow rate and collection volume are measured at the other end of the capillary (E).

**2.3. Influence of flow rate and temperature.** In a foundational paper for passive headspace concentration, Newman et al. examined the effects of sample volume, adsorbent capacity (strip size), temperature, and time [6]. In the current work, we employed a single sample volume (100  $\mu$ L) and adsorbent capacity (100 cm capillary length). Setting a constant oven temperature of 120 °C and a flow rate of 1 scc/min, we increased the collection volume until OD could be reliably



identified in the chromatogram with a signal-to-noise ratio of 5 or greater. Based on these preliminary studies (data not shown), we chose 40 scc as a reasonable collection volume. We note that the appropriate collection volume depends on the sample volume and anticipated concentration of analyte and is analogous to the sampling time during passive headspace concentration.

We first explored the effect of flow rate at 120 °C by assessing the following flow rates with the surrogate mixture: 0.5 scc/min, 1 scc/min, 1.5 scc/min, 2 scc/min, and 2.5 scc/min. We next assessed several sample temperatures with the surrogate mixture: 60 °C, 80 °C, 100 °C, and 120 °C. The sampling time was 30 min for a flow rate of 1.5 scc/min and 80 min for a flow rate of 0.5 scc/min. We repeated these experiments at the same four sample temperatures with neat diesel fuel. We evaluated the surrogate results by calculating relative peak areas for the five components. We first evaluated the diesel fuel results by total signal abundance, then by two secondary metrics that examined the composition of the collected vapor in more detail. By running the GC-MS program with an *n*-alkane ladder, we evaluated the carbon number distribution in each sample. We also applied ASTM Standard Test Method D2789, which generates quantitative information about the classes of carbon compounds in a sample from mass spectral data, to observe the effect of temperature on the types of hydrocarbons present in the samples [44].

**2.4 Spatial distribution of surrogate components.** We determined whether breakthrough occurred at 80 °C and 120 °C by bubbling the vapor exiting the capillary vapor trap through a breakthrough (autosampler) vial containing about 1 mL of acetone. The screw top of this vial was kept slightly unscrewed to prevent the vial from impeding the flow. Because the capillary was inserted into the breakthrough vial, we could not continuously monitor the flow rate or use the totalizer function on the flow meter to measure total collection volume; instead, we periodically removed the end of the capillary from the breakthrough vial and inserted it into the flow meter for a flow rate reading. At least eight flow rate measurements were made over the course of each ~30 min experiment. The averaged flow rate readings were multiplied by the collection time to determine the total collection volume, which was approximately 40 scc. We examined the distribution of surrogate compounds by segmenting the capillary into 20-cm lengths with a ceramic knife immediately after headspace collection. We eluted each segment separately with 1 mL of

acetone. We conducted this experiment in triplicate with a total collection volume of 40 scc, a flow rate of 1.5 scc/min, and a sample temperature of 80 °C.

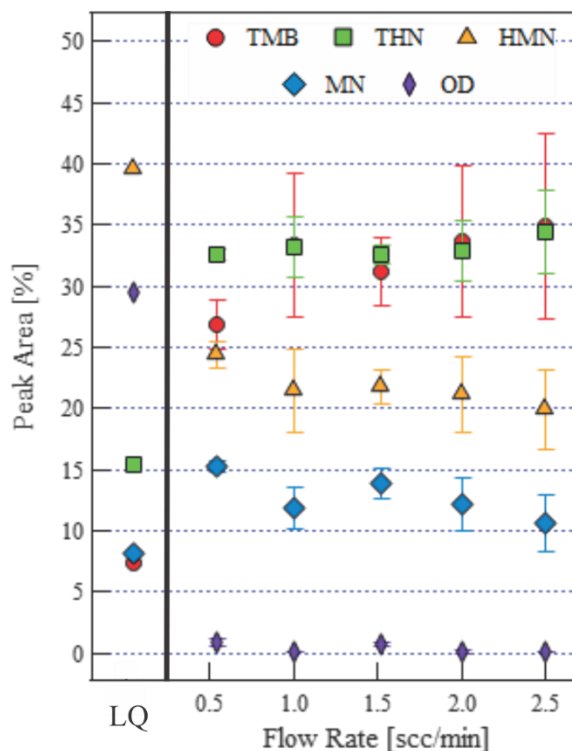
**2.5. Diesel fuel on debris.** We generated debris by heating Douglas fir wood blocks on a hot plate, then igniting them with an ethylene torch in the absence of any IL, allowing them to self-extinguish, and re-igniting them until they would not continue to burn. We have used this method of creating debris for several years and know that the resulting sample has no background signal. This debris resembling charcoal was homogenized into small pieces, and individual samples for PLOT-cryo collection were created by adding neat diesel fuel to a small amount of debris (approximately 1 mL) in a 2 mL vial. Samples were prepared with 15  $\mu$ L, 4  $\mu$ L, 0.5  $\mu$ L, and 30 nL of diesel fuel. After spiking, no liquid fuel was observable.

