# Analysis of arson fire debris by low temperature dynamic headspace adsorption porous layer open tubular columns ☆

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## ABSTRACT

In this paper we present results of the application of PLOT-cryoadsorption (PLOT-cryo) to the analysis of ignitable liquids in fire debris. We tested ignitable liquids, broadly divided into fuels and solvents (although the majority of the results presented here were obtained with gasoline and diesel fuel) on three substrates: Douglas fir, oak plywood and Nylon carpet. We determined that PLOT-cryo allows the analyst to distinguish all of the ignitable liquids tested by use of a very rapid sampling protocol, and performs better (more recovered components, higher efficiency, lower elution solvent volumes) than a conventional purge and trap method. We also tested the effect of latency (the time period between applying the ignitable liquid and ignition), and we tested a variety of sampling times and a variety of PLOT capillary lengths. Reliable results can be obtained with sampling time periods as short as 3 min, and on PLOT capillaries as short as 20 cm. The variability of separate samples was also assessed, a study made possible by the high throughput nature of the PLOT-cryo method. We also determined that the method performs better than the conventional carbon strip method that is commonly used in fire debris analysis.

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## 1. Introduction

Based on 2011 data (the most recent year for which data are available), a total of 1,389,500 fires were responsible for the loss of approximately US$ 11.7 billion in the United States, along with the loss of over 3000 civilian lives and 17,500 civilian injuries [1,2]. Of this total, approximately 306,300 of these fires were the result of arson (with 440 civilian deaths, 1360 civilian injuries, and US$ 1.3 billion in direct property damage) [3,4]. The investigation of arson fires results in a surprisingly low arrest rate (approximately 19%), and a very low conviction rate (approximately 2%) [5]. On the other hand, there is reason to think that many past convictions for arson and arson related homicides are in fact unjustified. The main reason for these problems is the absence of a clear profile of a typical arsonist, but sampling and chemical analysis of fire debris for residual accelerant (or the more modern term, ignitable liquid, abbreviated IL) can be a contributing factor as well. While the cause of a fire might be suspected (or in some cases known) before laboratory analysis of fire debris, such analysis is nonetheless a critical step. So important is the sampling and analysis process that a recent text on fire scene evidence asserted: "the confirmation or denial of arson cannot at present be determined at the fire scene, but only after forensic analysis of the samples collected at the scene" [6].

Many ILs can be used to start an arson fire, the most common being gasoline, diesel fuel, kerosene, charcoal lighter fluid, paint thinners and solvents; however, many less common fuels have been used as well [7,8]. Attention is even being paid to the new alternative fuels such as biodiesel fuel as potential ILs [9]. Forensic scientists and criminalists must routinely identify and characterize the accelerant or IL in a credible, defensible manner. The analysis of fire debris for the presence of residual IL has long been an accepted and routine aspect of arson investigations, and the techniques available for such analyses have evolved dramatically in recent years. The application of sophisticated techniques, such as nuclear magnetic resonance spectroscopy ($^1$H and $^{13}$C), fluorescence spectroscopy, second derivative ultraviolet spectroscopy, as well as gas and liquid chromatographic techniques, have been used [10–12]. We note that many of these reports are academic studies that have not been adopted in criminal investigations. The nature of ILs as multi-component, moderately volatile fluids makes the technique of gas chromatography the most important and widely used method for fire debris analysis [13,14]. Indeed, the majority of liquid residue analyses done in forensic labs utilize gas chromatography with some combination of detectors and peripherals [7,8,15–22]. The most common is gas chromatography with mass spectrometry as the detector [23–27]. In practice, the use of a single

quadrupole mass filter is most common; however, tandem mass spectrometric methods have been used as well [28].

Before any of the techniques described above can be used to detect ILs in fire debris, a method of extraction must be applied to isolate the components of the ILs. There are several approaches currently used for extraction, many of which are embodied in either standard practices or standard test methods [29,30]. The most common technique is passive headspace concentration with activated charcoal. A polymeric strip that holds the activated charcoal is the most convenient adsorbent used for this test. The sample (usually between several hundred g to approximately a kg) is collected and transported in a sealed paint can; upon reaching the laboratory, the can is opened and the carbon strip is suspended in the headspace above the fire debris. If the analyst notices a hydrocarbon odor while inserting the strip, the strip can be exposed for 2–3 h at 66 °C. If a slight odor or no odor is noted, the strip is exposed for 16 h at 66 °C [6]. Note that these procedures are general guidelines and many labs follow different but similar procedures. The analytes that are collected are then desorbed by a solvent into a sampling vial prior to analysis by gas chromatography; typical solvents include diethyl ether, pentane and most commonly carbon disulfide. Other solvents can interfere with analysis because they are themselves common ignitable liquids, although additional solvents are possible [31,32]. An advantage of this method is that it can be repeated if needed, since typically not all of the analytes in the fire debris are captured in a single carbon strip exposure. The obvious downside is that the method can therefore lack sensitivity. The timing is a critical variable when this technique is used because displacement of the lighter components from the strip will occur if the exposure is not stopped at the proper time [6].

Other headspace sampling methods that are less common include a standard dynamic purge and trap into a cartridge containing activated charcoal or another adsorbent such as p-2,6-diphenylphenyene oxide [13]. We call this a less common method in the present context of fire debris analysis; however, dynamic purge and trap has been one of the classical methods used for headspace analysis for decades. This method can be done with either positive or negative pressure, and the application to fire debris usually requires the placement of inlet and outlet fittings on the lid of a clean paint can that holds the sample of fire debris. This approach is faster and more sensitive than the passive activated charcoal strip collection described above. It can only be used once per sample; however, since the volatile components are typically swept into the adsorbent cartridge, and the adsorbent bed in the cartridge has a large capacity. Related to this method is the simple static headspace sampling technique, in which a gas tight syringe is used to penetrate into the interior of the sample can and withdraw a sample for direct injection into a gas chromatograph. This method is used primarily as a screening technique, because of a much lower sensitivity than other methods. The newer solid-phase microextraction methods (SPME) are a variant of this approach [33,34]. SPME methods are very sensitive and their use results in nondestructive sampling. Among the disadvantages of SPME are high displacement rates of heavier over lighter components (more pronounced than is observed with the activated charcoal strips), difficulty in automation and repetition, difficulty in sample preservation/archiving, and despite claims to the contrary, difficulty in obtaining repeatable and quantitative results [6]. Moreover, SPME requires more sophisticated equipment with a higher capital outlay than the other headspace sampling methods, and while the sample fibers can be used many times, a blank must be run before each use to ensure no carryover from prior samples. SPME fibers are easily damaged by rough handling and salting out procedures that make use of strong base.

Other methods of extracting the ILs from fire debris include simple solvent extractions, and these methods are sometimes used on a limited basis for specific situations. These destructive methods lack sensitivity and are messy, resulting in fair quantities of chemical waste (yielding a mud containing both solid and liquid). The primary advantage is that they consistently recover compounds containing 18+ carbons. Finally, the least common method of extraction is steam distillation, in which the fire debris is placed in a distillation flask equipped with a reflux condenser and a side arm. The method is used to extract liquids that are immiscible in water. The method is complex, results in a great deal of waste, and is low in sensitivity.

