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Extraction of Ignitable Liquid Residues by Dynamic Capillary Headspace Sampling and Comparison to the Carbon Strip Method

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Project Summary

Major Goals and Objectives

The primary goal for this project was to assess the value of an alternative headspace concentration method for the extraction of ignitable liquids (IL) related to fire debris. Headspace methods provide clean samples for analytical analysis, do not require direct contact with potentially dangerous artifacts, are non-invasive, and can be non-destructive. Dynamic vapor microextraction (DVME) is a small-volume purge and trap method that concentrates vapor phase analytes onto a short (1 m to 3 m) section of porous layer open tubular (PLOT) capillary coated with an adsorbent material. DVME has been successfully applied to the analysis of explosives (Lovestead & Bruno, 2010), grave soil (Lovestead & Bruno, 2011), and fuels (Burger et al., 2016a; Harries et al., 2021a) in the laboratory, and has been used to extract volatile compounds from a simulated shipping container in the field (Harries et al., 2019). To evaluate debris from structural fires for IL residue, forensic laboratories in the United States typically utilize passive headspace concentration onto activated carbon strips (ACSs) (ASTM E1412-19), followed by solvent elution and analysis. The high affinity of ACSs for hydrocarbons requires the use of carbon disulfide, a dangerous neurotoxic solvent, to recover these compounds. By contrast, DVME can recover characteristic compounds from laboratory-generated fire debris with a relatively benign solvent: acetone (Nichols et al., 2014). However, preliminary experiments were conducted with a small quantity of debris in crimp cap vials (the debris had to be pulverized prior to adding to the container) and employed instrument settings that would be unreasonable for the analysis of authentic fire debris (e.g., oven temperatures above 100 °C). This project will investigate whether DVME has potential as a practical alternative for fire debris analysis and lay the necessary groundwork for future validation, standardization, and implementation.

Research Questions

1. Can we adapt DVME for fire debris casework containers and realistic oven temperatures? DVME was developed with crimp cap vials that are not suitable for fire debris analysis. Containers with larger volumes are needed to account for the large and often irregularly shaped debris collected after a structural fire. Similarly, DVME was demonstrated for fire debris analysis at an oven temperature that is not compatible with water-soaked fire debris. Both modifications are required for DVME to progress towards IL extraction from authentic fire debris.
2. Can we utilize nuclear magnetic resonance (NMR) spectroscopy to quantitatively assess differences in the adsorptive properties of the materials used to trap headspace vapors in real time? It is well known that the activated carbon strips used for passive headspace concentration can lead to vapor distortion (Newman et al., 1996; Williams et al., 2005). While DVME and other dynamic headspace concentration

methods may be less reliant on the properties of the adsorbent material due to the possibility of cooling the capillary vapor trap, capillaries are available with different adsorbent materials such as activated carbon or alumina. Quantitating the difference in their adsorptive/desorptive properties can provide guidance for choosing the most appropriate material to trap headspace vapors.

3. Can we determine the DVME instrument settings that most impact IL extraction from authentic fire debris? Tunable instrument factors have not been investigated in conjunction with realistic differences in the composition of fire debris (e.g., water from firefighting efforts). Significant instrument factors direct future research on optimization, while non-significant factors identify elements that might be modified to facilitate adoption in forensic laboratories.

Research Design, Methods, Analytical and Data Analysis Techniques, and Experimental Data for Question 1

Research Design. DVME was first demonstrated for fire debris analysis with an instrument that repurposed a gas chromatography oven for temperature control and utilized the electronic pressure controller to set the inlet flow. Samples were prepared in crimp cap vials and the portion of the capillary vapor trap outside the oven was chilled with a vortex tube. The outlet flow passed through a breakthrough vial containing acetone and the flow rate was periodically measured with a mass flow meter. During the current project, we redesigned the apparatus to incorporate a mass flow controller (to replace the electronic pressure controller) and a thermoelectric cooler (to replace the vortex tube). With this apparatus, the inlet flowrate can be set in standard cubic centimeters per minute (sccm) and the outlet flowrate is measured. Figure 1 illustrates the new instrument. Carrier gas mixes with headspace vapors inside the container and then flows into a capillary vapor trap that can be cooled with the thermoelectric cooler. Flow leaving the capillary next passes through a breakthrough vial containing *n*-hexane to trap any headspace vapors that were not adsorbed by the capillary. Finally, the flow exiting the breakthrough vial passes through a mass flow meter to determine the total volume of headspace vapor that passed through the

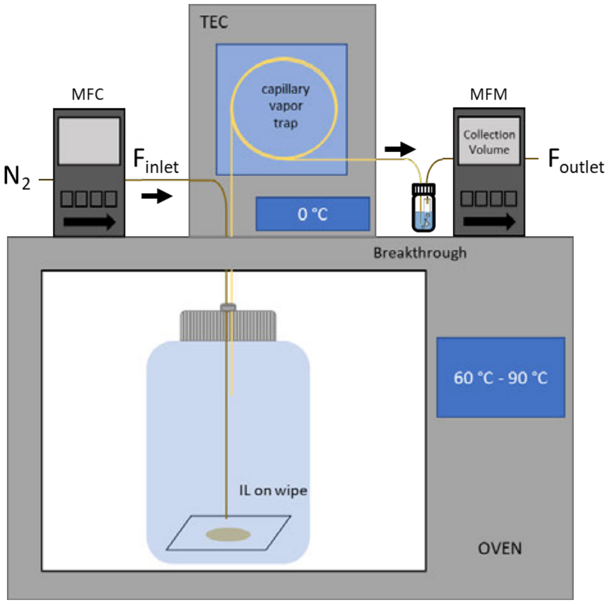

Figure 1: Dynamic vapor microextraction. Carrier gas flows through a non-adsorbent fused silica capillary into a casework container that is heated inside an oven. Flow into the container (F_{inlet}) is controlled by a mass flow controller (MFC). Carrier gas mixes with headspace vapors inside the container and then flows through a capillary vapor trap cooled by a thermoelectric cooler (TEC) within a rigid foam insulation block. Flow from the capillary vapor trap passes through a breakthrough vial containing 1.0 mL of *n*-hexane and the flow exiting the breakthrough vial (F_{outlet}) is measured by a mass flow meter (MFM).

capillary during the experiment, referred to as the collection volume and measured in standard cubic centimeters (scc). We first examined realistic temperatures with diesel surrogate or diesel fuel in crimp cap vials. These experiments were designed to monitor the effect of oven temperature on the composition and distribution of compounds in the capillary vapor trap. We next examined several possible casework containers, again at realistic temperatures, with weathered gasoline.

Methods. Samples consisted of neat liquids, specifically diesel surrogate, diesel fuel, or weathered gasoline. The five-component diesel surrogate (Burger et al., 2016b; Mueller et al., 2016) contained *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. The 50% weathered gasoline was prepared by room temperature evaporation. Diesel surrogate and diesel fuel were added directly to crimp cap vials with the capillary inserted through the septum. Weathered gasoline was spiked onto a laboratory wipe inside a casework container. The casework containers chosen were metal cans with friction sealed lids, metal cans placed within heat sealed polymer evidence bags, and glass jars with two-piece lids. For these containers, a stainless-steel port with a septum for capillary insertion was added and sealed with an O-ring. The capillary vapor traps were coated with alumina. We used 1 m / 320 μm diameter capillaries when the container was a crimp cap vial and 3 m / 530 μm diameter capillaries for casework containers because less pressurization was required to drive the flow. Following headspace concentration, the headspace vapors trapped on the capillary were recovered by elution. This was done by inserting the outlet of the capillary into a vial containing 1.0 mL of acetone, the elution solvent. The inlet was inserted into a second vial. Nitrogen gas, controlled by the mass flow controller, was then used to force the entire solvent volume through the capillary, recovering the trapped vapors. This eluate was analyzed by gas chromatography-mass spectrometry (GC-MS) with a single quadrupole mass spectrometer.

