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# Dynamic vapor microextraction of ignitable liquid from casework containers $\overset{\star}{}$



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#### ABSTRACT

Dynamic vapor microextraction (DVME) is a headspace concentration method that can be used to collect ignitable liquid (IL) from fire debris onto chilled adsorbent capillaries. Unlike passive headspace concentration onto activated carbon strips (ACSs) that must be eluted with a toxic solvent (carbon disulfide), DVME employs a relatively benign solvent (acetone) to recover the adsorbed IL residue, and each headspace collection is monitored for breakthrough. Here, for the first time, we extend DVME to casework containers while exploring a realistic range of oven temperatures and collection volumes. We investigated metal cans sealed with friction lids (container 1), metal cans sealed within polymer bags (container 2), and glass jars sealed with two-piece lids (container 3). Without additional containment, container 1 was found to leak so excessively that flow through the capillary was unreliable. Therefore, for containers 2 and 3 only, we determined the total number of target compounds collected from 50% weathered gasoline for oven temperatures from 54 °C to 96 °C and collection volumes from 47 standard cubic centimeters (scc) to 90 scc. Only high-volatility species with retention times  $(t_R) < n$ -decane on a non-polar column were recovered from polymer bags, whereas headspace concentration from glass jars led to the recovery of target compounds across the entire volatility range. DVME at 90 °C from 2-mL containers showed that the presence of polymer bag material leads to IL vapor losses, particularly for low-volatility species with  $t_R > n$ -decane. DVME was strongly influenced by the casework container, whereas oven temperature and collection volume had a minor influence for the IL samples explored here.

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# 1. Introduction

Fire debris from structural fires can be investigated by analysts to determine if ignitable liquid (IL) residue is present. Detecting IL residue is challenging because some of the IL is consumed or otherwise lost during the fire. Headspace can be directly sampled with a gas-tight syringe (ASTM E1388) [1], which removes some of the complexity of the debris matrix. However, due to the low concentration of IL residue, analysts mainly use headspace

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concentration techniques before instrumental analysis [2]. During headspace concentration, IL vapors are concentrated onto an adsorbent. In the United States (US), most fire debris analysts follow the ASTM E1412 method [3], which describes passive headspace concentration onto activated carbon strips (ACSs) followed by solvent elution, and then the ASTM E1618 method [4] for analysis by gas chromatography with mass spectrometry (GC-MS). Fire debris samples in the US are typically collected in 32 oz (1 quart or approx. 946 mL) or 128 oz (1 gallon or approx. 3785 mL) metal cans, and the extraction and concentration of IL vapors onto ACSs occurs within the cans. ACSs are suspended in the headspace of a sealed can, where they adsorb IL vapors over 2–24 h at oven temperatures of 50–80 °C. Longer time periods and higher temperatures are necessary to detect low-volatility species. Overall, the ACS method is sensitive with low detection limits [5], non-destructive, cost effective, compatible with a robust container for field sampling, and allows samples to be

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archived for later analysis [6]. Even with its many advantages, there are several ongoing challenges. In highly concentrated samples, the collected IL vapors may be distorted if low-volatility species displace adsorbed high-volatility species, causing a shift in the volatility range of detected IL vapors [7]. Additionally, activated carbon strongly binds to hydrocarbons and requires a strong elution solvent, which is typically carbon disulfide (CS<sub>2</sub>) [8]. CS<sub>2</sub> is dangerous to users because it is flammable and is a strong neurotoxin in low concentrations [9,10]. ASTM E1412 mentions *n*-pentane, diethyl ether, toluene, or tetrachloroethylene as alternative solvents [3], though their eluting efficiency may be lower [9]. Dichloromethane has higher eluting efficiency than other alternative solvents [10] and may be used by some analysts despite its carcinogenicity.

Although the ACS method is well established in US forensic laboratories, there are several other headspace concentration methods with associated ASTM standards. Solid-phase microextraction (SPME) is a passive headspace concentration method in which IL residue is concentrated onto fibers coated with a polydimethylsiloxane stationary phase (ASTM E2154) [11] and thermally desorbed for GC-MS analysis. This method is only recommended as a screening technique. Static headspace concentration (ASTM E3189) [12] draws headspace through an adsorbent tube; however it still requires elution with a solvent such as CS<sub>2</sub> if the adsorbent is activated carbon or a similarly strong equivalent. Dynamic headspace concentration (ASTM E1413) [13] is considered destructive, a disadvantage for evidence analysis, because such a large quantity of vapor is removed - typically multiple times the container volume potentially causing complete removal of any IL residue from the sample. Techniques like capillary microextraction of vapors (CMV) [14] and headspace sorptive extraction (HSSE) [15] are additional headspace concentration methods that allow thermal desorption. CMV has been used to sample from closed systems and for field detection, with a rapid ambient temperature protocol [16,17]. HSSE was found to be more sensitive than SPME [15]. While both techniques are promising, there are currently no ASTM standards in place for these methods.