**2.6. GC-MS Analyses.** We employed a gas chromatograph with mass spectrometer and a 5% phenyl polydimethylsiloxane capillary column (30 m x 250  $\mu$ m x 0.25  $\mu$ m). The instrument method for diesel surrogate was as follows: injection volume 1  $\mu$ L; inlet temperature 300 °C; 200:1 split ratio, initial oven temperature 100 °C, then 15 °C/min to 130 °C, then 0.1 °C/min to 130.7 °C, then 40 °C/min to 285 °C. (The very slow ramp in the middle of the method was required to separate HMN and MN.) The MS was operated in scan mode: 30-550 m/z. The instrument method for diesel fuel was as follows: injection volume 1  $\mu$ L; inlet temperature 325 °C; 100:1 split ratio; initial oven temperature 50 °C for 1 min, then 15 °C/min to 180 °C. The MS was operated in dual mode: scan 41-550 m/z and SIM ions 41, 43, 55, 57, 67, 68, 77, 78, 103, 104, 128, 141.

### 3. RESULTS AND DISCUSSION

**3.1. Influence of flow rate.** In general, dynamic headspace concentration cannot be assumed to be an equilibrium process, because vapor-liquid equilibrium (VLE) cannot be established if the vapor is too rapidly removed from the headspace. However, it is possible under certain conditions. We have previously demonstrated that at flow rates up to 10 scc/min, vapor-liquid or vapor-solid equilibrium can be established for pure compounds, permitting the determination of vapor pressure as a function of temperature [22, 42, 43]. Equilibrium is not a requirement for the extraction of IL residue from fire debris, but repeatability is an advantage. We tested the effect of flow rate to