A potential alternative to the above methods is the dynamic adsorption of headspace vapors on short porous layer open tubular (PLOT) columns maintained at low temperature, a technique called PLOT-cryoadsorption (PLOT-cryo) [35]. The method has proven to be sensitive and quantitative, with a sampling limit of detection below 1 ppb (mass/mass) of solute in the analyte matrix, and can provide results that are of low enough uncertainty to permit thermodynamic interpretation (by way of the equilibrium constant and associated enthalpy) of recovered concentrations through the van't Hoff equation. Naturally, the sampling limit of detection that will apply specifically to each analysis will depend upon the choice of detector. The low temperature that is used to improve efficiency and facilitate collection is generated with a vortex tube, a device that operates from a source of compressed air and has no moving parts [36–40]. This aspect in particular makes the approach attractive for environments with explosive or flammable materials [41]. The same vortex tube that is used to generate the low temperature air stream (that can be as low as −40 °C) can be used to generate a high temperature stream of air (that can be as high as 160 °C) to thermally desorb solutes from the PLOT capillary (or to assist the solvent desorption with more gentle heating). The capillaries that are used are robust and inexpensive, and unlike other headspace collection methods, PLOT-cryo is especially applicable for relatively involatile solutes because it has a large temperature operability range. Moreover, it is not limited to aqueous samples, as are some commercial headspace instruments. We have discussed the advantages of this method over conventional purge and trap (static and dynamic) [42–49], and even such modern techniques such as SPME [33–35]. A particularly attractive feature of PLOT-cryo is the ability to simultaneously sample headspace with multiple, different sorbent phases (selected for their specific functionalities). This has included the clay and organoclay phases developed at NIST [50–52]. We have in fact used up to seven separate phases, simultaneously, to collect vapor from a single sample. Alternatively, the approach allows sampling with multiple PLOT capillaries of the same phase, for repeatability and quality assurance. This advantage addresses one of the major shortcomings called out in the description of the other extraction methods that were discussed above. PLOT capillaries made from commercial columns presently cost approximately US$ 10 per unit, while the clay and organoclay capillaries can be made for approximately half that cost. The PLOT-cryo metrology has been demonstrated with applications to explosives, food safety, and cadaver detection [53–55]. A portable PLOT-cryo device has recently been developed, permitting the method to be used in remote locations and not simply in the laboratory. A further development was the introduction of pyrolysis-PLOT-cryoadsorption, in which a pyrolysis platform was incorporated with PLOT-cryo [56].

In this paper, we first compare the performance of PLOT-cryo with a conventional purge and trap (PT) method for the collection of ILs on selected substrates. Then, we present results on the application of PLOT-cryo for the collection of analytes present on fire debris. We examined fire debris produced by eleven different ILs (discussed below) on three substrates: Douglas fir (of the type used for studs in residential construction), hardwood plywood (of the type used for furniture construction and flooring), and a nylon

carpet. Selected comparisons of measurements made with conventional purge and trap cartridges and activated carbon strips are also presented.

## 2. Material and methods

### 2.1. Ignitable liquids (ILs)

A total of eleven flammable fluids were investigated in the course of this work, broadly divided into fuels and solvents (although the majority of results presented and discussed in this paper were obtained with gasoline and diesel fuel). While not all of these fluids are defined as ILs by the ASTM, for the remainder of this paper we will refer to them as such for simplicity. All of the ILs discussed here have been previously studied by use of the Advanced Distillation Curve method, a technique that couples the thermo-dynamic property of vapour–liquid equilibrium (that is, volatility) with composition to provide a prediction of weathering [57]. This body of previous work has provided a more detailed characterization of the fluids studied here than might otherwise have been available [58,59].

The gasoline used was a 91 antiknock index summer grade fuel obtained from a commercial supplier. The antiknock index (AI) cited is the average of the research octane number and the motor octane number. This fuel did not have any oxygenating additive, and had an initial boiling temperature of 44.4 °C (uncertainty of 0.3 °C). The diesel fuel used was a winter-grade, low-wax, ultra-low-sulfur diesel fuel that incorporated a red dye (specifying off-road use), and was refined locally from petroleum of the Denver-Julesburg field. The fuel had a relatively high cetane number of 45 (the typical range in the United States is 41–42). A diesel fuel with a high cetane number is typically associated with a high concentration of straight chain hydrocarbons and minimal branching. Such a fuel might differ in detailed compositional details from other commercial diesel fuels. The initial boiling temperature of this fuel was 215.1 °C (expanded uncertainty of 0.3 with a coverage factor $k = 2$ °C). Two aviation turbine kerosenes were studied as part of this work: Jet-A and JP-5. The sample of Jet-A (the most common domestic aviation turbine fuel) was obtained from the Fuels Branch at Wright Patterson Air Force Base, and was formulated as a typical composite fluid by mixing equal volume aliquots of five different batches of Jet-A from commercial sources. The fluid had an initial boiling temperature of 190.5 °C (expanded uncertainty of 0.3 with a coverage factor $k = 2$ °C), and the detailed composition has been presented elsewhere [60]. The sample of JP-5, also obtained from the Fuels Branch at Wright Patterson AFB, was a typical ship-board aviation turbine kerosene formulated to have lower volatility than the typical Jet-A or JP-8 formulations. This fluid had an initial boiling temperature of 200.1 °C (expanded uncertainty of 0.3 with a coverage factor $k = 2$ °C), and the detailed composition was presented elsewhere [61]. Another aviation fuel tested was 100LL, a 100 AI gasoline (treated with the antiknock compound tetraethyl lead). This fluid had an initial boiling temperature of 68.1 °C (expanded uncertainty of 0.3 with a coverage factor $k = 2$ °C), and the detailed composition is provided elsewhere [62]. A mixture of gasoline with a commercial two-cycle oil prepared in a 16/1 ratio (vol/vol) with the gasoline mentioned above was tested because it is also a common IL. This mixture had an initial boiling temperature of 68.8 °C (expanded uncertainty of 0.3 with a coverage factor $k = 2$ °C) and a composition similar to the gasoline discussed above, with some bis(2-ethylhexyl) esters in the base oil.

In addition to the fuels discussed above, several flammable solvents were studied [63]. These fluids are among those listed in the Ignitable Liquids Reference Collection (ILRC), maintained by The National Center for Forensic Science (University of Central Florida) [64]. This database is an up to date, comprehensive catalog of ignitable liquids and accompanying characterization data used for the analysis of fire debris samples in accordance with established practice, such as those embodied in ASTM practices and procedures. Each entry contains a gas chromatographic profile of the ignitable liquid for which mass spectrometry was used as the detector (gas chromatography–mass spectrometry). The ILRC categorizes ignitable liquids (based on ASTM E1618) into useful and distinct families to facilitate searching and reference.

The common light lubricant/cleaner WD-40 was obtained from a commercial source in a pressurized can, and was collected in a scintillation vial after flashing off the carrier, carbon dioxide. Classified as a medium petroleum distillate, this fluid had an initial boiling temperature of 190.8 °C (uncertainty of 0.3 °C), and had straight chain alkanes as major components (n-nonane, n-decane, n-undecane, n-dodecane, n-tridecane, n-tetradecane, n-pentadecane, and n-hexadecane). 3 M All-Purpose Adhesive Cleaner, classified as an aromatic, had an initial boiling temperature of 136.8 °C (uncertainty of 0.3 °C) and primarily aromatic components (1,3-dimethylcyclohexane, ethylbenzene, m-, o-, and p-xylene, and n-nonane). CRC Industrial Belt Dressing is a hexane(s) solution of polyisobutylenes that makes use of liquefied petroleum gas as a propellant. Vaporization data could not be measured for this fluid because the polyisobutylene further cross-linked upon heating to form a solid mass. A-9 Aluminum Cutting Fluid is a perfumed, mineral oil based fluid that includes an added green dye.

As mentioned in Section 1, this study included a comparison of conventional PT with PLOT-cryo. For these comparisons we used the gasoline and diesel fuel described above, as well as used motor oil (or drain oil, from an automotive shop) and used cutting oil (from the NIST-Boulder machine shop).

### 2.2. Solvents

In all of the work presented herein, spectroscopic grade acetone was used as the solvent for eluting PLOT capillaries, and spectroscopic grade n-hexane was used to elute conventional PT cartridges. These fluids were analyzed by GC–MS by use of established protocols in our labs. The same batch of acetone and n-hexane were used for all experiments; several batches with unacceptable levels of impurities were rejected by analysis. We note that acetone is considered to be an IL, and would not be used in typical forensic samples. We use it here because it has proven to be efficacious in eluting from alumina surfaces, and it is safer to use (especially by student workers) than carbon disulfide or diethyl ether.