Dynamic vapor microextraction (DVME) is a technique developed at the National Institute of Standards and Technology (NIST) that uses an inert carrier gas to push headspace vapors through a chilled adsorbent capillary vapor trap. The adsorbent phase of the capillary, along with the cold temperature, enhances vapor capture and stabilizes reactive species in the sample. The flow exiting the capillary vapor trap is measured for breakthrough, so potential distortion of the collected vapors can be monitored. Importantly, CS<sub>2</sub> solvent elution is not required. Following headspace concentration, adsorbed IL vapors are eluted from the capillary with acetone. While DVME is technically a positive-pressure dynamic (purge-and-trap) headspace concentration method, the flow rate through a single capillary vapor trap is low (up to 10 standard cm<sup>3</sup> per min (sccm)) and does not meet the definition of a dynamic method provided in ASTM E1413 (40 sccm to 400 sccm), which is typically destructive [13]. Due to DVME's low flow rate, the volume of headspace removed can be kept below 10% of the total volume, similar to the static method described in ASTM E3189 (2 sccm to 80 sccm), which is expected to be non-destructive [12]. Thus, samples can be archived for future re-analysis. Previous DVME studies with fuel surrogates and laboratory-generated fire debris have found that flow rates up to 1.5 sccm generate the most reproducible results and that the method recovered more IL vapors than a conventional purge-and-trap method with a poly(2,6-diphenylphenylphenylene oxide) adsorbent at room temperature [18,19]. A drawback of these studies is that IL vapors were concentrated from 2-mL glass vials, which are not practical for authentic fire debris samples owing to their small volume.

While the DVME method may address prominent issues of the ACS method, no research has been conducted on its performance for

the recovery of ILs from realistic casework containers. In this paper, we address this research gap. Metal cans with friction lids, which are the most commonly used container for fire scene evidence collection in the US [2], were first considered. Despite being robust and cost effective, metal cans are known to leak vapors [20]. While being a noticeable issue for passive and static methods, leaks will likely be exacerbated for dynamic methods like DVME due to the higher pressure. Therefore, we devised a secondary container to hold the metal can: a heat-sealed polymer evidence bag. Polymer bags were developed to hold large or oddly shaped debris (e.g., shoes) [2]. If this container system were adopted by forensic laboratories, fire investigators could continue using metal cans to collect evidence. This is advantageous because practitioner acceptance and procurement of new supplies are both impediments to the adoption of new technologies in the field. However, polymer bags may cause other issues. For example, cast nylon acrylonitrile/methacrylate can be changed irreversibly by heating above 80 °C [21], polyethylene can produce vapors similar to those from ILs [22], and nylon can be porous, leading to cross contamination of ILs [23,24]. Therefore, we also examined glass jars sealed with two-piece lids. While glass jars are still susceptible to leaks [20], they did not require secondary containment. Additionally, glass jars are a common casework container outside the US, such as in Canada [2] or the Netherlands [24]. To evaluate the performance of these containers, we varied oven temperature and collection volume and determined the number of target compounds identified from weathered gasoline. We conclude by presenting results from our investigation of vapor loss to the polymer bag material.

# 2. Materials and methods

# 2.1. Materials

Porous layer open tubular (PLOT) capillaries with alumina adsorbent (0.320 mm inner diameter (ID) with an 8.00 µm film thickness and 0.530 mm ID with a 15.0 µm film thickness), sold commercially as GC columns, were used to create traps by forming 9.5 mm diameter bundles of capillary loops. The number of loops was determined by the total length of the capillary vapor trap. Commercially obtained, un-oxygenated gasoline was weathered to 50% by volume at room temperature inside a chemical hood. Acetone (99.5%) and *n*-hexane ( $\geq$ 99%) were tested for purity by GC-MS, found to be consistent with reported purities, and used as received.