Analytical and Data Analysis Techniques. GC-MS analysis of the eluates employed total ion current (TIC) mode and a temperature ramp suited to each of the three neat liquids. Eluates resulting from a headspace concentration experiment of diesel surrogate were evaluated by calculating relative peak areas for each of the five surrogate compounds, if present, in the eluate. For diesel fuel, we separately injected an alkane ladder containing *n*-octane through *n*-eicosane. Eluates resulting from a headspace concentration experiment of diesel fuel were evaluated by calculating their carbon number distribution. For weathered gasoline, we separately injected a reference sample of 50% weathered gasoline in acetone and used the resulting retention times and ion spectra to identify 55 target compounds that ranged in volatility and represented different chemical classes. Eluates resulting from a headspace concentration experiment of weathered gasoline were evaluated for these 55 target compounds and the number of compounds detected served as the response variable.

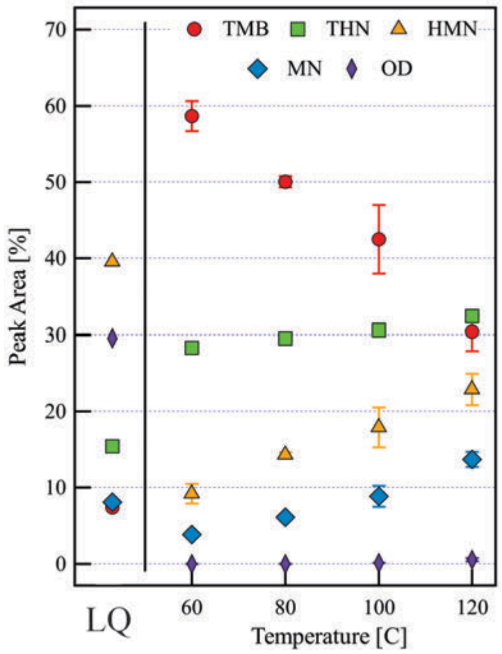

Figure 2: Temperature influences the distribution of each compound in the eluate. Each data point is the average of three replicates, with the exception of the data points at 120 °C, which are the average of nine replicates. Error bars are one standard deviation. The distribution of each compound in the neat liquid (LQ) is provided for reference. Total collection volume = 40 scc; flow rate = 1.5 scc/min.

Experimental Data. Replicate experiments from crimp cap vials containing diesel surrogate or diesel fuel were conducted at four oven temperatures. When diesel surrogate was employed, each compound in the eluate was chromatographically separated to examine its relative abundance as a function of oven temperature. Figure 2 shows the results of this experiment. Lower oven temperatures led to the collection of less total analyte and shifted its composition towards higher volatility compounds. Additionally, the vapor composition differed from the liquid composition for all instrument settings, an expected result based on vapor liquid equilibrium. Consistent with chromatographic theory, higher volatility compounds traveled furthest along the length of the capillary vapor trap and were more prone to breakthrough. Qualitative observations made with the diesel surrogate about the effect of oven temperature could be translated to diesel fuel. Specifically, decreasing the oven temperature from 120 °C to 60 °C led to an elevenfold decrease in total abundance and a shift in the carbon number towards higher volatility compounds. The vapor composition again differed from the liquid composition, as indicated by a carbon number distribution that centered on C10-C11 for eluates resulting from headspace concentration at 80 °C, vs. C14-C15 for diesel fuel.

Replicate experiments from casework containers containing 50% weathered gasoline were conducted at multiple oven temperatures and collection volumes. These experiments could not be done with metal cans sealed with a friction lid. We found that leaks through the lid were so pervasive that typical inlet flow rates (≤ 10 sccm) did not result in any flow through the capillary vapor trap. Thus, headspace concentration is impossible. We therefore devised a second container, a heat-sealed polymer evidence bag, to enclose an open metal can. After sealing, the bags were pre-filled with 450 scc of nitrogen, resulting in a headspace volume of approximately 3.1-3.2 L. The third container was a 950 mL glass canning jar sealed with a two-piece lid. We compared the suitability of metal cans in polymer bags vs. glass jars by adding the same volume (10 µL) of 50% weathered gasoline to each container and varying oven temperature and collection volume in a randomized factorial design. In total, 14 experiments were performed with metal cans in polymer bags and 21 experiments were performed with glass jars. Figure 3 shows that 42-50 of the target compounds could be recovered when the container was a glass jar, whereas only 10-20 compounds could be recovered when the container was a metal can inside a polymer bag. The compounds recovered from polymer bags also had lower retention times, i.e., had higher volatility, than those recovered from glass jars. The difference in performance may be due to the loss of headspace vapors to the polymer bag, potentially due to adsorption, the focus of Research Question 2.

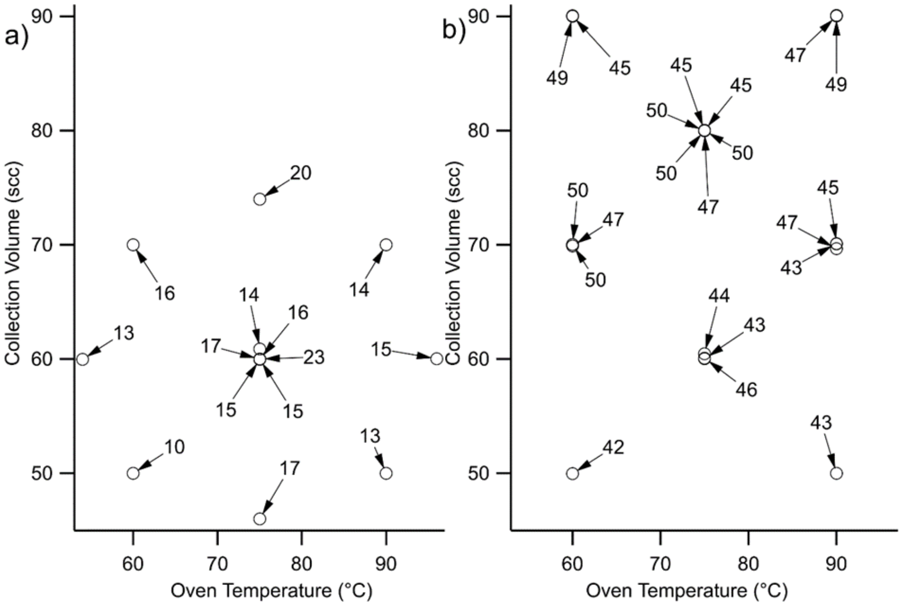

Figure 3: Target compounds identified as a function of oven temperature (x axis) and collection volume (y axis) after headspace concentration from metal cans in polymer bags (a) or glass jars (b) containing 10 µL of 50% weathered gasoline spiked onto a wipe. Replicates with the same instrument settings are indicated by multiple labels showing total target compounds.

Research Design, Methods, Analytical and Data Analysis Techniques, and Experimental Data for Question 2

Research Design. NMR spectroscopy is most often employed qualitatively to probe the structure of organic molecules in solution. However, quantitative measurements of composition are possible in liquids and were recently demonstrated in the vapor phase (Suiter et al., 2019, Suiter et al., 2020, Miller et al., 2023). An advantage of these measurements is that they are absolute, with the peak areas in a given spectrum being directly proportional to the number of atoms contributing to the peak area. In this portion of the project, we developed two NMR based approaches to quantitatively probe adsorptive interactions between vapor phase molecules and adsorbent materials in real time. The first approach mimicked passive headspace concentration (ACS method), while the second approach mimicked dynamic headspace concentration (DVME method). Figure 4 and Figure 5 provide details on the experimental configurations for these approaches.