### 2.3. Substrates

Measurements of residual IL were made on three different matrices: Douglas fir, oak plywood and Nylon carpet; however, most of the work focused on the two wood substrates. Douglas fir (DF), ubiquitous in residential and industrial construction, is commonly used for the erection of stud walls. The sections of DF used were cut from a length of commercial stud into trapezoidal sections (9 cm × 3.5 cm base, 4 cm × 3.5 cm top). Oak plywood (PW) is used in the construction of furniture and flooring. The plywood samples were cut from a commercial sheet into squares that measured 5 cm on a side. After some experimentation, we found it optimal to form a series of depressions into the top surface of each section of both DF and PW, to hold the IL during burning. This was done with an automatic center punch. While the number and pattern of holes was identical for all substrates, the size varied slightly because of the grain density of the wood; this variability is discussed in Table 1. Carpet (NC) is a very variable substrate not amenable to easy representation by a single sample. Nevertheless, we have measured one type of carpet as a substrate: an Anso BCF Nylon cut into squares

**Table 1**
The size of holes typically formed in the wood substrates by use of the automatic center punch. The average width and depth of punches in each type of wood are indicated. The volume was approximated assuming each hole is conical.

| Substrate | Width (mm) | Depth (mm) | Volume (µL) |
| --- | --- | --- | --- |
| Oak Plywood | $2.98 \pm 0.04$ | $2.0 \pm 0.1$ | $4.5 \pm 0.1$ |
| Douglas Fir | $2.99 \pm 0.04$ | $3.1 \pm 0.1$ | $7.2 \pm 0.1$ |

measuring 2.5 cm on a side. We note that the substrate samples used for our laboratory measurements are small compared with the substrates encountered at fire scenes. We note further that the recovered fire debris samples resulting from our experimental substrates yield samples that are smaller than those typically recovered from a fire scene.

The substrate used for the direct comparison of PT with PLOT-cryo (in contrast to the fire debris samples) was clay soil (designation by the United States Geological Survey) obtained from an unimproved section of the NIST-Boulder campus. A soil sample was chosen because we desired, as part of other work, to evaluate the performance of PLOT-cryo in environmental sampling.

### 2.4. Dynamic purge and trap cartridges

The dynamic purge and trap (PT) cartridges used for comparison with PLOT-cryo were prepared from 8 mm sections of thin walled stainless steel tubing equipped with custom made low dead volume fittings, packed with p-2,6-diphenylphenyene oxide porous polymer. These are the same adsorbent cartridges that have been used in concatenated gas saturation vapor pressure measurements, and are fully described elsewhere [65]. The vapor flow dynamics and solvent elution geometry of these cartridges have been optimized to permit the measurement of thermodymically consistent reference quality vapor pressures for low vapor pressure materials [66,67]. All transfer lines between the cartridge and the sample were made from 316 stainless steel. Because of the short residence times and relatively rapid flow rates, no attempt was made to passivate the interior of the tubing.

### 2.5. PLOT-cryo capillaries

In previous work, dynamic headspace vapor collection on short (0.5–3 m), PLOT capillary columns maintained at low temperature was introduced (see the references cited in Section 1) [35,37]. This approach, called PLOT-cryoadsorption (or PLOT-cryo), is sensitive and quantitative, with a sampling limit of detection below 1 ppb (mass/mass) of solute in the analyte matrix. Since details are found elsewhere, no further general discussion on operation and construction will be provided here. The PLOT capillaries used in this work were uniformly 80 cm in length and had an internal diameter of 0.32 mm; the only exception was the collection of shorter lengths studied to assess the limits of the method.

### 2.6. Activated carbon strips

The activated carbon strips used in this work were obtained from a commercial supplier. They were rectangular, 1 cm × 2 cm, and were typically suspended in the paint can by a corner with a magnetic paper clasp. Unfortunately, scarcity and supply/delivery problems (there being only one supplier) prevented us from performing extensive comparisons with these strips. The usual paint can approach was used for the work described here, but with one variation. A septum cap was installed in the lid of the paint can so that a PLOT capillary could be inserted to allow comparison of PLOT-cryo with the carbon strips. In keeping with the established practice in many labs, the sample temperature was maintained at 66 °C (in

a surplus gas chromatographic oven) for these comparisons, and since residual IL was known to be present, the 2 h (rather than the 16 h) collection period was employed. While many methods call for washing the carbon strip with $CS_2$, we used the same solvent as with the PLOT capillaries: 0.75 mL of acetone.

### 2.7. Production and vapor sampling of fire debris

The individual samples of fire debris were prepared by applying 2 mL of each IL onto the substrate by use of a disposable pipette. The substrate, with the applied IL, was placed on a 1018 steel platform (4 cm × 10 cm × 1 cm) housed inside of a brass chimney (a cylinder 15 cm in diameter, 20 cm high) that was equipped with two 7 cm access ports in the wall. The access ports allowed for safe ignition and observation of the burning, and also allowed for videography. The videography, while not specifically included as part of this paper or the supporting information, was used to document the qualitative observations of the fires discussed below. In general, each IL appeared to be better absorbed into the PW than the DF, no doubt because of the higher grain density of the DF. Once applied, the IL was then allowed to remain on the substrate before ignition for a latency period. The latency period was intended to probe what effect a delay between the application of liquid and the time of ignition might have in the suite of compounds that are recoverable from the fire debris vapor. We used latencies of 1, 10 and 30 min in this work (recognizing that an arsonist may apply IL and then delay ignition in order to affect escape). After the desired latency, the IL and substrate was ignited by use of a propane torch. The torch was applied for the minimum time required to achieve ignition, typically 1–3 s. For ILs of low volatility, sometimes multiple ignition attempts were needed. Following ignition, the sample was allowed to burn until the active flame was self-extinguished. Once no flame or glowing embers were visible, one re-ignition was attempted with the propane torch. Any flames or glowing embers produced upon re-ignition were then allowed to burn out.

During the process of burning the ILs on the substrates, some qualitative observations of the fires were made. These observations are presented here rather than in the discussion of results because they are more concerned with the preparation of the samples, rather than being central to the measurements that were made. As might be expected, the liquids of lower volatility (as characterized by the ADC method mentioned above) were more difficult to ignite than liquids of higher volatility. Once ignited, the lower volatility fluids burned for a longer time period than the higher volatility fluids, and they produced flames that were shorter in height (8–10 cm) than the more volatile fluids. These fluids tended to produce more smoke and left behind more glowing embers, and re-ignition was often possible. Examples of fuels that behaved in this manner include diesel fuel and jet fuel (both Jet-A and JP-5). ILs of intermediate volatility were, in general, easy to ignite and produced larger initial flames, but burned for less time. Re-ignition of samples with ILs of intermediate volatility was occasionally possible but the resulting fires were of short duration. Examples of liquids that showed this behavior were the leaded aviation gasoline, the MR Paraffinic Solvent, gasoline, and the 2-cycle oil/gasoline mixture. The highest volatility liquid we examined was 3 M adhesive cleaner. Upon ignition, substrates treated with this liquid immediately produced a large flame (20–23 cm high, extending above the top of the chimney) that quickly shrank and extinguished. One fluid that we examined, WD-40, showed characteristics of both high and low volatility fluids. This fluid was easy to ignite, but produced intermediate sized flames (approximately 10 cm), and produced a bubbling foam beneath the flame. This was the only fluid we examined in this work that showed this behavior.