# 2.2. DVME

Dynamic vapor microextraction (DVME) has been used to concentrate headspace from diesel fuel surrogates [18], laboratorygenerated fire debris [19], explosives [25], and natural gas [26]. DVME has been extensively covered elsewhere [27], so only a brief description follows. Fig. 1 shows a general schematic of DVME as used in this paper. Ultra-high purity (UHP) nitrogen (N<sub>2</sub>) flows through an uncoated capillary into a casework container (described in Section 2.3) that is heated to the desired temperature within a repurposed GC oven. The carrier gas flow rate into the container  $(F_{inlet})$  is controlled by a precise (  $\pm$  0.6% of the reading or  $\pm$  0.1% of the full scale, whichever is greater) mass flow controller (MFC). Carrier gas mixes with headspace vapors inside the container and then flows through a capillary vapor trap that is cooled to 0 °C with a thermoelectric cooler (TEC) contained within a rigid foam insulation block. Foam insulation is used to hold the capillary in direct contact with the cooler surface and to prevent moisture in the air from freezing to the surface of the cold plate or capillary vapor trap. Flow from the capillary vapor trap passes through a breakthrough vial containing 1.00 ( $\pm$  0.01) mL of *n*-hexane to trap any vapors that were not captured by the capillary. By analyzing the breakthrough



**Fig. 1.** (a) Dynamic vapor microextraction (DVME) from a casework container with an ignitable liquid (IL)-spiked wipe. The inlet flow (F<sub>inlet</sub>) is set by a mass flow controller (MFC) while the outlet flow (F<sub>outlet</sub>) is measured via a mass flow meter (MFM). The capillary vapor trap is chilled to 0 °C with a thermoelectric cooler (TEC). (b) Container 1: a metal can sealed with a friction lid. (c) Container 2: a metal can sealed within a polymer bag. (d) Container 3: a glass jar sealed with a two-piece lid.

solvent, users can determine whether the vapors trapped in the capillary vapor trap were distorted. The flow exiting the break-through vial ( $F_{outlet}$ ) is measured by a precise (  $\pm$  0.6% of reading or  $\pm$  0.1% of full scale, whichever is greater) mass flow meter (MFM) utilizing a vapor correction for *n*-hexane. The total volume of vapor that has passed through the capillary vapor trap during an experiment is referred to as the collection volume.

There are several expensive, low-uncertainty controllers and meters used in this design, because of the precision needed to investigate our specific research questions. For example, precise measurements of  $F_{inlet}$  and  $F_{outlet}$  allow for the detection of leaks within the system. However, many instrumental factors could be controlled by simpler and less costly means. For example, a pressure-controlled inlet such as those found in GC ovens could be used, and cold water could suffice as a cooling system. As GC ovens are commonly found in forensic laboratories, DVME could be modified to suit many different laboratory requirements and available resources to translate this method to forensic laboratories.

# 2.3. Casework containers

Three casework containers were explored in this study: a metal can sealed with a friction lid (container 1, Fig. 1b), a metal can sealed within a polymer bag (container 2, Fig. 1c), and a glass jar sealed with a two-piece lid (container 3, Fig. 1d). For all containers, the stainless-steel inlet was sealed with an o-ring and contained a septum for capillary insertion. Container 1 (referred to as a metal can, Fig. 1b) was a 32 oz (946 mL) metal paint can closed with a mallet. Preliminary tests revealed leaks around the entirety of the friction lid where it contacts the can body to form a sealing surface. The leaks were so pervasive that  $F_{inlet}$  up to 10 sccm did not consistently produce measurable  $F_{outlet}$  through the capillary vapor trap. DVME requires flow to be pushed or pulled through the capillary vapor trap, therefore a secondary container was devised to hold the metal can. Container 2 (referred to as a polymer bag, Fig. 1c, Fig. S1a)

was a polymer bag sealed around an open metal paint can. Polymer bags were made from a 2-ply structure of polyester and polyethylene by sealing 2.5-mil thick roll stock with an impulse heat sealer to a 25 cm × 25 cm size. Metal cans were sealed within the polymer bags without a lid. After sealing, the bags were pre-filled with 450 scc of N<sub>2</sub>. This was done because no vapor can flow through the capillary vapor trap until the container is slightly pressurized; pre-filling brings each flexible container to a similar internal volume and allows them to reach pressures sufficient to drive flow within minutes. Pre-filling results in a headspace volume of approximately 3.1-3.2 L for this container. Container 3 (referred to as a glass jar, Fig. 1d, Fig. S1b) was a 32 oz (946 mL) glass canning jar with a two-piece lid (flat-lined lid with a plastic gasket and metal jar ring). No pre-filling was needed for the glass jars because of their rigidity.