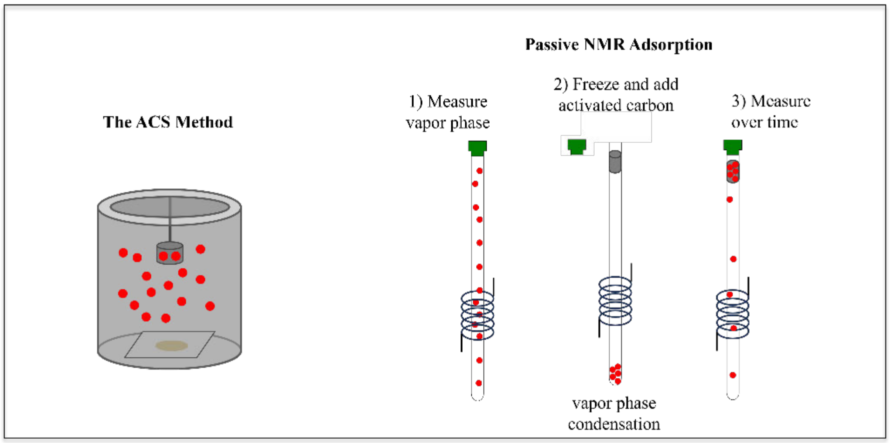

Figure 4: The passive NMR adsorption experiment closely resembles the ACS method and was developed to probe the adsorptive properties of activated carbon strips. First, the sample of interest is added to a tube and sealed, and the initial vapor peak area(s) are measured. Next, the sample is frozen using liquid nitrogen to prevent vapor loss, the cap is removed, an adsorbent is added to the headspace (i.e., outside the detectable region of the NMR magnet, indicated by the coil), and the cap is replaced. Finally, the vapor peak area(s) are measured over time to quantify the adsorption.

To mimic passive headspace concentration, we used a single NMR tube sealed with an air-tight cap and monitored compounds in the vapor phase. Figure 4 details the experimental procedure. This experimental approach was tested with propane and a binary mixture of propane and acetone. Although this mixture is not a traditional ignitable liquid, it serves as a good proxy as it has both a liquid and vapor phase at room temperature and the two compounds differ in volatility with propane boiling at -42.0 °C and acetone at +56.2 °C. The adsorbent material for both experiments was an activated carbon strip.

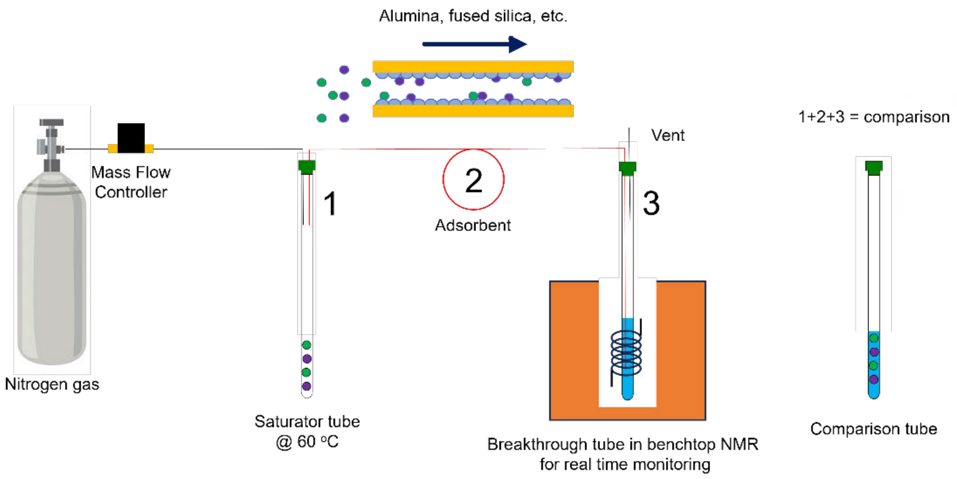

Figure 5: The dynamic NMR adsorption experiment closely resembles the DVME method and was developed to probe the adsorptive properties of capillaries. First, the sample of interest is added to a saturator tube and an identical comparison tube. Next, nitrogen carrier gas flows through a non-adsorbent fused silica capillary into the saturator tube, which is held at 60 °C in a water bath. This container replaces the crimp cap vials or casework containers used in the DVME method. Flow (0.2 sccm – 0.5 sccm) is controlled by a mass flow controller. Carrier gas mixes with headspace vapors inside the saturator tube and then flows into a capillary vapor trap

with an adsorbent material. The capillaries are not temperature controlled. Flow continues into a breakthrough tube containing acetone. NMR spectroscopy is used to measure the composition in the breakthrough tube in real time; each composition measurement requires several minutes. After the flow of gas is stopped, acetone is added to the saturator tube so the composition that remains can be measured. Finally, the capillary vapor trap is eluted with acetone (as described in the method section for Research Question 1) so its composition can be measured.

To mimic dynamic headspace concentration, we used two NMR tubes sealed with air-tight caps, connected by a capillary vapor trap, and monitored compounds in the liquid phase. Figure 5 details the experimental procedure. Our assumption for these experiments is that each analyte can only be in three places: the saturator tube where it is placed at the start of the experiment, the capillary where it could be trapped due to adsorption, or the breakthrough tube where analytes are trapped by a small volume of solvent. This experimental approach was tested with a five-component mixture of hydrocarbons and a binary mixture of toluene and isooctane. The mixtures were chosen to provide a range of chemical classes and boiling points and do not simulate any specific ignitable liquid. The adsorbent material inside the capillary was either alumina or activated carbon. Fused silica capillaries without an adsorbent were also used to test the experimental approach.

Methods. For passive adsorption measurements, data were collected on a 14.1 T NMR spectrometer operating at a ^{1}H frequency of 600.130 MHz with a commercial NMR probe. The probe temperature was set to 26 °C during data collection. Tuning, matching, and shimming were all performed automatically through instrument routines. A high-power 90^o pulse was used with a width of 16.5 μs. A recycle delay that was 10 x T_1 was used to ensure quantitative NMR peak areas. A spectral width of 2400 Hz (4 ppm) was used and 16k data points were collected. The offset frequency was placed in the center of the spectral window. The acquisition time was 3.41 s. Four scans were collected at each timepoint for samples that did not contain an adsorbent. Once the adsorbent was added to the headspace, one scan was collected at each timepoint. Samples consisted of propane and a binary mixture of propane and acetone. Propane vapor was introduced by a home-built gas transfer apparatus and acetone liquid was added (if used) by a gas tight syringe. The commercial NMR tubes were sealed with air-tight caps with a pressure rating to 1.5 MPa.

For dynamic adsorption measurements, data were collected on a 1.4 T benchtop NMR spectrometer operating at a ^{1}H frequency of 61.9 MHz. The probe temperature was set to 26.5 °C during data collection. Tuning, matching, and shimming were all performed automatically through instrument routines. Either 90^o or 30^o pulse lengths of 14.8 μs or 4.93 μs were used. Either 30 s or 10 s recycle delays were used between scans. The spectral width and offset frequencies were chosen automatically by the instrument. The number of scans ranged from 8 to 64 and was chosen based on the size of the peaks for a given sample. Samples consisted of neat liquids: a five-component mixture (3.65 mol% hexane, 5.88 mol% 1-methyl naphthalene, 41.52 mol% acetone, 44.19 mol% 2-propanol, and 4.76 mol% toluene) and several binary mixtures of toluene and isooctane (with varying initial compositions). The commercial NMR tubes were sealed with rubber septa caps designed to limit the samples' interaction with air.

Analytical and Data Analysis Techniques. Data were processed using a Fourier transform to convert between the time and frequency domain. When needed, the data were zero-filled and a 0.3 Hz exponential multiplication was applied. This process enhances the NMR data allowing for peak areas to more easily be defined. The processed spectra were phased manually, and an automatic baseline correction was applied. The peak areas were determined manually without overlap corrections.

For passive NMR adsorption measurements on the 14.1 T instrument, NMR peak areas from the analyte (i.e., propane) were compared to the peak area of the ^{1}H signal from a D_2O/H_2O mixture. This reference signal remains constant over the entire experiment because the D_2O/H_2O mixture is contained within a flame-sealed capillary placed in the NMR tube. This water peak area was set to a value of 1.00 in each spectrum and acts as an internal standard. For example, if the propane peak area has decreased by 50% over time when compared to a stable water peak area, this indicates that 50% of the propane has adsorbed.