After the burning was complete, the sample was allowed to cool for 3 min. The charred material, along with loose underlying

substrate from the burned section was then removed and collected on an aluminum tray. All coarse char and substrate removal was done with a wood rasp, and fine removal was done with a dental scaler. The material removal process required several minutes. The collected material was then placed in a 2 mL automatic sampler vial that was sealed with a crimp cap. The quantity of fire debris that could be recovered was variable, however, in adherence with the protocols and capability of the PLOT-cryo metrology, samples were much smaller than what is usually taken by investigators in paint cans from fire scenes. In general, our samples reached the 0.5 mL mark on the automatic sampler vials, and had masses between 0.3 and 0.1 g. The substrates were used only once and then archived.

Vapor collection by PLOT-cryo was done with the apparatus described in earlier work. The fire debris samples contained in the automatic sampler vials were placed in the oven (of the PLOT-cryo apparatus, as described earlier) and the sweep gas (helium) inlet was connected to the electronic pressure control via a length of uncoated fused silica tubing. Once inside the oven, the PLOT capillary (which was 80 cm long for most measurements) extending from the cryostat (set at 5 °C, uncertainty of 2 °C) was then connected to the vial, and the vial temperature was then set to 175 °C (uncertainty of 1 °C). While competitive adsorption on char or charcoal can make desorption of the ILs difficult, our collection at 175 °C proved to eliminate most such problems.

We usually sampled from eight separate vials, with eight separate PLOT capillaries, simultaneously. Pressure and flow were established for each vial–capillary pair (1.4 kPa above atmospheric pressure, flow rate average of 1.3 mL/min). Because multiple PLOT capillaries were used simultaneously, no breakthrough volumes were employed. For most of the work presented here, a collection time period of 30 min was used. Time was measured with a digital stopwatch, and given the ramp up and ramp down of flow, the uncertainty in time period was typically 0.05 min. Flow and pressure were monitored during the collections; pressure was measured with a strain gauge transducer with an uncertainty of 0.1 kPa, and flow was measured with an electronic bellows flow meter with an uncertainty of 0.1 mL/min. After collection, the PLOT capillaries were eluted with approximately 0.75 mL of acetone, by pressure flowing into another automatic sampler vial. Experimentation showed that additional elution with larger volumes of solvent did not produce additional detectable analyte, so repeat elutions were not generally done. Although the elutions effectively cleaned the PLOT capillaries, before a subsequent vapor collection, each capillary was rinsed with an additional 1.5 mL of acetone, and then the capillary was conditioned at 200 °C under a head pressure of 14 kPa of helium.

The eluted samples were analyzed by gas chromatography with mass spectrometry (30 m column of 5% phenyl polydimethylsiloxane). Survey analyses were done in scan mode (from 33 to 550 relative molecular mass units); this allowed for peak identification. Since most of the recovered analytes were hydrocarbon species, a selected ion monitoring method was used for our data analysis, a method that permitted highly repeatable chromatograms, identification of all important peaks and the elimination of unnecessary background. The ions that were monitored are listed in Table 2.

## 3. Results and discussion

### 3.1. Comparison of PT with PLOT-cryo

While we realize that a direct comparison of the low efficiency–high capacity of conventional PT with the high efficiency–low capacity of PLOT-cryo is necessarily limited (rather like comparing packed chromatographic columns with open tubular columns), it is nevertheless of interest especially in defining optimum

**Table 2**
A listing of ions monitored for GC–MS analyses of the vapors collected above the fire debris samples.

| $m/z$ | $m/z$ | $m/z$ |
|-------|-------|-------|
| 39.1  | 112.1 | 134.1 |
| 43.1  | 113.1 | 141.1 |
| 51.1  | 114.1 | 142.1 |
| 55.1  | 115.1 | 155.1 |
| 56.1  | 116.1 | 156.1 |
| 57.1  | 117.1 | 165.1 |
| 65.1  | 118.1 | 166.1 |
| 71.1  | 119.1 | 167.1 |
| 77.1  | 120.1 | 169.1 |
| 78.1  | 121.1 | 170.1 |
| 83.1  | 123.1 | 183.1 |
| 84.1  | 124.1 | 184.1 |
| 85.1  | 125.1 | 198.1 |
| 91.1  | 127.1 | 211.1 |
| 96.1  | 128.1 | 212.1 |
| 99.1  | 129.1 | 226.1 |
| 105.1 | 131.1 | 239.1 |
| 106.1 | 132.1 | 240.1 |
| 109.1 | 133.1 |       |

performance regimes. Soil (a 2.5 cm layer, approximately 65 g) spiked with gasoline, diesel fuel, used motor oil, and used cutting oil was maintained in 250 mL Nalgene bottles at ambient temperature (23 °C) for the tests. Five such bottles were prepared for each spiked analyte. For PT, the adsorbent cartridge was also maintained at ambient temperature, while for PLOT-cryo, the capillaries were chilled to approximately 0 °C. The spiked soil samples were allowed to equilibrate for approximately 1 h before sampling; this was sufficient time to develop the headspace concentration of analyte. For the PT cartridges, a gas tight syringe was used to draw 50 mL of headspace volume through the cartridge (a negative pressure sampling procedure). The cartridge was then removed from the bottle and placed on a syringe pump, and 1 mL of *n*-hexane solvent was passed through the adsorbent bed and collected in an automatic sampling vial. Unlike the PT sampling process, when using PLOT-cryo capillaries the bottles were swept with 50 mL of helium (positive pressure sampling procedure, flow calculated by a measured flow rate and a measured time period, uncertainty 1.5 mL) to collect the head space. Subsequent to the sweep, the capillaries were eluted with 1 mL of *n*-hexane solvent.

The solutions collected by both methods were analyzed by gas chromatography mass spectrometry (2 µL injection via automatic sampler into a splitless injector, 0.01 m coating of 5% phenyl polydimethylsiloxane, temperature program of 50 °C for 2 min with split vent closed, followed by a 20 °C/min ramp to 300 °C, with a 2 min hold at 300 °C to prepare for subsequent analysis, scan $m/z$ from 35 to 550).