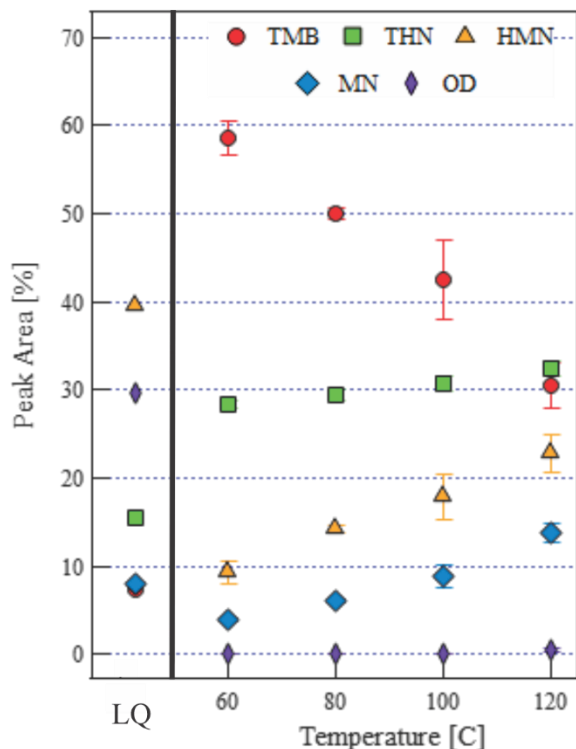
identify conditions that led to stable and repeatable vaporization inside the sample vial. We anticipated that the kinetics of vaporization for each compound would cause its enrichment or depletion in the headspace as a function of flow rate. Figure 2 shows the effect of flow rate on the relative distribution of surrogate components collected by the capillary vapor trap. The flow rates investigated here replace the entire headspace volume (2 mL) in 4 min (0.5 scc/min) or in less than 1 min (2.5 scc/min). The relative quantity of the most volatile component, TMB, appears to increase with flow rate, while the relative quantity of lower-volatility components appears to remain constant or slightly decrease with increasing flow rate. For example, the relative quantity of the least volatile component, OD, decreased by nearly an order of magnitude from 0.5 scc/min to 2.5 scc/min. However, the observed differences (30 % increase for TMB; 30 % decrease for MN) were not statistically significant due to large relative standard deviations. In fact, the most prominent feature of this data is the increase in the scatter in the relative peak areas with flow rate. This result suggests mechanical disturbance of the liquid sample due to turbulence. Larger sample containers such as quart cans may be able to tolerate higher flow rates because the duration of contact between sweep gas and sample is a function of container volume. The surrogate is a useful tool to empirically determine the maximum flow rate as a function of headspace volume, as each component can be separated and quantified. Based on the results in Figure 2, all subsequent experiments utilized flow rates of 0.5 scc/min or 1.5 scc/min.



**Figure 2.** Flow rate influences the distribution of each component in the collected headspace. Each data point is the average of six replicates, and error bars represent one standard deviation. The distribution of each component in the neat liquid (LQ) is provided for reference. Total collection volume = 40 scc (time = 80 min, 40 min, 30 min, 20 min, or 16 min); temperature = 120 °C.

**3.2. Influence of temperature.** Higher temperatures increase the availability of lower-volatility compounds in the vapor phase. Figure 3 shows that temperature has the expected effect on relative quantities of the surrogate components, which have a wide range of volatilities. Note that the vertical axis is area percent, not total absolute signal; that is, the quantity of TMB collected at 120 °C is not *less* than at 60 °C—it is only a less dominant component relative to the others. TMB and THN are enriched in the vapor at all temperatures, whereas HMN and OD are depleted compared to the neat liquid. MN is depleted at 60 °C, but enriched at 120 °C. Although it is difficult to discern due to the vertical axis in this figure, OD is present at 100 °C and is most abundant at 120 °C. This finding demonstrates the difficulty of recovering low-volatility compounds from mixtures containing higher-volatility compounds. We used a large volume of diesel surrogate (100  $\mu$ L) such that the liquid phase remained essentially constant in volume and composition. Smaller volumes

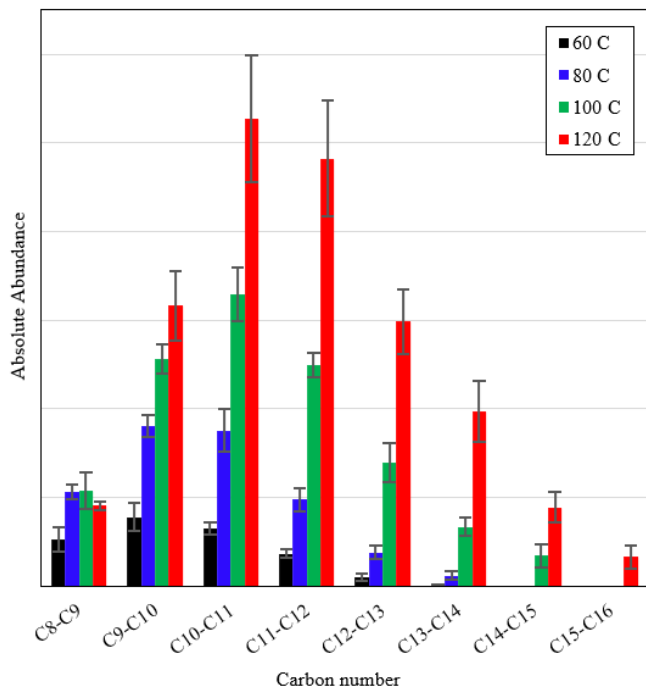
of surrogate, which might be fully vaporized under some temperatures and collection volumes, should be investigated in future experiments.