For dynamic NMR adsorption measurements on the 1.4 T instrument, NMR peak areas from the analytes in the saturator tube, capillary rinse, and breakthrough tube were compared to an acetone internal standard. First, a comparison tube was prepared with a known mass of analyte and acetone. This was used to determine the initial peak areas of the analytes with respect to the peak area of acetone, which was set to a value of 1.00. Next, an identical mass of the analyte was placed into the saturator tube (corrected to account for small differences) and an identical mass of acetone was placed into the breakthrough tube (corrected to account for small differences) before starting the carrier gas flow. After the experiment concludes and the flow is stopped, an identical mass of acetone was added to the saturator tube and the capillary is removed from the experimental apparatus and analytes were desorbed from the capillary with a second identical mass of acetone. From this, the peak area of a given analyte within the comparison tube is compared to the analyte peak areas in the saturator tube, capillary rinse, and breakthrough tube. The peak areas from the latter three locations should combine to equal the magnitude of the peak area determined from the comparison tube. An alternative approach was investigated where relative peak areas, rather than total peak areas, are compared. This approach removes the reliance on acetone as an internal standard. For example, the peak area of isooctane within the breakthrough tube was compared to the peak area of toluene. This ratio was then compared to the ratio for these analytes in a comparison tube. This simplifies the experiment, allowing us to understand how analytes pass through the capillaries without having to track the absolute amount of each analyte throughout the experiment.

Experimental Data. The passive NMR adsorption experiment was first tested with vapor phase propane and then with vapor phase propane plus liquid phase acetone. Figure 6 shows the results for both experiments. In the experiment with vapor phase propane, the normalized propane peak area (blue circles) decreases over the experiment, indicating adsorption, which can be quantified. Over the first ~0.4 h, more than 50% of the propane adsorbed to the activated carbon strip and greater than 98% of the propane adsorbed after ~22 h. In the experiment with vapor phase propane and liquid phase acetone, the data were more complex to interpret. The normalized propane peak area (black triangles) decreases over the first ~0.5 h of the experiment, indicating adsorption. Intriguingly, after 0.5 h, the normalized propane peak area begins to increase, indicating desorption. After ~19 h, the entirety of the propane that initially adsorbed has returned to the vapor phase.

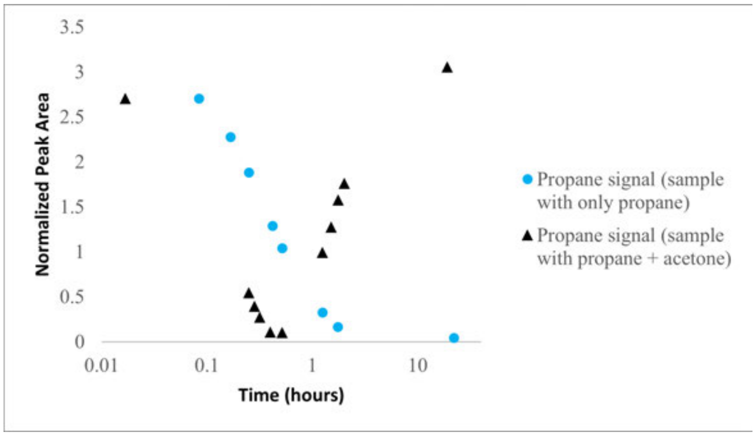

Figure 6: Results from two passive NMR experiments. The blue circles show the decrease of the normalized peak area for propane over time for a sample containing propane (0.171 MPa) and an activated carbon strip. The black triangles are for a sample containing propane (0.103 MPa), acetone (5 μL), and an activated carbon strip. In the absence of acetone, propane adsorbs to the activated carbon and remains adsorbed during the entire measurement. When acetone is present, propane adsorbs similarly but is displaced by acetone vapor over time.

The dynamic NMR adsorption experiment was first tested with a five-component mixture and a non-adsorbent fused silica capillary. This experiment was designed to probe how each analyte evaporates into the headspace and flows through the apparatus, including breakthrough times, without the complicating factor of adsorption to the capillary. Figure 7 summarizes the results from this experiment. Breakthrough is observed for four of the five components after only ~0.1 h, with 1-methylnapthalene being the only compound that isn't detected. As higher volatility compounds will be enriched in the headspace and none of the compounds should be retained by the fused silica capillary, their enrichment in the breakthrough tube is expected. After ~1 h we detected the presence of 1-methylnapthalene, the compound with the highest boiling point, and after ~6 h, the overall composition of the five-component mixture, except for 1-methylnapthalene, begins to normalize towards the initial composition. We note that 1-methylnapthalene has a boiling point of ~240 °C, which is more than 100 °C higher than any other compound.

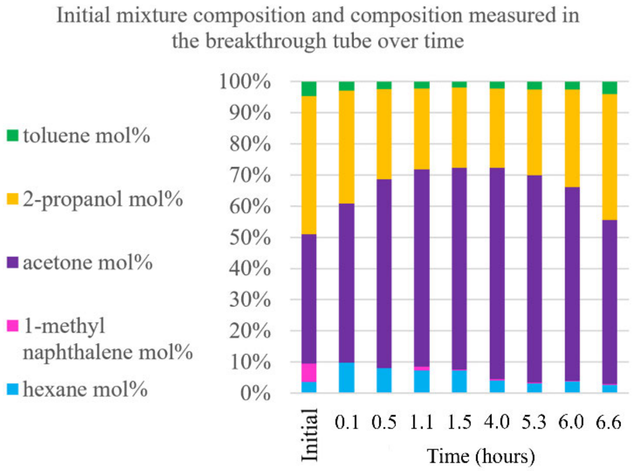

Figure 7: Results from the dynamic NMR adsorption experiment with a 5-component mixture and a non-adsorbent fused silica capillary. The initial composition is the composition before the flow of carrier gas, equivalent to that of the comparison tube. After starting the flow, the composition in the breakthrough tube was measured over time. At earlier times the composition is enriched in higher volatility compounds and depleted in lower volatility compounds. At later times the composition in the breakthrough tube begins to resemble the initial composition.

Next, adsorbent alumina and carbon capillaries were tested with a binary mixture of toluene and isooctane. Table 1 highlights the results from these experiments. For alumina capillaries, the total toluene recovery (where total = saturator + capillary rinse + breakthrough) ranged from 70% – 90% while the total isooctane recovery ranged from 59% – 100%. Isooctane was 100% recovered in only two of the six trials. For carbon capillaries, both toluene recovery and isooctane recovery were calculated to be greater than 100% (range from 105% –140%). Switching to the non-adsorbent fused silica capillary did not improve recovery or consistency.

To better understand the dynamic NMR adsorption experiment, a simplified design was investigated. Here, only the relative peak areas for the analytes are considered and the acetone peak area is not used as an internal standard. This avoids complications due to leaking. For this design, a binary mixture of toluene and isooctane was placed into three separate saturator and comparison tubes and all

Table 1: Results from dynamic NMR adsorption experiments with adsorbent and non-adsorbent capillaries. The recovery of toluene and isooctane was calculated by combining the quantities measured in the saturator, capillary rinse, and breakthrough. Six trials were conducted for alumina capillaries, two trials for activated carbon capillaries, and five trials for fused silica capillaries. If the experiment works as designed, 100% of each compound should be recovered during each trial.

Adsorbent	**Toluene Recovered (mol%)**	**Isooctane Recovered (mol%)**
Alumina 1	89.70	59.25
Alumina 2	90.60	86.72
Alumina 3	85.02	66.27
Alumina 4	85.34	100.71
Alumina 5	70.64	95.55
Alumina 6	85.33	100.71
Carbon 1	104.55	105.61
Carbon 2	112.56	139.86
Silica 1	86.52	64.74
Silica 2	88.31	71.67
Silica 3	84.90	60.76
Silica 4	105.65	116.31
Silica 5	92.56	99.52

experimental conditions (e.g., carrier gas flow rate, saturator temperature, capillary length, etc.) were equivalent. The only difference was the capillary connecting the saturator and breakthrough tubes. After starting the carrier gas flow, we measured the composition in the breakthrough tube at five time points. After stopping the flow, the saturator tube and capillary were rinsed with equivalent volumes of acetone and the composition was measured. Table 2 shows results from this experiment.

Table 2: Results from a simplified dynamic NMR adsorption experiment with adsorbent and non-adsorbent capillaries. The data show that the initial composition was nearly identical. The compounds in the mixture appear to pass through the capillary depending on the adsorbent material present. This is based on the composition detected at different time points in the breakthrough tube.