# 2.4. Flow limitations in polymer bags

Polymer bags cannot be pressurized to the same extent as rigid glass jars. We found that the pressure required to drive flow through a capillary vapor trap can cause the bag to burst at the heat seals, leading to loss of flow and sample. Poiseuille's equation can be used to mathematically determine the pressure drop in an incompressible fluid across a pipe as a function of viscosity, volumetric flow rate, length, and diameter, but would require many approximations to apply to the geometry of our capillary vapor trap at different temperatures. Our primary interest was in knowing what Finlet are feasible in our system, and we chose to investigate this question empirically by varying the capillary vapor trap length and diameter to determine the  $F_{\text{outlet}}$  at which the bags fail. For these flow restriction experiments,  $F_{inlet}$  was set to 10.00 (  $\pm$  0.05) sccm and measurement of F<sub>outlet</sub> continued until it showed a precipitous drop, signifying a failure of the polymer bag. Fig. 2 shows the maximum Foutlet measured before the bags burst for three different capillaries. The length of the capillary vapor trap (2 m vs. 3 m) has a smaller



**Fig. 2.** F<sub>outlet</sub> measured before bags burst from over pressurization. These "failure" F<sub>outlet</sub> provide guidance on the maximum  $F_{inlet}$  to use for headspace concentration from polymer bags. Dashed gray lines indicate two standard deviations below the average of the replicate failure  $F_{outlet}$  and indicate the maximum  $F_{inlet}$  with a low probability of polymer bag failure.

influence on pressure and therefore  $F_{\rm outlet},$  than ID (530  $\mu m$  vs. 320  $\mu m$  ).

Based on the results in Fig. 2, we chose 3-m, 530-µm ID capillaries with a  $F_{inlet}$  of 2.00 ( ± 0.01) sccm for all subsequent experiments. The 3-m capillaries provide 50% more adsorbent than 2-m capillaries with only a small decrease in the  $F_{inlet}$  setpoint. While  $F_{inlet}$  was controlled and held constant,  $F_{outlet}$  depends on the container. Temperature causes the air within each container to expand, potentially adding to  $F_{outlet}$ , but flexible polymer bags can accommodate the expansion compared to rigid glass jars.  $F_{outlet}$  from polymer bags stayed below 2 sccm.  $F_{outlet}$  from glass jars were larger, varied with temperature, and maximum values ranged from 4 sccm to 9 sccm. Despite the variability in  $F_{outlet}$  measured from glass jars, no gasoline compounds were found in the breakthrough vial, and we therefore assumed that  $F_{outlet}$  did not impact headspace concentration from these containers.

# 2.5. DVME from polymer bags and glass jars

Casework containers were prepared as described in Section 2.3 and non-abrasive laboratory wipes spiked with 10.0 ( $\pm$  0.1) µL of 50% weathered gasoline were placed at the bottom of each container. Containers were sealed, pre-filled (polymer bags only), and then thermally equilibrated at the desired oven temperature ( $\pm$  1%) for 10 min while the capillary vapor trap was chilled to  $0.00 (\pm 0.01)$  °C. Air within the containers was found to reach the temperature setpoint in less than 3 min, so the IL vapors were assumed to be fully equilibrated within 10 min. The uncoated capillary introducing the carrier gas was positioned above the IL-spiked wipe, whereas the capillary vapor trap was positioned far above the IL-spiked wipe (Fig. 1). Flow was started via the MFC and monitored via the MFM until the desired collection volume was reached. The capillary vapor trap was then removed, and the adsorbed IL vapors were eluted for GC-MS analysis (described in Section 2.6). Oven temperatures from 54 °C to 96 °C and collection volumes from 47 scc to 90 scc were investigated.

After each experiment, the metal cans (from inside the polymer bags) and the glass jars were rinsed with acetone and baked in a vacuum oven for at least 6 h at 150 °C and 100 °C, respectively, and a negative gauge pressure of at least -8 kPa, to clean them before reuse. The metal lids of the glass jars were washed with soap and warm water. After cleaning, blank samples were collected from both

containers at an oven temperature of 90 °C and a collection volume of 90 scc. The blanks showed that our cleaning process was sufficient for both containers; the only contaminants were two compounds produced from acetone, most likely 4-methyl-3-penten-2-one and 4-hydroxy-4-methyl-2-pentanone that eluted between 4.6–5.2 min and 6.1–6.6 min, respectively. These contaminants were not included in the target compound analysis described below. The consistency of the blanks collected before each subsequent experiment showed that both containers had all IL vapors removed by the thorough cleaning process.