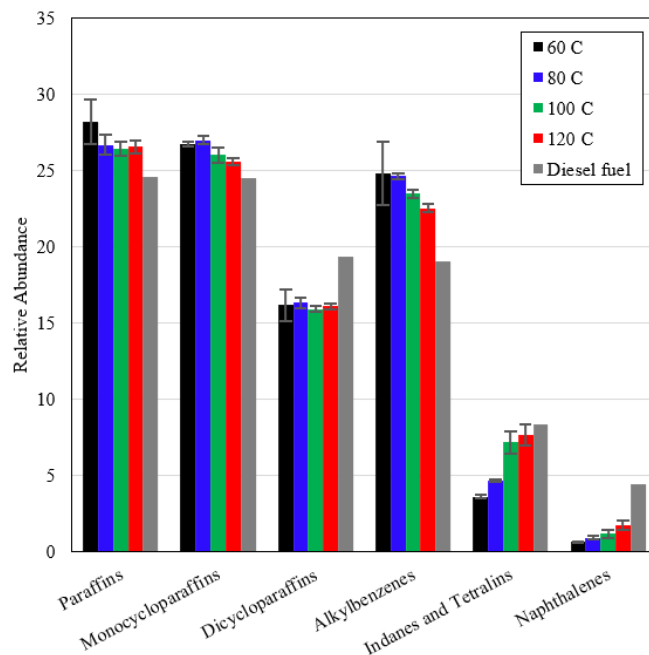


**Figure 3. Temperature influences the distribution of each component in the collected headspace. Each data point is the average of three replicates, with the exception of the data points at 120 °C, which are the average of nine replicates. Error bars represent one standard deviation. The distribution of each component in the neat liquid (LQ) is provided for reference. Total collection volume = 40 scc; flow rate = 1.5 scc/min.**

In the absence of breakthrough, PLOT-cryo recovers all compounds from the collection volume, and therefore, higher temperatures should yield a higher total mass of recovered compounds, whether the IL being sampled is diesel surrogate or diesel fuel. For constant sample volume, collection volume, and flow rate, increasing the temperature from 60 °C to 120 °C leads to an eleven-fold increase in total signal abundance for diesel surrogate and a four-fold increase for diesel fuel. Figure 4a shows the magnitude of this effect for diesel fuel; the vertical axis represents absolute abundance. Temperature also has a strong effect on the carbon number distribution of the collected vapor. As temperature increases, the average carbon number of the

vapor increases (average volatility decreases). Neat diesel fuel, although not plotted in Figure 4a, has a carbon number distribution centered around a peak in the C14-C15 region. By comparison, the vapor composition at all temperatures is shifted towards more volatile compounds, but only the vapor collected at the higher two temperatures contain any compounds in that region. These results are consistent with our findings in the surrogate experiments. For example, HMN, a 16-carbon compound, shows a dramatic increase in relative abundance with increased temperature—doubling from 60 °C to 120 °C (Figure 3)—predicting the differences observed in Figure 4a. Interpreting the surrogate results is clearly a simpler task while being predictive of subtler effects of temperature on real diesel fuel samples.