		Fused Silica		**Alumina**		**Carbon**	
	Time	Toluene (mol%)	Isooctane (mol%)	Toluene (mol%)	Isooctane (mol%)	Toluene (mol%)	Isooctane (mol%)
Comparison	Initial	48.58	51.42	48.58	51.42	48.56	51.44
Breakthrough	1 min	32.79	67.21	0.00	100.00	0.00	100.00
Breakthrough	11 min	37.15	62.85	0.00	100.00	0.00	100.00
Breakthrough	21 min	36.12	63.88	11.66	88.34	20.26	79.74
Breakthrough	31 min	37.97	62.03	18.96	81.04	24.87	75.13
Breakthrough	41 min	41.09	58.91	21.05	78.95	27.49	72.51
Saturator	Final	59.17	40.83	59.19	40.81	60.80	39.20
Capillary Rinse	Final	68.32	31.68	57.18	42.82	55.75	44.25

The composition in the comparison tubes is equivalent within 0.02 mol%. This highlights our motivation to use NMR spectroscopy for quantitating the differences between adsorbent materials. The composition in the saturator tubes, measured after the flow of carrier gas was stopped and after the addition of acetone, is within 1.6 mol%, suggesting that the mixture is evaporating similarly. The time course through the capillary to the breakthrough tube is different for the three capillary materials. Both toluene and isooctane are detected in the breakthrough tube within 1 min when a non-adsorbent fused silica capillary is used. For alumina and carbon capillaries, toluene is not detected in the breakthrough tube until 21 min. After 41 min, the breakthrough tubes have started to normalize towards the initial composition but are always enriched in isooctane. Conversely, the capillary rinses are enriched in toluene, but the percentages differ between the fused silica capillary and the two adsorbent capillaries.

Research Design, Methods, Analytical and Data Analysis Techniques, and Experimental Data for Question 3

Research Design. In this portion of the project, we explored instrument settings, the necessity of precise controllers, the influence of variables that are uncontrollable in real-world fire debris, and the interaction between instrument and debris variables. Isolating the influence of individual factors is challenging due to the highly variable nature of fire debris, including even laboratory-generated fire debris (Vergeer et al., 2020). Therefore, simulated fire debris was created by adding woodchips (the debris matrix) onto wipes that were spiked with weathered gasoline. Five debris factors were considered. Debris characteristics represented in the design include unburnt wood vs. burnt wood (x1), debris quantity (x2), IL volume (x3), and IL weathering (x4). As fire debris is expected to contain water due to firefighting efforts, the final debris factor, water addition (x5), compared "dry" debris matrices, containing only the water inherently present in the wood, with matrices soaked in water and drained. Six controllable instrument factors were simultaneously investigated. Sorbent (x6) refers to the adsorbent material coating the capillary vapor traps (3 m in length, 530 µm inner diameter), comparing polydimethylsiloxane (PDMS) vs. alumina. Oven temperature (x7) was set to 60 °C or 80 °C and equilibration time (x8) refers to time in the oven at one of those temperatures. Capillary temperature (x9) refers to the "trap" portion of the capillary, which was cooled to 3 °C or 20 °C with the thermoelectric cooler. Finally, the headspace concentration time was indirectly varied by setting the inlet flowrate (x10) and continuing until the collection volume (x11) reached 5% (47.3 scc) or 10% (94.6 scc) of the container volume, respectively.

Table 3 summarizes the factors investigated, the two settings selected as "low" and "high" values, and the factor class. Experiments with full factorial designs, in which each factor is varied independently, consume time and scarce resources. Specifically, evaluating 11 two-level factors would require 2048 separate experiments (2^{11} experiments). Here, we selected an orthogonal two-level fractional factorial design (Box & Hunter, 1978) consisting of 128 experiments to efficiently evaluate 11 main effects and 55 two-term interactions. Main effects represent the effect due to one of the factors in Table 3 while two-term interactions represent the combined effect of two factors.

Table 3: List of debris characteristics (D) and instrument setting (I) factors considered in the experiment and the values chosen for their two levels. The debris matrix was hickory woodchips for all experiments.

Factor Number	Factor Name	Low Value (-)	High Value (+)	Factor Class
1	Debris processing	unburnt	burnt	D
2	Debris quantity	5 g	50 g	D
3	IL volume	10 µL	100 µL	D
4	IL weathering	50%	80%	D
5	Water addition	no	yes	D
6	Sorbent	PDMS	Alumina	I
7	Oven temperature	60 °C	80 °C	I
8	Equilibration time	10 min	30 min	I
9	Capillary temperature	3 °C	20 °C	I
10	Inlet flow rate	5 sccm	10 sccm	I
11	Collection volume	47.3 scc	94.6 scc	I

Methods. Hickory woodchips were used as received to simulate unburnt debris. To simulate burnt debris, 100 g of woodchips were placed into a furnace and ignited using a propane torch. After 5 min, the woodchips were extinguished, stirred, and reignited for an additional 5 min. This resulted in debris consisting of burnt and partially burnt woodchips. Simulated fire debris was prepared by spiking IL onto a lint-free wipe inside a glass jar, adding the chosen debris matrix, and sealing the glass jar. Individual headspace concentration experiments (128 in total) followed a randomized order, with elution and GC-MS analysis of the eluates on the same day. To evaluate each headspace concentration experiment, we utilized covariance mapping (Sigman & Williams 2006; Sigman et al., 2007), which required that eluates were analyzed in conjunction with a reference sample injected just prior to the eluate. Reference samples contained IL in 1.00 (±0.01) mL of acetone. The IL weathering in the reference sample was matched to the experiment and the IL volume was one tenth the volume used in the corresponding experiment (e.g., 100 μL in experiment, 10 μL in reference).

Analytical and Data Analysis Techniques. Eluates and reference samples were analyzed by GC-MS in selected ion monitoring (SIM) mode, with the following ions chosen to represent the known classes of gasoline (Stauffer et al., 2008): 55 *m/z*, 57 *m/z*, 69 *m/z*, 71 *m/z*, 83 *m/z*, 85 *m/z*, 91 *m/z*, 99 *m/z*, 105 *m/z*, 117 *m/z*, 118 *m/z*, 119 *m/z*, 128 *m/z*, 131 *m/z*, 132 *m/z*, 142 *m/z*, and 156 *m/z.* Each eluate resulted in a retention time – ion abundance matrix, $\boldsymbol{Y}$, comprised of 949 rows and 17 columns corresponding to retention time (denoted t_i) and *m/z* (denoted m_j), respectively. The values in this matrix, $y(t_i, m_j)$, are the ion abundances. The covariance map of $\boldsymbol{Y}$ was generated by use of the equation $\boldsymbol{Z} = \boldsymbol{Y}^T\boldsymbol{Y}$, and the resulting matrix was normalized such that the sum of elements equaled 1.0, yielding $\boldsymbol{Z}_{run}$. The corresponding normalized covariance matrix, $\boldsymbol{Z}_{ref}$, was similarly constructed from the reference sample. Each eluate was compared to its reference by calculating a distance between the two matrices through the equation:

$$D = \frac{\sum_i \sum_j \left| z_{run}(i,j) - z_{ref}(i,j) \right|}{2},$$

where $z_{run}(i,j)$ and $z_{ref}(i,j)$ denote the elements of the normalized covariance matrices. D values range from 0 to 1, corresponding to matrices that are identical and non-overlapping, respectively. Smaller values of D are desirable as they indicate eluates that are more similar to the idealized reference sample. D_{rep} repeats the calculation described above for replicate reference samples (same IL volume, same IL weathering) analyzed on the same day, which are nominally identical. D_{rep} values represent variability due to sample preparation and instrumental analysis that is unavoidable.