# 2.6. Target compound analysis

The elution solvent, 1.00 (  $\pm$  0.01) mL of acetone, was sealed within a 2-mL screw-top autosampler vial and connected to an MFC via an uncoated silica capillary inserted through the septum into the headspace. The outlet end of the capillary vapor trap was placed into this vial into the bottom of the solvent volume and the inlet end was placed into an empty 2-mL screw-top autosampler vial. N<sub>2</sub> flowed into the solvent vial at  $5.00 (\pm 0.05)$  sccm, forcing the entire solvent volume through the capillary vapor trap and into the second vial at a consistent velocity. A second acetone elution followed the same procedure. The eluate (acetone) and breakthrough (*n*-hexane) samples were analyzed by GC-MS with a single guadrupole mass spectrometer. The GC column was 5% phenyl dimethyl siloxane (30 m initial length, 250 µm ID, 0.25 µm film thickness). The following GC program was employed: inlet temperature = 300 °C; split ratio 20:1; flow rate = 1 mL/min; initial oven temperature = 35 °C for 2 min, then increased at 2.5 °C/min to a final temperature of 170 °C and held for an additional 2 min at 170 °C. The MS was operated in scan mode (33-300 m/z). An alkane ladder containing *n*-octane through *n*-eicosane was run to compare retention relative to *n*-alkanes and compare the instrument used here and a different instrument of the same model used in Section 2.7. Liquid samples (1 µL) were injected by autosampler, and the tray was not temperature controlled.

Target compounds were first identified by GC-MS analysis of 50% weathered gasoline in acetone. There were 55 total compounds (Table 1). Breakthrough samples were examined for the presence of target compounds, but no breakthrough samples contained any target compounds. Similarly, none of the second eluate samples contained any target compounds. For the first eluate samples, the total number of target compounds with signal-to-noise ratios greater than 20 were determined. Peaks were identified from their retention time ( $t_R$ ), and their signal was taken as the peak maximum. Noise was calculated from the average signal from 25.0 min to 25.5 min for each individual chromatogram, as no peaks appeared in this range.

# 2.7. Vapor interaction with polymer bags

We conducted a separate set of experiments to investigate whether the bag material adsorbed or absorbed gasoline compounds, which we suspected led to IL loss. Varying amounts of bag material were placed within 2-mL crimp-top autosampler vials containing 1.00 (  $\pm$  0.01) µL of 50% weathered gasoline. To generate vials containing 4 cm<sup>2</sup>, 8 cm<sup>2</sup>, and 16 cm<sup>2</sup> of bag material, multiple 1 $cm \times 2$ -cm rectangles of bag material were placed above the IL volume within the vials. During preparation, the pieces of bag curled inside the mouth of the vial and stayed suspended without touching the IL at the bottom of the vial. The vials were then placed in a 90.0  $(\pm 0.9)$  °C oven for 60 min, chosen to represent the most extreme conditions described in Section 2.5. After this equilibration period, each vial was removed from the oven and immediately used as the DVME sample container. For these experiments, the capillary vapor trap was 1 m in length, 320 µm ID, and 8.00 µm film thickness. The oven temperature was 90.0 (  $\pm$  0.9) °C with a TEC temperature of

#### Table 1

Peak number, proposed general peak identity that is consistent with resulting ion spectrum, and retention time (min) for the 55 target compounds used in the analysis. Detection rate is explained in Section 3.1 and is used to classify each target compound as vigorous (V), receptive (R), or stagnant (S).