**Figure 4. Temperature influences the carbon number distribution of the diesel fuel headspace (a) but has a minor influence on the compound class distribution (b). In (a), each carbon number range is defined by the chromatographic retention times of the relevant alkanes in the *n*-alkane ladder. In (b), carbon class distribution was calculated according to ASTM Standard Test Method D2789 [44]. Each bar represents the average of five measurements. Total collection volume = 40 scc; flow rate = 0.5 scc/min.**

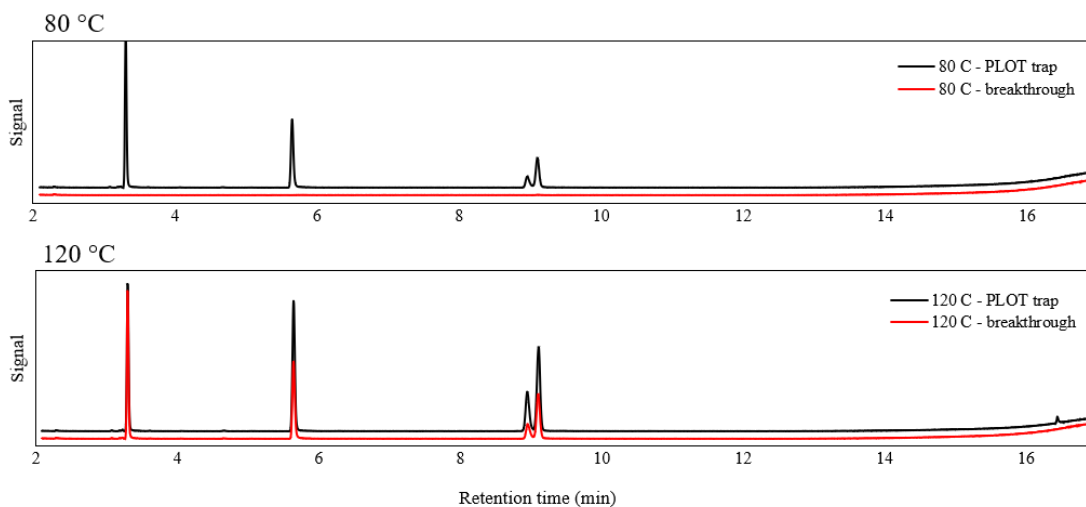
Figure 4b shows that temperature does not have a major effect on hydrocarbon class distribution. Indanes/tetralins and naphthalenes both moderately increase with temperature; however, this is explained by the lower volatility that characterizes those classes of bicyclic compounds. Because all the classes are observed at each temperature, and in the same approximate relative quantities, a fire debris analyst using hydrocarbon classification as part of their assessment would be able to identify diesel fuel regardless of which of these temperatures were used in collection. Notably, these findings could not be predicted with the five-component surrogate. Because the mixture is so simple, it lacks the distribution of hydrocarbon classes that are required to generate a meaningful D2789 analysis.

For single components, the natural log of the mass recovered by a PLOT-cryo collection (measured in grams per liter of carrier gas) was previously shown to be proportional to the inverse sample temperature, consistent with the van't Hoff equation [21, 22]. These papers demonstrated

that PLOT-cryo measurements can provide order-of-magnitude estimates of the enthalpy of vaporization; however, mixture or matrix effects led to variable results from complex multicomponent samples. Figures 2 and 3 are the first-ever PLOT-cryo measurements of a simple fluid mixture and the consistency in the relative peak areas suggest that it may be possible to modify PLOT-cryo for use in vapor-liquid equilibrium (VLE) measurements with the addition of standard curves. Our group has previously measured VLE of complex mixtures using a distillation approach [45]; however, a PLOT-cryo VLE measurement would provide access to a much wider range of temperatures. Although data from Figure 2 indicates that stable vaporization can be achieved at moderate flow rates, the system is capable of lower flow rates if they are required. Of course, VLE is a simplification of fire debris headspace, which is subject to matrix effects and multiple partitioning relationships. Still, measuring the VLE of complex mixtures like ILs is an important research area relevant to thermal weathering of arson fire debris [45, 46].