Typical comparative total ion chromatograms of headspace collected by PT and PLOT-cryo are provided in Fig. 1a and b for gasoline and diesel fuel on soil (1% spike, mass/mass). We also provide similar chromatograms for used cutting oil and drain oil on soil in supporting information, Figs. S1a and S1b. An examination of the chromatograms shows that for both diesel fuel and gasoline spiked on soil, a much larger number and variety of components (alkanes, branched alkanes and aromatics) are collected by PLOT-cryo than are collected by PT. This is especially striking for the case of gasoline. Moreover, a much larger total integrated area is obtained for the samples collected by PLOT-cryo. In the case of the diesel fuel collections, this was typically a ratio of 4:1. Again, even more striking is the comparison with gasoline, in which the peak area ratio is 40:1. It is clear that PLOT-cryo performs better than conventional PT, at least for the 50 mL sample volumes drawn, primarily because of the high efficiency. This is especially apparent for the more volatile gasoline components, in which high efficiency is required
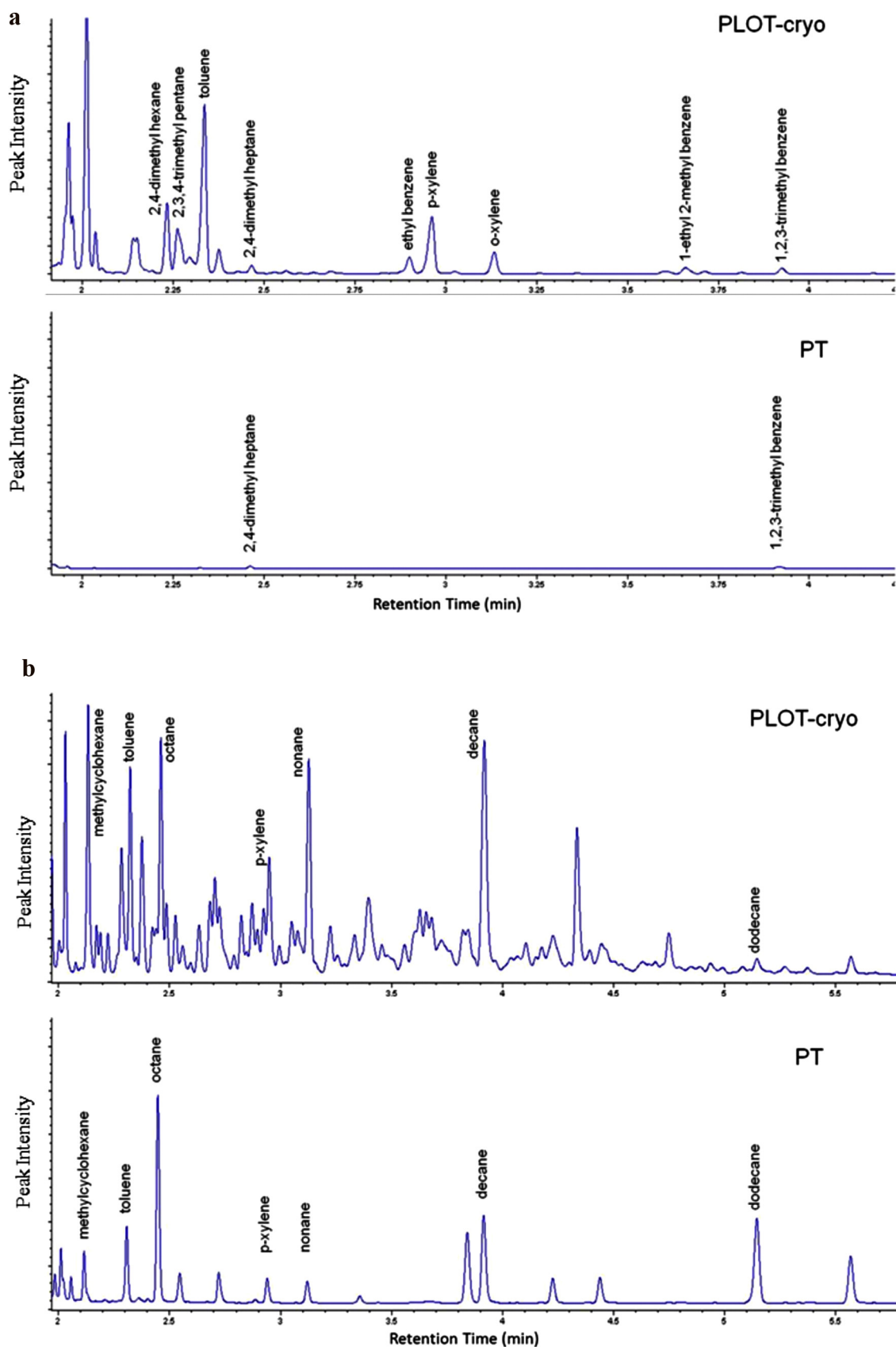
**Fig. 1.** (a) Representative chromatograms measured at the same scale (analysis conditions described in the text) showing components collected from the headspace allowed to develop from a 1% (mass/mass) spike of gasoline on clay soil. (b) Representative chromatograms measured at the same scale (analysis conditions described in the text) showing components collected from the headspace allowed to develop from a 1% (mass/mass) spike of diesel fuel on clay soil.

**Table 3**

Representative suite of compounds collected from fire debris made from burning DF treated with gasoline after a latency of 10 min. The chromatographic conditions and the uncertainties are discussed in the text. The area percents provided are on the basis of uncalibrated area measurements. Where the positional isomerism could not be determined by mass spectrometry, substitution is indicated by x-, x, y-, etc.

| Compound | Retention time (min) | Area percent |
|---|---|---|
| o, m-xylene[1] | 3.814 | 0.25 |
| 1,2,4-trimethylbenzene | 5.044 | 5.48 |
| 3-ethyl-3-methylbenzene | 5.353 | 2.46 |
| 1,3,5-trimethylbenzene | 5.584 | 17.38 |
| x-methyldecane | 6.083 | 0.54 |
| indane | 6.397 | 2.18 |
| 1-methyl-2-propylbenzene | 6.665 | 4.48 |
| 1-methyl-3-propylbenzene | 6.761 | 2.34 |
| 4-ethyl-1,2-dimethylbenzene | 6.808 | 3.52 |
| 1-methyl-3-propylbenzene | 7.001 | 0.98 |
| 2-ethyl-1,3-dimethylbenzene | 7.213 | 1.53 |
| 1-ethyl-2,4-dimethylbenzene | 7.252 | 1.93 |
| x-ethyl-y,z-dimethylbenzene | 7.391 | 3.82 |
| x-methylindane | 7.458 | 0.85 |
| 2-ethyl-1,4-dimethylbenzene | 7.871 | 0.71 |
| 1,2,3,5-tetramethylbenzene | 8.085 | 2.67 |
| x,y,z,w-tetramethylbenzene | 8.186 | 3.78 |
| x-methylindane | 8.637 | 1.49 |
| x,y-diethyl-methylbenzene | 8.738 | 1.53 |
| x-methyl-y-(methylpropyl)-benzene[a] | 9.243 | 1.44 |
| naphthalene | 9.747 | 7.12 |
| pentamethylbenzene | 10.049 | 0.79 |
| x,y-dimethylindane | 11.383 | 0.70 |
| 2-methylnaphthalene | 12.541 | 5.75 |
| 1-methylnaphthalene | 12.986 | 2.94 |
| 2,7-dimethylnaphthalene | 15.387 | 0.87 |
| 1,2-dimethylnaphthalene | 15.777 | 0.97 |
| 2-methoxy-4-(2-propenyl)phenol (eugenol) | 16.539 | 0.55 |

[a] Co-elution of multiple peaks.

above high capacity. The capacity of the PT approach is typically much higher than that of PLOT-cryo, however, so one must balance the competing advantages and also the intended purpose of the vapor collection. Thus, collections by PLOT-cryo for extended periods of time are not indicated (more discussion on limitations will be provided in Section 3.5). The clear ability of PLOT-cryo to efficiently collect headspace vapors of hydrocarbons (as demonstrated in these figures) prompted our application of the metrology to fire debris. We note that other adsorbent beds (activated carbon, silica, molecular sieve, etc.) were tested, this was merely a survey and comparisons beyond the porous polymer mentioned must be regarded as speculative.

### 3.2. Headspace collection of fire debris vapor by PLOT-cryo

Fire debris was generated on DF, OP and (to a more limited extent) NC by use of the method discussed in the Experimental section. We typically performed 10 burnings for each IL/substrate pair. In addition, we tested three different IL latencies: 1, 10 and 30 min. While it is not possible within the confines of this paper to discuss all of these data in detail, we will begin with the presentation of representative product suites collected on DF and OP, with the goal of assessing the ability of PLOT-cryo to determine the identity of the IL. In Table 3, we provide a representative data set taken for gasoline on DF after a latency of 10 min, and a representative chromatogram is provided in Fig. 2. These data were taken for one collection, in one automatic sampler vial, however this suite was typical of the recovery. The repeatability of replicate chromatographic retention times is excellent, typically within 0.02 min. The uncertainty in replicate peak areas is acceptably low, ranging from 1% for the midrange molecular mass compounds to approximately 3% for the lighter and heavier components. Sample to sample
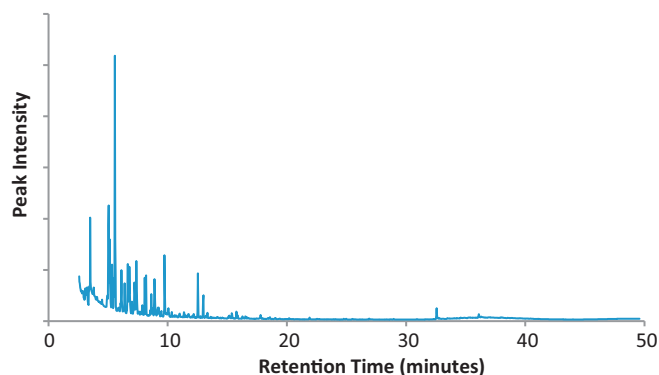