Peak No.	Proposed General Peak	Retention	Detection Rate		
	Identity	Time	Polymer Bag Glass Jar		
		(t <sub>R</sub> , min)	- 0		
1	dimethylhexane	3.3	1.00	1.00	V
2	dimethylnexane	3.4	0.00	0.95	ĸ
3	trimethylpentane	3.6	1.00	1.00	V
4	trimetnyipentane	3./	1.00	1.00	V
5	dimethylnexane	3.9	1.00	1.00	v
5	toluene	4	1.00	1.00	V
/	trimethylhovane	4.2	1.00	1.00	v
0	trimethylhevane	4.4 5 2	0.20	1.00	V D
9	dimethylheptape	5.5	0.29	1.00	R D
10	trimothylhoyano	69	0.21	1.00	R D
11	athulhanzana	0.0	1.00	1.00	K V
12		0.9	1.00	1.00	v
15	dimethylectane	7.2	0.14	1.00	V D
14	trimethylbontane	7.4	0.14	1.00	R D
15	dimethylactane	7.0	0.14	1.00	R D
10		7.9	1.00	1.00	K V
1/	0-xylelle	8.1	1.00	1.00	V
18	trimethymeptane	8.4	0.07	1.00	ĸ
19	lion athula atawa	8.0	0.00	1.00	ĸ
20	athul mathulhannana	9.3	0.00	1.00	ĸ
21	ethyl-methylbenzene	9.6	0.00	1.00	ĸ
22	propulbonzono	9.8	0.00	1.00	K D
25	athul mathulhanzana	11 2	0.07	1.00	R D
24	ethyl-methylbenzene	11.3	0.93	1.00	ĸ
25	ethyl-methylbenzene	11.4	0.93	1.00	ĸ
20		11.7	0.79	1.00	ĸ
27	pentamethymeptane	12.1	0.00	1.00	ĸ
28	etnyl-metnylbenzene	12.2	0.36	1.00	ĸ
29	trimethyldecane	12.0	0.00	0.95	ĸ
30		12.9	0.93	1.00	ĸ
31	mathul	14.4	0.07	1.00	ĸ
32	metnyl-	14.6	0.00	0.57	ĸ
22	methylethylbenzene	14.0	0.00	1.00	р
33	indene	14.9	0.00	1.00	K
34	Indane	15.1	0.00	1.00	ĸ
30 26	diathulhan	13.3 16	0.00	0.52	ĸ
36	dietnyibenzene	16	0.00	1.00	ĸ
3/	methyl-propylbenzene	16.1	0.00	1.00	K
38 20	othul dimothulhorser	10.3	0.00	1.00	K D
39 40	etiiyi-uiiietnyibenzene	10.0 17	0.00	1.00	K
40	methyl-propyidenzene	17	0.00	1.00	ĸ
41	ethyl-dimethylbenzene	17.5	0.00	1.00	ĸ
42	ethyl-dimethylbenzene	17.0	0.00	1.00	K
43	etnyi-aimethyibenzene	17.9	0.00	1.00	K
44	etiiyi-uiiietnyibenzene	19.1 10.6	0.00	0.29	K
45	tetrametnylbenzene	19.6	0.00	1.00	K
40 47	tetrametnylbenzene	19.8	0.00	1.00	ĸ
4/	dihudaa mathulia tara	20.4	0.00	0.00	5
48 40	dihudro-methylindene	20.8	0.00	0.33	K
49	uinyaro-methylindene	21.3	0.00	0.95	ĸ
50	tetramethylbenzene	21.5	0.00	0.33	K
51	naphthalene	23	0.00	0.81	ĸ
52	aihydro-methylindene	25.7	0.00	0.00	S
53	aihydro-	26.3	0.00	0.00	S
- 4	aimethylindene	26.6	0.00	0.00	6
54	methylnaphthalene	26.6	0.00	0.00	S
55	methylnaphthalene	26.8	0.00	0.00	S

-10.00 (  $\pm$  0.01) °C, F<sub>inlet</sub> of 1.00 (  $\pm$  0.01) sccm, and collection volume of 10.00 (  $\pm$  0.05) scc. Under these conditions, the entire IL volume is extracted from the 2-mL vial and no detectable IL residue remains in the container. The capillaries were eluted and analyzed by GC-MS as described in Section 2.6. While the same GC-MS program was utilized here and in Section 2.6, a different instrument of the same model was used here and thus the two columns had different lengths and retention times due to routine maintenance. Repeatability within each set of three replicate DVME experiments was

good; however, the most variability was observed for high-volatility species. We suspect that these compounds demonstrated the largest variation because they were most impacted by any leaking that took place during the 60-min equilibration period. Crimp-cap seals were achieved with a manual crimper, which likely resulted in variability across the samples.

# 3. Results and discussion

# 3.1. Comparison of DVME headspace concentration from polymer bags and glass jars

We quantitatively compared headspace concentration from polymer bags and glass jars by adding the same amount of 50% weathered gasoline to each container and varying oven temperature and collection volume across a realistic range of instrumental conditions. Oven temperatures covered the recommended range (ASTM E1412) [3] and were below the boiling point of water, ranging from 54 °C to 96 °C. Collection volumes were less than 10% of the volume of either container, which conforms to the recommendation for nondestructive sampling by leaving most of the original headspace for potential resampling (ASTM 3189) [12], ranging from 47 scc to 90 scc. The different instrumental conditions were tested for each container in randomized order.