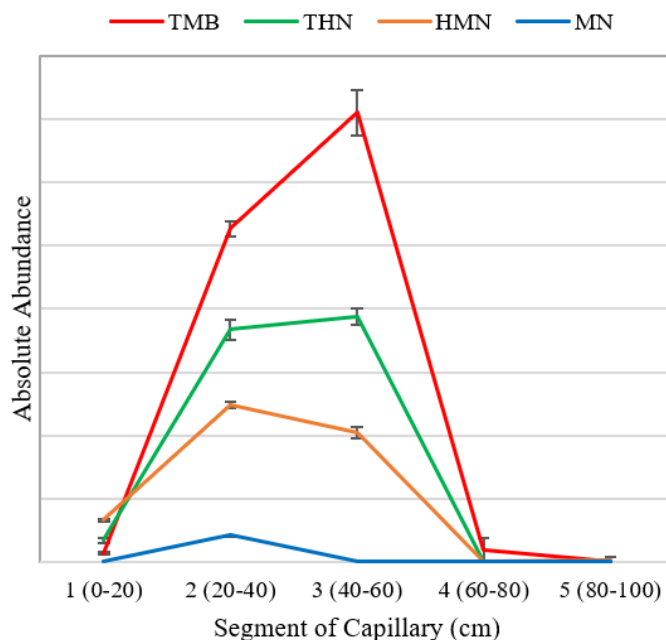
**3.3. Spatial distribution of analytes.** At 80 °C, the breakthrough vial was free from surrogate compounds, indicating that breakthrough did not occur. At 120 °C, however, it was evident from GC-MS analysis that significant breakthrough occurred, with TMB, THN, MN, and HMN appearing in the breakthrough vial (Figure 5). Volatility clearly influenced the composition of the mixture found in the breakthrough vial. TMB, the most-volatile component, was enriched in the breakthrough vial relative to the capillary. OD was detected in the capillary (Figure 5, bottom, 16.4 min) but did not break through due to its low volatility. Notably, there was a point during the experiment at which the end of the capillary between the cryostat and flow meter began to darken in color as analytes reached this section of the capillary vapor trap. This real-time indication of imminent breakthrough, even in the absence of GC-MS analysis, might be used to maximize signal while avoiding breakthrough. More experiments would be required to show that this visual indication occurs prior to every instance of breakthrough; if so, this could be a major advantage of PLOT-cryo over other types of headspace analysis.





**Figure 5. Representative chromatograms indicate that breakthrough did not occur at 80 °C (top); however, at 120 °C (bottom), breakthrough compounds include TMB (3.3 min), THN (5.7 min), MN (8.9 min), and HMN (9.1 min). Signal traces are offset for clarity.**

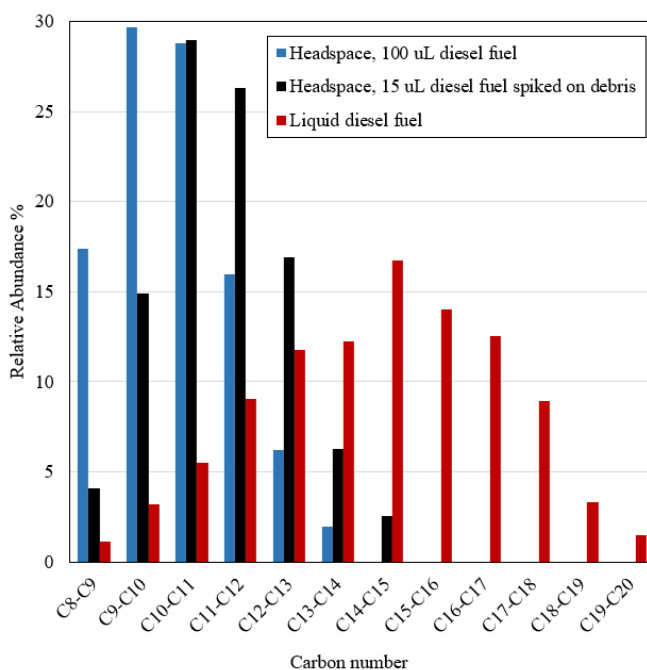
The retention of analytes on the capillary vapor trap is dependent on their relative affinities for the gas phase and the sorbent phase, which is a function of temperature, analogous to chromatography. Figure 6 shows the spatial distribution of surrogate components based on individual analysis of five segments of the capillary after headspace collection. TMB, the most volatile component, was present in a lower quantity than THN and HMN in segment 1, but most abundant in segments 2 and 3. Consistent with its high volatility, it was the only component that traveled far enough through the capillary to be present in segment 4. The quantities of HMN and MN, which have very similar boiling points (Table 1), both peaked in segment 2; while MN was only detected in segment 2, HMN was much more abundant and also detected in segments 1 and 3. Confirming and extending our earlier finding that breakthrough did not occur at 80 °C (Figure 5), no analytes were detected in segment 5. By contrast, at 120 °C, TMB, THN, HMN, and MN were abundant in segments 3, 4, and 5 (data not shown).