**Fig. 2.** A representative chromatogram of the vapor recovered from the headspace of fire debris generated on DF with gasoline as the IL. Chromatographic conditions are discussed in the text.

variability is a different issue that will be treated separately below. As is well known, it is not often possible to distinguish branching by mass spectra alone, and where ambiguity in the substitution exists, we indicate such by x-, x, y-, etc., as a prefix to the root name. We note the recovery of predominantly aromatic compounds, consistent with a premium (that is, high antiknock index) gasoline. We also note the somewhat surprising presence of eugenol (2-methoxy-4-(2-propenyl)phenol, with a relative molecular mass of 164.2), an antioxidant compound commonly associated with clove oil. This compound, which was identified on the basis of the mass spectrum and retention index, was found only in samples in which the gasoline (or gasoline mixed with 2-cycle oil) was used as the IL, regardless of the substrate considered. We attempted to confirm with the gasoline supplier whether this compound was used as an antioxidant additive, but we were unsuccessful. It is nonetheless remarkable that PLOT-cryo allows the identification of what is possibly a fuel treatment compound, recovered in the vapor over fire debris.

In Table 4, we provide a representative data set taken for diesel fuel on DF after a latency of 10 min, and a representative chromatogram is provided in Fig. 3. As with the gasoline sample presented above, these data were for one collection in one automatic sampler vial. We note the predominance of linear and branched alkanes in the vapor when diesel fuel is used as an IL. In contrast with the gasoline sample, we observe very little aromatic content. This is consistent with the compositions of the samples; high AI gasoline has a high aromatic content for antiknock, while the high cetane number diesel fuel we used has mostly alkanes for compression ignition.

A final example will be discussed here because it represents an IL with properties intermediate between the low and high volatility
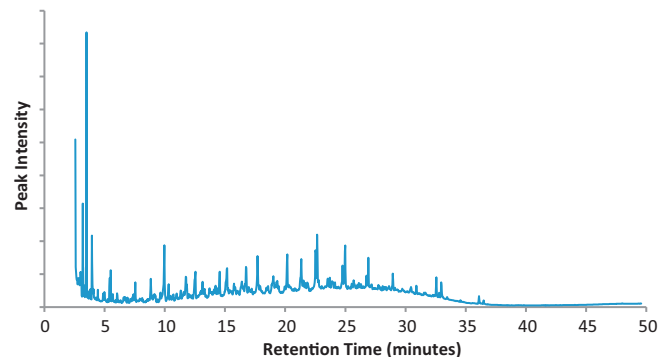


**Fig. 3.** A representative chromatogram of the vapor recovered from the headspace of fire debris generated on DF with diesel fuel as the IL. Chromatographic conditions are discussed in the text.

**Table 4**

Representative suite of compounds collected from fire debris made from burning DF treated with diesel fuel after a latency of 10 min. The chromatographic conditions and the uncertainties are discussed in the text. The area percents provided are on the basis of uncalibrated area measurements. Where the positional isomerism could not be determined by mass spectrometry, substitution is indicated by *x*-, *x*, *y*-, etc.

| Compound | Retention time (min) | Area percent |
|---|---|---|
| *n*-decane | 5.599 | 0.57 |
| *n*-undecane | 7.628 | 1.13 |
| *n*-dodecane | 10.023 | 2.24 |
| 2,6-dimethylundecane | 10.374 | 0.79 |
| 3,6-dimethylundecane | 10.529 | 0.32 |
| 1,4-diethyl-2-methylbenzene | 11.043 | 0.50 |
| *x*,*y*-dimethylindane | 11.397 | 0.77 |
| 2-methyldodecane | 11.649 | 0.72 |
| *x*-methyl-tetralin | 11.799 | 1.26 |
| *x*,*y*-dimethyl-dodecane | 11.888 | 0.72 |
| *n*-tridecane | 12.59 | 4.02 |
| 1,2-dimethyltetralin | 12.598 | 0.94 |
| 2-methyltridecane | 13.176 | 1.57 |
| 3-methyltridecane | 14.6 | 1.23 |
| *x*,*y*-dimethyltetralin | 15.11 | 0.83 |
| *n*-tetradecane | 15.2 | 3.27 |
| *x*,*y*-dimethyl-tridecane | 15.38 | 0.54 |
| *x*,*y*-dimethylnaphthalene | 15.78 | 0.56 |
| *x*,*y*,*z*-trimethyltetralin | 15.91 | 0.54 |
| *x*-methyltetradecane | 15.78 | 0.68 |
| octylcyclohexane | 16.438 | 0.79 |
| *x*,*y*,*z*-trimethyltetralin | 16.56 | 0.56 |
| *n*-pentadecane | 17.76 | 5.7 |
| nonylcyclohexane | 19.05 | 0.95 |
| *x*-methylpentadecane[a] | 19.37 | 1.97 |
| *n*-hexadecane | 20.12 | 4.19 |
| *x*,*y*-diethyldodecane | 20.38 | 0.74 |
| *x*,*y*,*z*-trimethylpentadecane | 21.37 | 2.11 |
| decylcyclohexane[b] | 21.55 | 1.05 |
| *x*-methylhexadecane | 21.71 | 0.66 |
| *x*,*y*,*z*-trimethyl-hexadecane | 22.70 | 2.92 |
| *x*,*y*-dimethyl-biphenyl | 22.79 | 0.58 |
| *n*-octadecane | 24.80 | 2.64 |
| *x*,*y*,*z*,*w*-tetramethyl-hexadecane | 25.01 | 2.73 |
| nonadecane | 26.94 | 2.64 |

[a] Three unresolved peaks.
[b] Uncertain assignment.

**Table 5**

Representative suite of compounds collected from fire debris made from burning DF treated with WD-40 after a latency of 10 min. The chromatographic conditions and the uncertainties are discussed in the text. The area percents provided are on the basis of uncalibrated area measurements. Where the positional isomerism could not be determined by mass spectrometry, substitution is indicated by *x*-, *x*, *y*-, etc.

| Compound | Ret. time (min) | Area percent |
|---|---|---|
| furfural | 3.473 | 1.07 |
| *n*-decane | 5.534 | 1.09 |
| 3-methyl-decane | 6.926 | 0.50 |
| *n*-undecane | 7.57 | 3.88 |
| *x*-methyl-undecane | 8.984 | 0.75 |
| *x*-methyl-undecane | 9.087 | 0.91 |
| *x*-methyl-undecane | 9.252 | 0.94 |
| *n*-dodecane | 9.991 | 4.43 |
| *x*-methyl-dodecane | 11.631 | 0.76 |
| *x*-methyl-dodecane | 11.809 | 0.96 |
| *n*-tridecane | 12.585 | 7.98 |
| *x*-ethylundecane | 13.991 | 0.84 |
| *x*,*y*-dimethyldodecane | 14.119 | 1.36 |
| *x*-methyltridecane | 14.248 | 1.59 |
| *x*-methyltridecane | 14.431 | 1.25 |
| *x*,*y*,*z*-trimethyldodecane | 14.593 | 1.94 |
| *n*-tetradecane | 15.206 | 11.70 |
| 1-heptadecene | 16.449 | 2.89 |
| *x*-methyltetradecane | 16.699 | 1.67 |
| 4-methyl-tetradecane | 17.011 | 1.66 |
| *n*-pentadecane | 17.762 | 15.46 |
| *n*-hexadecane | 18.914 | 3.00 |
| 6-methyl-pentadecane | 18.963 | 0.52 |

and 30 min on the suite of compounds recovered in the vapor phase. For this, we studied three ILs (gasoline, 2-cycle oil/gasoline mixture, and diesel fuel) on DF and PW substrates. Chromatographic analyses on the recovered samples were performed in triplicate, and the uncertainties were always within the limits discussed earlier. We present an example of the results as histograms in Fig. 4a and b, representing the vapor suite collected with diesel fuel as the IL on DF and PW, respectively. In Figs. S3a, S3b, S4a and S4b of the supporting information, we provide similar histograms for the vapor suites collected with gasoline and the 2-cycle oil/gasoline mixture. We conclude from the latency studies that in the most general sense, lighter or more volatile components were present in higher concentrations at lower latencies than at higher latencies. Heavier or less volatile components were present in lower concentrations at lower latencies than at higher latencies. We also noted that the recovered vapor suites samples tended to vary less with latency when prepared on DF than on PW. We speculate that this is related to grain density; each IL was observed to absorb far more into the PW than the DF, thus the time allowed for such absorption would be expected to have a greater effect.