The distances calculated via covariance mapping must be combined to calculate the effect of each factor. The main effect of a factor, f, is calculated from $E_f = \overline{D}_f(+) - \overline{D}_f(-)$, where $\overline{D}_f(+)$ denotes the mean experimental response, D, from all experiments conducted when factor f was set to its high value, and

$\overline{D}_f(-)$ is the mean when f was set to its low value. The two-term interaction effect between factor f and factor g is similarly calculated from $E_{fg} = \overline{D}_{fg}(+) - \overline{D}_{fg}(-)$, where $\overline{D}_{fg}(+)$ is the mean experimental response of all experiments where factors f and g were both set to their (respective) high or low settings, and $\overline{D}_{fg}(-)$ is the mean when the two factors were set to opposite settings. Three types of interactions are possible: interactions involving two controllable factors (instrument/instrument), interactions involving two uncontrollable factors (debris/debris), or factors involving one controllable and one uncontrollable factor (instrument/debris).

Experimental Data. Figure 8 provides the absolute effect for the 40 largest effects (main effects or two term interactions). The dashed horizontal line is an empirical significance threshold for factor effects. This analysis reveals that there are six factors and two interactions of statistical significance, which is confirmed by comparison to 95% confidence intervals (Berry, Gregg et al., 2023). It is worth noting that the factors with the highest absolute effects are IL volume (x3) and oven temperature (x7), which matches practical experience with passive headspace concentration (Newman et al., 1996; Williams et al., 2005). This observation confirms the importance of holding IL volume constant to compare casework containers in Research Question 1. It also emphasizes the shortcomings of target compound identification as a response variable, as oven temperatures from 60 °C to 90 °C could not be differentiated.

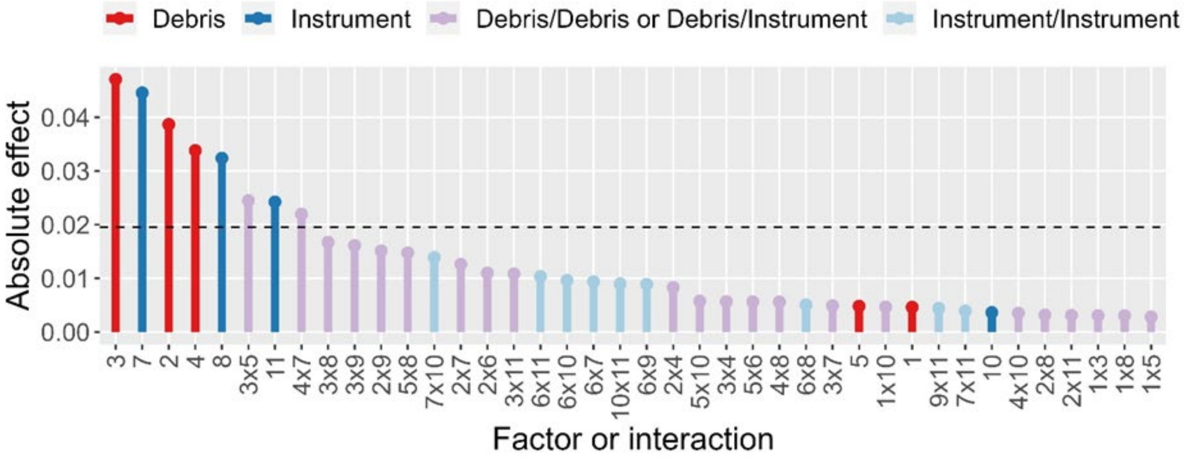

Figure 8: Main factor effects (E_f) and two-term interaction effects (E_{fg}), ranked by magnitude. The height of the bars shows the absolute effect for a factor or interaction, while the color differentiates the various factor classes and interaction types. $D_{rep} = 0.006 \pm 0.005$ and the dashed line is an empirical significance threshold set to three standard deviations above D_{rep} (replicate reference samples).

Main effects can be visualized within individual plots for each factor of the mean experimental responses $\overline{D}_f(-)$ and $\overline{D}_f(+)$. Figure 9 shows these results, providing a qualitative assessment of factor effects; important factors have large slopes while less influential factors have small slopes. DVME performance was significantly affected by three instrument settings (Figure 9a): oven temperature, equilibration time, and collection volume, with optimal performance achieved at the high settings. DVME performance was also significantly affected by three uncontrollable debris characteristics (Figure 9b): IL volume, debris quantity, and IL weathering, with optimal performance achieved at the low settings.

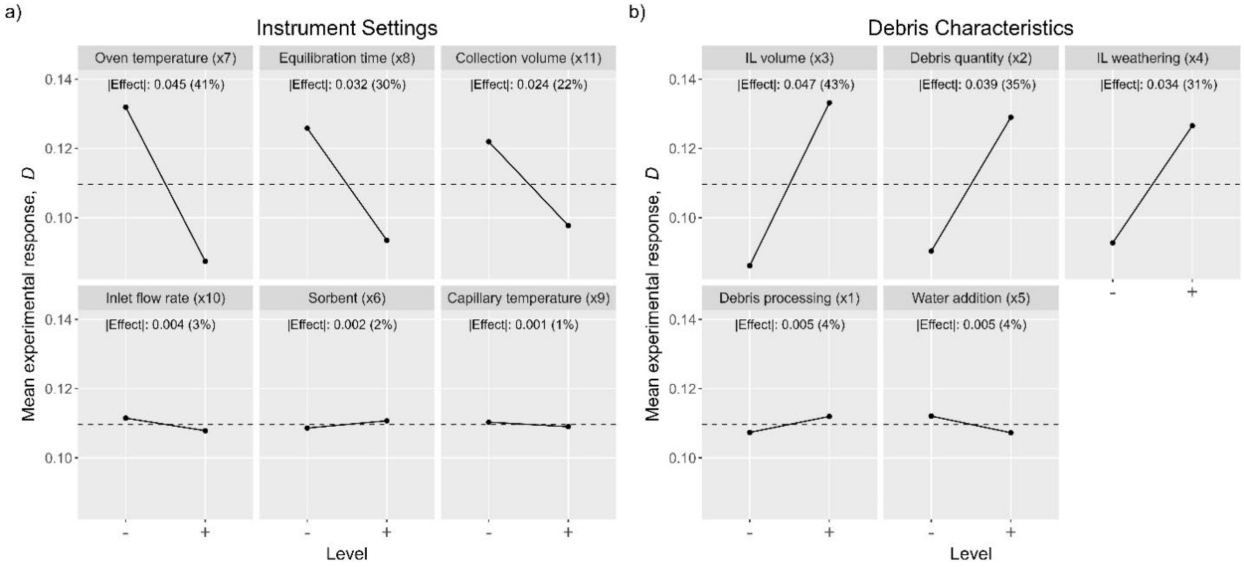

Figure 9: Main effects plots reveal the importance of three instrument settings (a) and three debris characteristics (b) on the similarity of experimental eluates resulting from headspace concentration from simulated fire debris to reference samples. Each panel shows the mean experimental response (D_f) resulting from the previously described low (-) and high (+) settings (Table 3). The dashed line is the overall mean response. For each set of factors in (a) and (b), the estimated absolute effect and relative effective size are in decreasing order of magnitude.

Expected Applicability of the Research

Debris from structural fires is assessed for the presence of ignitable liquid (IL) residue by headspace concentration followed by instrumental analysis. In the United States, headspace concentration is primarily conducted with the activated carbon strip (ACS) method. While this method has low detection limits and is non-destructive and cost-effective, it requires the use of a toxic extraction solvent and is subject to vapor distortion. Over two decades, headspace concentration methods have been investigated to avoid toxic solvent use (i.e., drop in replacements) or avoid solvents altogether, but an equivalent method is yet to be established. Dynamic vapor microextraction (DVME) offers a potential alternative. This method uses precise controllers to concentrate headspace vapors onto a capillary vapor trap and acetone as an elution solvent. Replacement of carbon disulfide will have a positive impact on the health and safety of the criminalists and forensic chemists who are part of the criminal justice system. However, implementing safer methods for trace evidence analysis requires that emerging methods be quantitatively compared to current methods. This project modified DVME to match the needs of fire debris analysis, specifically by demonstrating the use of realistic oven temperatures and casework containers, investigated novel methods to quantify the properties of adsorbent capillaries, and evaluated the effect of instrument settings and debris characteristics with a fractional factorial design. Importantly, this project provides a path towards unbiased, quantitative comparisons of headspace concentration methods through its use of simulated fire debris to mimic some of the complexity of authentic fire debris, while still providing the consistency needed to evaluate instrument settings.