Fig. 3 shows the results from the polymer bag and glass jar experiments. The number of target compounds identified from the polymer bags varied from 10 to 23 compounds with  $t_R < n$ -decane. When concentrating headspace from glass jars, 42 to 50 target compounds were identified spanning the full range of the chromatogram with  $t_{R} < n$ -dodecane. One factor that may influence this result is the approximate three-fold difference in headspace volume caused by enclosing a metal can inside a fully-inflated polymer bag. This means that identical collection volumes do not represent the same fraction of the headspace volume. The volume of the polymer bag cannot be decreased as it must contain the metal can and be fully inflated to generate flow through the capillary vapor trap. If the chromatograms from glass jars are modified with a simple three-fold dilution calculation, the number of target compounds identified from glass jars is still greater than the number identified from polymer bags. Furthermore, we cannot know that the concentration of vapors differs by a factor of three because of the different adsorptive and/or absorptive properties of the container materials. For these reasons, the results discussed below are the original findings for each casework container.

Fig. 4 compares the detection rate for polymer bags and glass jars for the 55 individual target compounds. Ten target compounds were detected in all the experiments, regardless of container. These "vigorous" compounds correspond to compounds with higher volatility (t<sub>R</sub> < n-octane) or the C<sub>2</sub>-alkylbenzenes (ethylbenzene, m/pxylene, and o-xylene). Likewise, five "stagnant" compounds were detected in none of the experiments, which is most likely related to their lower volatility ( $t_R > n$ -undecane) and generally lower abundance in gasoline. The remaining compounds exhibited various degrees of detection across the containers. Of these "receptive" compounds, thirteen were detected at varying rates in the polymer bag experiments while being successfully detected in all the experiments conducted in glass jars. Seventeen were identified in all of the glass jar and none of the polymer bag experiments. The remaining ten were detected in some (but not all) of the glass jar experiments, but in none of those conducted with polymer bags.

For the range of oven temperatures and collection volumes examined here, the variability in the number of target compounds identified is similar for both casework containers. However, the minimum number of compounds identified from glass jars (42) was 19 more than the maximum number identified from polymer bags (23). Additionally, the detection rate in glass jar experiments was



Fig. 3. Number of target compounds identified when concentrating IL vapors from (a) polymer bags and (b) glass jars as a function of oven temperature and collection volume. Both containers held 10.0 µL of 50% weathered gasoline spiked onto a wipe. Replicates with the same instrumental conditions are indicated by multiple labels showing total target compounds.



Fig. 4. Detection rate for the 55 target compounds reported in Table 1 from two casework containers. Peak numbers are grouped by detection rate and then listed in order of retention. Detection rate is calculated as the proportion of experiments a compound was detected out of the 21 glass jar and 14 polymer bag experiments, respectively.

elevated across all receptive compounds, suggesting glass jars to be uniformly, rather than differentially, preferable to polymer bags for this collection of compounds. We therefore investigated the effect of the polymer bag material on target compound recovery with a more controlled DVME sampling design.

# 3.2. Vapor loss to polymer bags

The observation that compounds recovered from polymer bags had low  $t_R$  compared to compounds recovered from glass jars (Table 1 and Fig. 4) led us to investigate adsorptive and/or absorptive vapor loss to the polymer bag material. To investigate how the presence and amount of bag material impacts the compounds recovered from 50% weathered gasoline, we concentrated vapors from 2-mL autosampler vials. While these containers are not suitable for authentic fire debris samples, they offer greater experimental control by minimizing the thermal expansion volume and ensuring that the entire headspace volume flows through the capillary vapor trap.

Fig. 5 summarizes how the presence of polymer bag material dramatically affected the concentration of gasoline compounds available in the vapor phase for collection onto the capillary vapor trap. Losses increased monotonically with the amount of bag material added to the vial. While losses to the bag occurred across the entire chromatogram, including high-volatility species ( $t_R < n$ -

octane) like iso-octane and toluene, low-volatility species showed the most dramatic decrease in abundance. For example, naphthalene  $(n-undecane < t_R < n-dodecane)$  was abundant in the samples collected in the absence of bag material but was not detected in the samples that contained 16 cm<sup>2</sup> of bag material. This suggests that polymer bags do not allow for the successful collection of low-volatility species in gasoline, even at high oven temperatures. Preliminary experiments suggest that the equilibration time was not a significant factor; that is, loss of gasoline compounds to the bag occurred in as little as 10 min and did not change significantly for equilibration periods up to 90 min. Additionally, the bag area  $(cm^2)$ to gasoline volume (µL) ratio used here ranged from 4:1–16:1, while the experiments in Section 3.1 used 25 cm  $\times$  25 cm bags with 10  $\mu$ L of gasoline for an approximate ratio of 130:1. This suggests that the loss of IL vapors to the polymer bag material may be almost an order of magnitude greater than what is shown in Fig. 5.