### 3.4. Effect of fire debris sample variability

When considering the uncertainty of an analytical method, sampling variability is often not considered because either it is not an issue (as with a parent population comprising a homogeneous liquid) or because the sampling problem is intractable (as with a parent population of bags of sugar in a warehouse). In the case of headspace vapor sampling, the problem can be approached by generating replicate individual samples for separate analysis, with the understanding that each measurement is a separate experiment. Thus far, we have discussed the uncertainty in terms of the chromatographic measurement on the eluted sample. Here, we address the variability that might be expected from different samples prepared in essentially the same way. We used six separate burnings of diesel fuel on PW after a 10 min latency, and we selected a 13 component suite for comparison. We chose PW because, as noted above, it showed more variability than DF. The
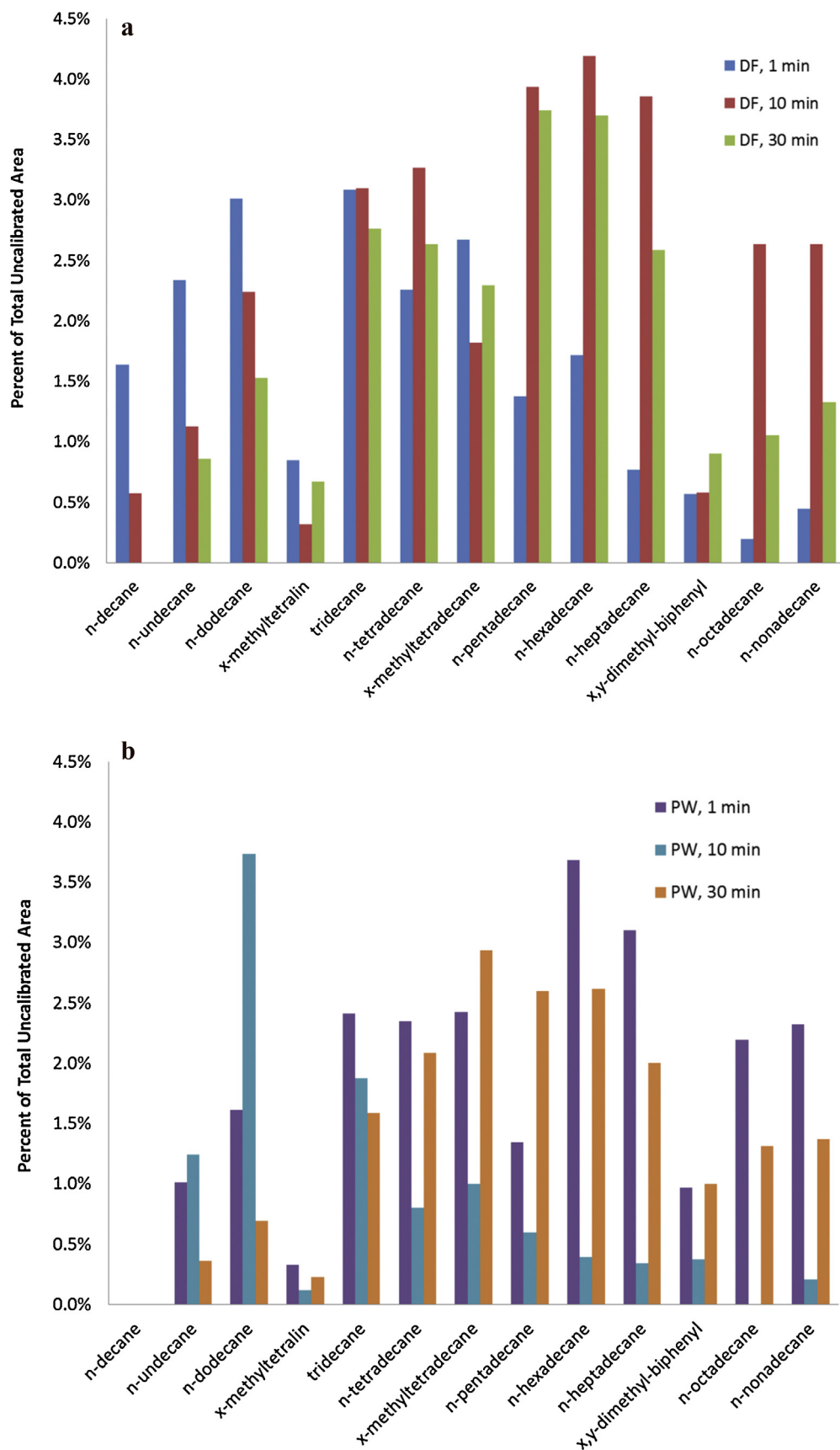
fluids we examined. As discussed earlier, WD-40 produced intermediate sized flames (approximately 10 cm), and produced a bubbling foam beneath the flame. While the suite of compounds recovered (Table 5) appears somewhat similar to that recovered for diesel fuel, some distinct characteristics may be observed. We note the presence of a small quantity the industrial solvent furfural (which is also a natural wood product), and we note that of the *n*-alkanes present, *n*-tetradecane and *n*-pentadecane are dominant. In the diesel fuel, we noted a more distributed suite with no dominant compounds. Representative chromatograms for other ILs we measured are provided in supporting information, Figs. S2a–S2f.

It is clear that fire debris generated with gasoline, diesel fuel and WD-40 as the IL can easily be distinguished from one another through vapor phase sampling by use of PLOT-cryo. Moreover, the collection is completed with a very small sample in 30 min. While we did not explicitly test for the effect of a delay between the time of flame burn out and scraping of the fire debris (recall that 3 min were allowed for cooling before scraping was begun), we do not expect modest delays to greatly alter the results because the carbon char produced is an effective adsorbent. In many cases, the odor of the IL could be noted on the archived blocks weeks after use.

### 3.3. Effect of latency

As we mentioned in the experimental section, the latency is the time period that an IL is allowed to remain on a substrate before ignition. In this work, we examined the effect of latencies of 1, 10