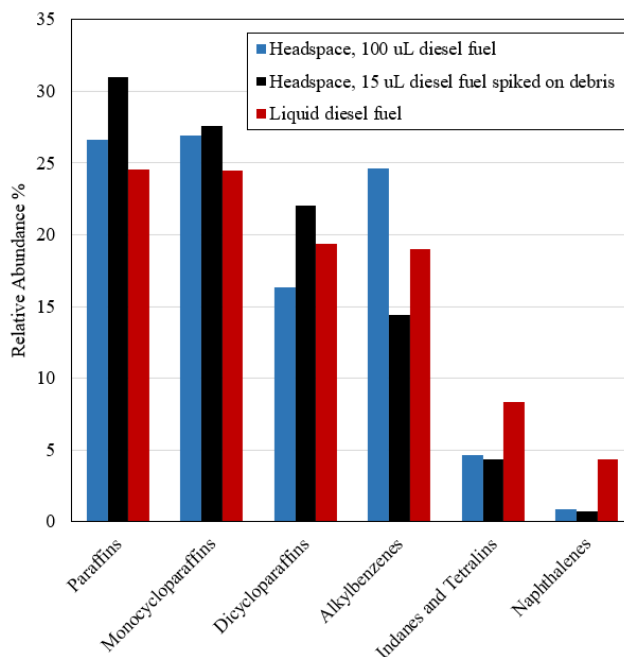


**Figure 6.** The spatial distribution of surrogate components. The first 20 cm of the capillary after the sample vial (segment 1) is within the oven (80 °C). Most of the final 20 cm of the capillary travels from the cryostat to the flow meter (segment 5) and is at room temperature (20 °C). Segments 2 – 4 are within the cryostat (0 °C). OD was not detected in any segment and is not plotted. Each data point is the average of three replicates, and error bars represent one standard deviation. Total collection volume = 40 scc; flow rate = 1.5 scc/min; temperature = 80 °C.

**3.4. Modifications for simulated debris experiments.** While the primary goal of this work has been to examine the influence of PLOT-cryo sampling parameters on the composition and spatial distribution of the collected headspace by employing a surrogate mixture, real fire debris is a complex mixture of IL residue (if present), partially burned material (such as carpeting, vinyl flooring, and/or wood subfloor), and often residual water from firefighting efforts. Fire debris can be created by spiking IL onto wood (or other materials) and igniting it [29]; however, the resulting debris will be variable. We examined spiking IL onto charcoal debris to replicate some of the characteristics of laboratory-generated fire debris while being nominally identical. Based on the limitations revealed by Figure 4, we chose real diesel fuel for these experiments. We first determined the limit of detection, which was 0.5  $\mu$ L of diesel fuel spiked onto ~0.09 g (about 1 mL) of crushed wood debris resulting in a concentration of 0.5 %. Charcoal debris has a negative

effect on the total mass collected, suggesting that vaporization is inhibited. These experiments represent the maximum of this effect, because the debris used here was completely converted to charcoal with no visible unburned wood material remaining. The presence of debris also affects carbon number and class distributions. Relative to diesel headspace in the absence of debris, these experiments show an average carbon number shift towards heavier hydrocarbons (Figure 7a). The presence of debris also shifts the carbon classification (Figure 7b) away from alkyl benzenes and towards paraffin classes relative to diesel headspace without debris. This suggests not only that some compounds are adsorbed to the debris but that preferential adsorption of aromatic species occurs, decreasing the abundance of those species in the vapor. These experiments demonstrate the importance of partitioning and preferential adsorption, and ongoing work to optimize PLOT-cryo sampling parameters includes IL-spiked debris.