Participants and Other Collaborating Organizations

Experiments and instrumental analysis were conducted by the Applied Chemicals and Materials Division (ACMD) within the Material Measurement Laboratory (MML) at NIST. Contributors included Dr. Jennifer L. Berry (post-doctoral), Dr. Adam J. Friss (post-doctoral), Dr. Megan E. Harries (post-doctoral), Dr. Christopher L. Suiter, and Dr. Kavita M. Jeerage (PI). Statistical analysis was conducted by the Statistical Engineering Division (SED) within the Information Technology Laboratory (ITL) at NIST. Contributors included Dr. Mary E. Gregg (post-doctoral) and Dr. Amanda A. Koepke. Reta Newman, Director, Pinellas County Forensic Laboratory provided expert consultation on the analysis of fire debris in forensic laboratory settings.

Changes in Approach from Original Design

We made three important changes from our original design. First, we did not anticipate that switching to the standard casework container, the metal can, would result in the complete loss of flow through the capillary vapor trap due to pervasive leaks around the lid. This observation led to a more extensive examination of casework container options, resulting in the investigation of glass jars and metal cans enclosed in polymer bags. Glass jars were ultimately selected for subsequent experiments based on their superior performance here. Second, we discovered that the proposed metric to compare instrument settings, target compound identification, is not sensitive enough to evaluate differences in performance, in part, due to its discrete nature. Therefore, we examined alternatives and identified covariance mapping as a continuous metric with promising sensitivity. To apply this approach, eluates were analyzed in conjunction with reference samples. Third, to systematically evaluate instrument settings, we decided to utilize simulated fire debris that mimicked only a subset of the characteristics of authentic fire debris.

Outcomes

Activities and Accomplishments

- DVME can be adapted to concentrate headspace vapors from casework containers at realistic oven temperatures, but target compound identification is not sensitive to realistic differences in oven temperature or collection volume (Harries et al., 2021b; Berry et al., 2022).
- Passive adsorption NMR experiments provide quantitative real time adsorption measurements for vapors but cannot be utilized when both a vapor phase and a liquid phase are present.
- Dynamic adsorption NMR experiments provide quantitative real time composition measurements of breakthrough that could indicate differences in adsorbents, but more work is necessary to determine the source of losses in the apparatus.
- DVME eluates from simulated fire debris can be quantitatively evaluated via covariance mapping to identify important instrument settings and debris characteristics via a fractional factorial design (Berry, Gregg et al., 2023).

Results and Findings

DVME can be adapted to concentrate headspace vapors from casework containers at realistic oven temperatures, but target compound identification is not sensitive to realistic differences in oven temperature or collection volume (Harries et al., 2021b; Berry et al., 2022). DVME is a positive pressure purge and trap method that requires an airtight container to achieve pressures sufficient to drive flow through a capillary vapor trap. While this was not possible with metal cans, both polymer bags (enclosing an open metal can) and glass jars could be pressurized sufficiently when 530 μm diameter capillaries were employed – an increase from the original 320 μm diameter capillaries. The glass jars were found to be a more effective container. Headspace concentration from glass jars resulted in the identification of at least 19 additional target compounds when compared to polymer bags for experiments with equivalent instrument settings. Importantly, when using glass jars, compounds across the entire chromatogram and full range of volatilities were recovered. This contrasts with polymer bags, where only higher volatility compounds were recovered. Our data suggest that lower volatility compounds are lost to the polymer bag before headspace vapors flow through the capillary vapor trap, likely during thermal equilibration. Therefore, the only feasible casework container we identified is the glass jar. Although identifying target compounds was sufficient to observe the dramatic differences in performance between polymer evidence bags and glass jars, this discrete metric could not identify performance differences due to realistic differences in oven temperature or collection volume, motivating the identification of a continuous metric with greater sensitivity.

Passive adsorption NMR experiments provide quantitative real time adsorption measurements for vapors but cannot be utilized when both a vapor phase and a liquid phase are present. Propane is a vapor phase molecule under the conditions of this experiment and the decrease in its peak area with time suggests that it is adsorbed by an activated carbon strip. When propane is combined with liquid acetone, our results suggest that a competitive process is occurring. Initially propane adsorbs to the carbon strip due to its overwhelming presence in the vapor phase. Over time, as more and more acetone evaporates from the liquid pool, it begins to displace propane on the carbon strip. Observation of this competitive process is encouraging and could be a starting point for understanding the behavior of vapor distortion or displacement. Unfortunately, the measurement we describe is only able to monitor the vapor phase; we do not observe the liquid phase with the current experimental design. When a sample contains a liquid, as is the case for acetone and for ILs, quantitative measurements are no longer possible. This is due to a complex process of liquid/vapor/solid equilibrium. We suspect that as acetone leaves the vapor phase due to adsorption, liquid acetone is driven to evaporate, leading to replenishment of the acetone vapor. Potentially, the acetone vapor peak area could increase over time if the rate of evaporation is faster than the rate of adsorption. Conversely, if acetone adsorbs rapidly and evaporation is a slower process, no acetone vapor would be detected. The experiment was designed to correlate the decrease in the vapor peak area to the quantity of analyte adsorbed, but the presence of a liquid prevents us from achieving this. The reason the measurements work for propane is because all the molecules that are not adsorbed to the activated carbon strip remain in the vapor phase. When considering pertinent ILs, each compound in the mixture is likely to have both a liquid phase and a vapor phase at meaningful temperatures.

Dynamic adsorption NMR experiments provide quantitative real time composition measurements of breakthrough that could indicate differences in adsorbents, but more work is necessary to determine the source of losses in the apparatus. Our results indicate that there are differences between the three types of capillaries tested (alumina, carbon, fused silica); however, the reasons for these observations are unclear. The differences could be due to adsorption or another factor prohibiting the passage of the toluene/isooctane mixture from the saturator tube to the breakthrough tube. There are three primary concerns preventing a concrete understanding of our observations. (1) There are cases where less than 100% of the analyte is recovered, which could indicate a leak in the saturator tube's rubber septa cap or capillary connection, allowing the mixture to bypass the capillary and escape into the air. Alternatively, the adsorbent materials are acting as effective adsorbents, but the elution solvents are inadequately desorbing the mixture. (2) The percentage recovered varies greatly for a given capillary type. This could suggest that conditions during the flow of carrier gas are inconsistent and/or that each individual capillary has different adsorbent behavior. (3) There are also cases where more than 100% of the analyte is apparently recovered, which could indicate that the vent placed in the breakthrough tube allows acetone (the internal standard in the experiment) to escape and leads to inflated analyte peak areas during quantitation.

Concerns (1) and (2) were addressed with control experiments where a non-adsorbent fused silica capillary is used in place of an adsorbent capillary. In four out of five trials for fused silica capillaries, less than 100% of the analyte was recovered (Table 1). This suggests that a leak is the primary cause for these observations. These trials still lack consistency with recovered quantities ranging from 85 – 105% for toluene and 60 – 116% for isooctane, however, this is not caused by differences in adsorption by individual capillaries. Concern (3) was addressed by altering the design of the experiment to include a second breakthrough tube and/or chilling the breakthrough tube, but these modifications did not improve the results. Replacing connections where leaks were possible also did not improve results. In aggregate, these experiments are of finite value, showing only modest differences in the adsorptive behaviors of the three materials tested. Due to the challenges described, a fundamental understanding of the differences in the adsorptive properties of different capillary materials remains elusive.