These experiments confirmed our hypothesis that one cause of the difference between the number of target compounds identified under the same instrumental conditions when concentrating headspace from glass jars and polymer bags is the loss of IL vapors to the polymer bag material. Headspace concentration from polymer bags did not result in the detection of compounds with  $t_R > n$ -decane. This matches well with the finding that low-volatility species were almost completely lost during headspace concentration of 50%



**Fig. 5.** Average GC-MS chromatograms resulting from three replicate DVME experiments at 90 °C of 1.00  $\mu$ L of 50% weathered gasoline from 2-mL vials with and without polymer bag material. With even small amounts of bag material in the vial, losses of IL vapors across the chromatograms were seen, but the losses were highest for the low-volatility species with later t<sub>R</sub>, as seen in the figure inset.

weathered gasoline with small amounts of bags in 2-mL sample vials. This result suggests that the low-volatility species that were not detected with DVME headspace concentration from polymer bags were lost to the bag material before concentration onto capillaries could be accomplished, most likely during temperature equilibration. Since glass is more inert, IL vapors that partition onto the glass surface would be more likely to partition back into the gas phase where they are accessible for collection and concentration by DVME.

It is important to note that polymer bags have been successfully used as sampling containers for the ACS method, but the results presented here show that sampling from polymer bags is not equivalent to glass jars for the DVME method. We speculate that one possibility for this difference is a vapor-solid equilibrium occurring between the analytes and the polymer bag. In the DVME method, where sampling is rapid, vapors flow through the sample container and capillaries in a matter of minutes. In the ACS method, where vapors are passively adsorbed over 2-24 h, the concentration of the headspace decreases and creates a favorable scenario for vapors to desorb from the polymer bag, return to the vapor phase, and adsorb to the activated carbon. The equilibrium likely occurs on a timescale longer than DVME sampling times, potentially explaining why DVME is strongly influenced by the polymer material. This speculation would align reasonably well with observations of displacement and vapor distortion in highly concentrated samples and warrants future exploration.

# 4. Conclusions

DVME may offer an alternative to the standard ACS method for extracting and concentrating IL residue from fire debris samples. DVME allows samples to be monitored for breakthrough and uses acetone, a relatively benign solvent, for elution. In the US, the standard casework container is a metal paint can, which is known to leak vapors. Preliminary experiments demonstrated that this leaking prevents the unmitigated use of metal cans with the DVME method. Therefore, we investigated the use of two alternate containers: polymer evidence bags to enclose the metal can that fire debris is typically collected into and glass canning jars. The polymer bags required flow rate limitations to avoid over-pressurization, bag failure, and sample loss. Polymer bags were also found to cause losses of many of the compounds that comprise gasoline. This was particularly true for low-volatility species, like naphthalene, that are important components of heavily weathered gasoline. Even at an oven temperature of 90 °C, low-volatility species with  $t_R > n$ -decane were lost from 1  $\mu$ L of 50% weathered gasoline with as little as 4 cm<sup>2</sup> of bag material in a 2-mL vial. While polymer bags have been successfully used as sampling containers for the ACS method, the

results presented here show DVME sampling from polymer bags is not equivalent to glass jars. The influence of vapor loss is apparent when comparing headspace concentration from polymer bags to glass jars. For all oven temperatures and collection volumes examined, headspace concentration from glass jars resulted in at least 19 more compounds than headspace concentration from polymer bags. Headspace concentration from glass jars resulted in detection across the entire chromatogram and, therefore, the full range of volatilities of 50% weathered gasoline, while headspace concentration from polymer bags only resulted in detection of abundant or high-volatility species. While glass jars were superior to polymer bags for IL recovery by the DVME method, our experiments were limited to a single IL (50% weathered gasoline) and volume (10  $\mu$ L). Authentic fire debris samples include wood, carpet, and other partially burned materials and water from firefighting efforts may be present. IL residue may have a larger or smaller volume than examined here and ILs from different classes have different volatility ranges. Further experiments with samples spanning a realistic range of these factors will be needed.

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# **CRediT authorship contribution statement**

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# **Conflict of Interest**

The authors have no conflicts of interest to declare.

# Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.forsciint.2022.111315.

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