**Figure 7. The carbon number distribution (a) and carbon class distribution (b) of diesel fuel headspace is compared to diesel fuel headspace in the presence of fire debris and neat diesel fuel. Carbon class distribution was calculated according to ASTM Standard Test Method D2789 [44]. These results represent a single sample collection. Total collection volume = 40 scc; flow rate = 0.5 scc/min; temperature = 80 °C.**

The quantity of charcoal debris used above was limited by the sample vials. To utilize more realistic quantities of debris, we must sample from larger containers, such as steel cans. However, when a sample container is heated, air within the container expands and causes flow through the vapor trap (if present), or pressurization of the container. For a headspace volume of 2 mL, the ideal gas law predicts an expansion of 0.25 mL (at 60 °C) or 0.39 mL (at 80 °C). These expansion volumes are negligible compared to the 40 scc collection volume, so we collected the small amount of vapor generated while the container thermally equilibrated. For a quart-sized steel can that is half full of debris, the headspace volume is approximately 500 mL. The ideal gas law predicts an expansion of 63 mL (at 60 °C) or 97 mL (at 80 °C). These expansion volumes are greater than the collection volume used here; therefore, these containers must be thermally equilibrated before sampling without losing any headspace vapors.

We examined leaks by measuring expansion volumes from different containers. Expansion volume measurements from crimp-capped vials were highly reproducible (standard deviation

equal to 0.01 mL) and indicated that less than 3 % of the expanded volume was lost during heating to 60 °C or 80 °C. Expansion volume measurements from quart-sized steel cans were inconsistent (standard deviation greater than 1 mL) and indicated the loss of 10 % or more of the expanded volume. Leak rates during passive headspace concentration have been quantified in other studies [47], and dynamic headspace concentration driven by positive pressure places a greater demand on the sample container. To prevent the loss of headspace vapors, we have developed the following procedure for sampling large amounts of debris: IL-spiked debris is placed inside a quart-sized steel can and is then heat-sealed into an evidence bag with attached fittings, which is known to have a low leak rate [48]. The evidence bags are partially prefilled with the inert carrier gas and heated to the desired temperature. This procedure, which we have adopted for ongoing work to optimize PLOT-cryo sampling parameters, allows for thermal equilibration and expansion without vapor loss.

#### **4. CONCLUSION**

Surrogate mixtures designed to represent complex fluids with fewer components have long been used to simplify fuels research, but their potential contributions to forensic science have not yet been fully explored. We demonstrated here that a five-component diesel fuel surrogate was a valuable tool for developing PLOT-cryo adsorption for headspace concentration of ILs from fire debris. The thousands of components in diesel fuel lead to data analysis challenges, especially when looking for subtle differences in the results of different sampling parameters. With a surrogate, we easily determined the maximum flow rate as a function of headspace volume, as each component could be separated and quantified. We were also able to elucidate temperature-dependent trends in carbon number distribution that were borne out in subsequent experiments using actual diesel fuel. For constant sample volume, collection volume, and flow rate, increasing the temperature from 60 °C to 120 °C led to an eleven-fold increase in absolute abundance for diesel surrogate and a four-fold increase for diesel fuel. Higher sample temperatures were able to capture octadecane, the lowest-volatility compound, but the highest temperature was also subject to breakthrough. We studied the spatial distribution of analytes inside the PLOT capillary vapor traps by segmenting them immediately after headspace sampling and observed darkening of the final segment, which is a promising real-time indicator of imminent breakthrough of high volatility compounds. We found that using a simple surrogate mixture to explore experimental parameters

was a useful approach, although the surrogate we chose was so simple that it could not be used to predict hydrocarbon class trends. For ongoing work to optimize experimental parameters, we demonstrated the importance of burned debris by its effect on carbon number and carbon class distribution of the collected headspace and developed methods to thermally equilibrate realistic fire debris containers without vapor loss.

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