DVME eluates from simulated fire debris can be quantitatively evaluated via covariance mapping to identify important instrument settings and debris characteristics via a fractional factorial design (Berry, Gregg et al., 2023). DVME has more controllable instrument settings than passive headspace concentration, which creates a challenge for evaluating its performance, especially in conjunction with varying debris characteristics. Oven temperature is controlled in both methods, but DVME independently controls the temperature of the capillary vapor trap and also requires equilibrating casework containers at the oven temperature. Capillary length and adsorbent thickness are analogous to the size of the activated carbon strip, but the adsorbent material can also be varied. Collection volume is somewhat analogous to the headspace concentration time, but DVME additionally requires setting the inlet flow rate. Important instrument settings were identified through the use of simulated fire debris, a fractional factorial design, and a sensitive metric. This design allowed us to quantify expected effects, e.g., due to oven temperature and equilibration time, both of which increase the quantity of lower volatility compounds in the capillary vapor trap by increasing their concentration in the headspace. Employing a higher collection volume leads to a higher quantity of trapped vapors and more correspondence between eluates and reference samples. The other instrument settings (inlet flow rate, sorbent, and capillary temperature) had only limited effects.

Debris characteristics had both expected and surprising effects. Simulated debris with smaller IL volume and IL weathering leads to eluates that better match the reference samples due to more complete evaporation. The effect of a small volatility difference between two weathered gasolines was readily apparent, indicating the sensitivity of the covariance mapping metric. Debris quantity also had the expected effect, with more debris leading to less correspondence between eluates and reference samples due to the loss of headspace vapors to surfaces. The most surprising finding was the limited effect of water addition, although water did increase the outlet flow rate through the capillary vapor trap approximately threefold. The observation that performance is essentially unchanged for debris that is dry or soaked in water for all instrument settings considered in this analysis is an important finding because wood will always contain trapped water. Importantly, authentic fire debris could be soaked in water from firefighting efforts. While covariance mapping was used here to investigate instrument settings over a range of debris characteristics, its use naturally extends to a comparative analysis, as it allows two headspace concentration methods to be quantitatively assessed relative to the reference "truth" contained in simulated fire debris. Conducting this experiment over a range of debris characteristics while mimicking realistic sampling scenarios, could result in a meaningful and equitable comparison between methods.

Limitations

The primary motivation for adapting dynamic vapor microextraction (DVME) for fire debris was the potential to eliminate neurotoxic carbon disulfide in favor of acetone. We discovered that while DVME can be adapted to concentrate headspace vapors from casework containers, some of its advantages are lost in the process. When a sample container is heated, air within the container expands and causes pressurization of the container and flow through the capillary vapor trap. For an empty crimp cap vial, the maximum headspace volume is approximately 2 mL; therefore, the small quantity of vapor generated while the vial thermally equilibrates is negligible for typical collection volumes. This is not true for casework containers where the vapor generated during thermal equilibration can be larger than the desired collection volume. Therefore, casework containers must be thermally equilibrated before sampling. Furthermore, the outlet flow rate for crimp cap vials is equivalent to the inlet flow rate – this is not true for glass jars or other casework containers. Therefore, although crimp cap vials are not suitable for authentic fire debris, they offer greater experimental control by minimizing the thermal expansion volume and by ensuring that all headspace vapors flow through the capillary vapor trap. These features are critical to a separate challenge related to forensic science – measuring the vapor pressure of large and/or unstable compounds such as cannabinoids (Harries, Beuning et al., 2020; Beuning et al., 2023).

This project advanced DVME such that we could quantitatively evaluate headspace concentration from a casework container with simulated fire debris via a sensitive metric. While we didn't progress to the point of working with authentic fire debris, our investigations did move from surrogate mixtures to fuels, and ultimately to fuels spiked onto a debris matrix (i.e., simulated fire debris). The debris matrix was created from burnt and unburnt wood chips and included water, but additional matrices such as carpet were not examined. DVME is not at the technology readiness level required for implementation in forensic practice; however, our experimental design enabled us to develop greater insight into each instrument setting and debris characteristic that was considered. Importantly, we demonstrated that covariance mapping provides a means to quantitatively and sensitively compare different instrument settings when simulated fire debris is employed. This approach could easily be extended to identify nuanced effects resulting from different headspace concentration methods, though we note that no other metrics were evaluated for this purpose.

Artifacts

Peer-reviewed Publications

1. M.E. Harries, S.S. Wasserman, J.L. Berry, K.M. Jeerage. Characterization of a headspace sampling method with a five-component diesel fuel surrogate. *Forensic Chemistry* **22** (2021) 100301
2. J.L. Berry, M.E. Gregg, A.J. Friss, A.A. Koepke, C.L. Suiter, R. Newman, M.E. Harries, K.M. Jeerage. Dynamic vapor microextraction of ignitable liquid from two realistic casework containers. *Forensic Science International* **336** (2022) 111315
3. J.L. Berry*, M.E. Gregg*, A.A. Koepke, R. Newman, K.M. Jeerage (*equal contribution). Concentration of ignitable liquid residue from simulated fire debris by dynamic vapor microextraction: sensitivity to instrument settings and debris characteristics. *Forensic Chemistry* **35** (2023) 100511

Data Sets: None.

Dissemination Activities

1. Christopher L. Suiter, J.A. Widegren, M.E. Harries, K.M. Jeerage, T.M. Lovestead. Analysis of gaseous mixture adsorption by nuclear magnetic resonance (NMR) spectroscopy: improving our understanding of arson debris investigations, *Poster presentation at the 72nd Annual Meeting of the American Academy of Forensic Sciences (AAFS)*, Anaheim, 2020.
2. Jennifer L. Berry, M.E. Gregg, M.E. Harries, A.A. Koepke, A.J. Friss, C.L. Suiter, K.M. Jeerage. Optimization of dynamic vapor microextraction for ignitable liquid extraction, *Virtual oral presentation at the 21st Symposium on Thermophysical Properties*, Virtual, 2021.
3. Mary E. Gregg, J.L. Berry, A.A. Koepke, K.M. Jeerage, M.E. Harries, A.J. Friss, C.L. Suiter. Optimization of headspace sampling parameters for forensic fire debris analysis with discrete outcomes, *Virtual oral presentation at the Women in Statistics and Data Science Conference (WSDS)*, Virtual, 2021.
4. Jennifer L. Berry, M.E. Gregg, A.A. Koepke, C.L. Suiter, R. Newman, K.M. Jeerage. Sensitivity analysis of dynamic vapor microextraction with simulated fire debris, *Oral presentation at the 74th Annual Meeting of the American Academy of Forensic Sciences* (AAFS), Seattle, 2022.

5. Kavita M. Jeerage, J.L. Berry, M.E. Gregg, A.A. Koepke, C.L. Suiter, R. Newman, A.J. Friss, M.E. Harries. Dynamic vapor microextraction and its potential for fire debris analysis, *Virtual poster presentation at the NIJ Research Symposium*, Virtual, 2022.

6. Mary E. Gregg, J.L. Berry, A.A. Koepke. K.M. Jeerage. An investigation of differential factor effects amongst ion groupings in the performance of dynamic vapor microextraction, *Oral presentation at the Women in Statistics and Data Science Conference (WSDS)*, St. Louis, 2022.

7. Jennifer L. Berry. Optimizing ignitable liquid recovery from simulated fire debris without carbon disulfide, *Invited oral presentation at Forensics @ NIST*, Virtual, 2022.

8. Mary E. Gregg. An investigation of differential factor effects amongst ion groupings in the performance of dynamic vapor microextraction, *Invited oral presentation at Forensics @ NIST*, Virtual, 2022.

9. Jennifer L. Berry. Vapors and aerosols: NIST's forensic approach to arson and cannabis intoxication. *Invited seminar at the University of Colorado – Boulder, Dept. of Chemistry, 2022*.

10. Jennifer L. Berry, M.E. Gregg, A.A. Koepke, K.M. Jeerage. Differential performance of dynamic vapor microextraction for recovery of ignitable liquid compounds investigated within a sensitivity analysis, *Oral presentation at the 75th Annual Meeting of the American Academy of Forensic Sciences* (AAFS), Orlando, 2023.

11. Christopher L. Suiter, J.L. Berry, M.E. Gregg, A.J. Friss, A.A. Koepke, R. Newman, M.E. Harries, K.M. Jeerage. Characterization of ignitable liquids in simulated fire debris using dynamic vapor microextraction, NMR spectroscopy, and sensitivity analysis. *Oral presentation at the 22nd Symposium on Thermophysical Properties Symposium, Boulder, 2024*.

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