**Fig. 4.** (a) Histogram showing the recovered vapor suite of fire debris generated with diesel fuel as the IL, on DF. Chromatographic conditions and uncertainty is discussed in the text. (b) Histogram showing the recovered vapor suite of fire debris generated with diesel fuel as the IL, on PW. Chromatographic conditions and uncertainty are discussed in the text.
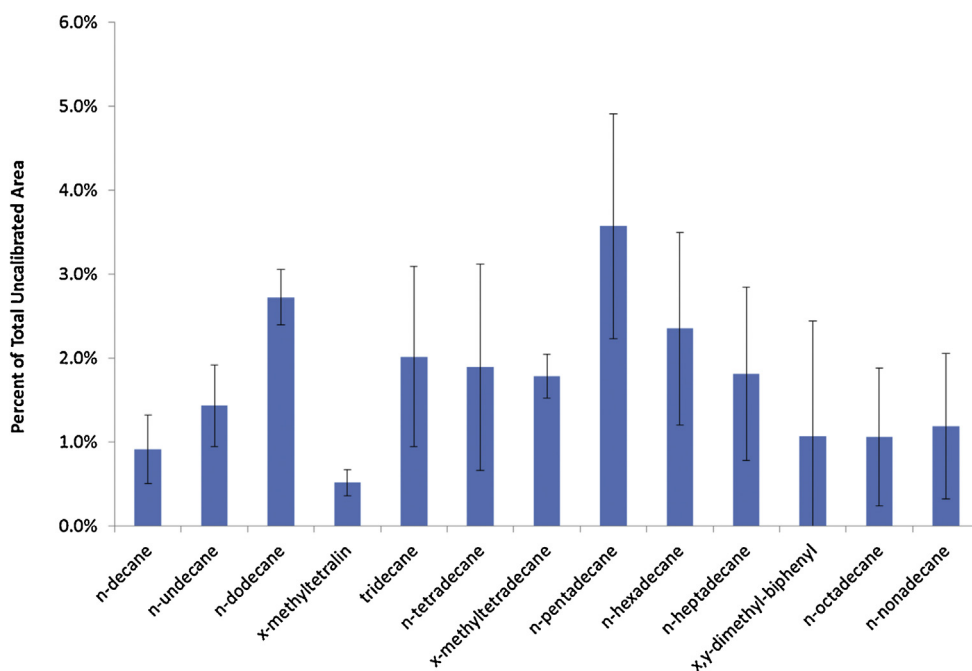
**Fig. 5.** A histogram showing the variability among a suite of 13 compounds recovered from the vapor of six different burnings of diesel fuel on PW after a 10 min latency. The error bars describe the variability; details on how these were determined are provided in the text.

eluted samples were analyzed six times each, and the chromatographic analyses were within the repeatability discussed earlier. The variability among these six individual burnings cannot be considered an uncertainty in the traditional sense, but rather this must be taken to represent the quantitative variability that, at best, can occur with the vapor analysis of fire debris. We say "at best" because the presence of firefighting chemicals, water, other chemical background at the scene, and the distinct possibility of spilled fuel from firefighting equipment can further complicate the picture. The variability among the suite of 13 compounds recovered from the vapor of our six burnings is shown as a histogram in Fig. 5. The "uncertainty" bars (perhaps better stated as being variability bars) represent one standard deviation of the mean of the area counts for each compound. We recognize that the use of the standard deviation as a measure of variability is questionable because we cannot ascertain whether the distribution is normal; however, for a small data set such as this, it is nevertheless instructive. We used the q-test (at the 99% confidence level) to identify any potential outliers among the measured areas, but none were indicated. We found from this series of measurements that the sample to sample variability (as measured by the coefficient of variation) averaged 44%. Work is ongoing at NIST to develop a more comprehensive approach to uncertainty (i.e., an uncertainty machine) that will take explicit account of sampling uncertainty. Until that effort is complete, we will use measures such as the coefficient of variation among separate experiments to understand or predict expected variability. We emphasize that the PLOT-cryo method is particularly suited to assess this variability because of the ability to collect vapor from many small samples simultaneously.

### 3.5. Assessing the limitations of PLOT-cryo

As part of the work on fire debris, we undertook a study of the limitations of the PLOT-cryo method, focusing on PLOT-capillary lengths and vapor collection time periods. While the collection times for the fire debris samples discussed above was uniformly 30 min, we measured vapor recovery at 15, 10 and 3 min of diesel fuel on PW burned after a 10 min latency. To reduce variability,

the samples were prepared from a single burning that was homogenized in the aluminum collection tray, described in Section 2. We present in Fig. 6 an overlay of typical chromatograms at all four collection times. We found that reducing the collection time period to 3 min did not significantly change the product suite or the recovery of vapor. Reduced collection time periods resulted in somewhat higher concentrations of high-volatility components, while the longest collection time periods resulted in somewhat higher concentrations of low-volatility components. This difference is evident in the relative height and areas of the peaks distributed over the chromatograms. We concluded that short collection time periods did not affect our ability to correctly identify the IL from the collected vapor. This is a favorable outcome since shorter analyses are highly desirable.

We also assessed our ability to use shorter PLOT capillaries than the typical 80 cm lengths used for the measurements described heretofore. This study was more challenging than simply changing the collection time periods (above) because very short PLOT capillaries are difficult to connect inside the cryostat as it is
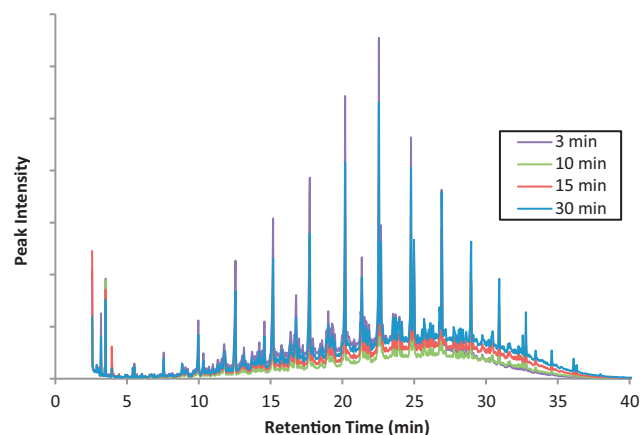


**Fig. 6.** An overlay of chromatograms of vapor collected from fire debris collected from diesel fuel on PW ignited after a 10 min latency, with vapor collected for 30, 15, 10 and 3 min collection times.
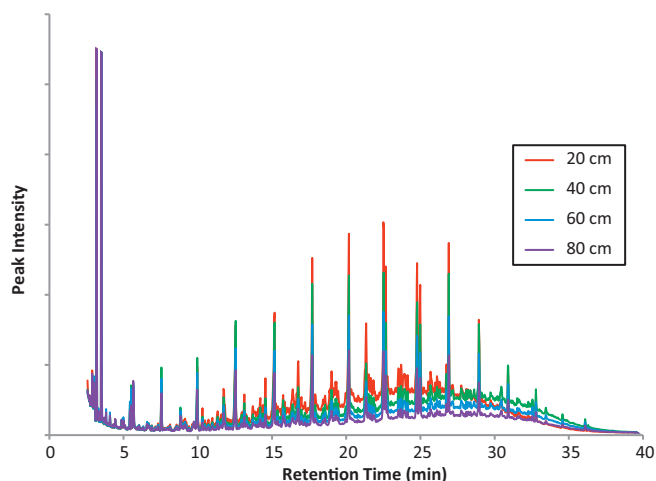
**Fig. 7.** An overlay of chromatograms of vapor collected from fire debris collected from diesel fuel on PW ignited after a 10 min latency on PLOT capillaries having lengths of 20–80 cm.

presently configured. Nevertheless, we were able to determine the performance of PLOT capillaries of 20, 40, and 60 cm to compare with our usual length of 80 cm. As with the temporal study above, the samples used for the length study were done with the same collection of fire debris, prepared with diesel fuel on PW after a 10 min latency. In Fig. 7 we present an overlay of chromatograms showing the results of collections on different length capillaries. The data show that shorter column lengths collected a slightly higher concentration of high-volatility solutes from the headspace than longer column lengths. In each case, the recovered vapor was still readily identifiable as diesel fuel.

### 3.6. Comparison of PLOT-cryo with the carbon strip technique

As discussed in the experimental section, the 1 cm × 2 cm activated carbon strips were used for comparison with PLOT-cryo with the paint can approach usually used by criminalists. Supply and availability difficulties associated with the carbon strips prevented us from making extensive comparisons. We generated 6.1 g of fire debris (far more than needed for PLOT-cryo) by burning diesel fuel on PW after a 10 min latency. A typical result is presented in Fig. 8, in which we overlay chromatograms taken with both approaches. It is evident that while the carbon strip performs admirably, it is outperformed by the PLOT-cryo method. We do note, however that
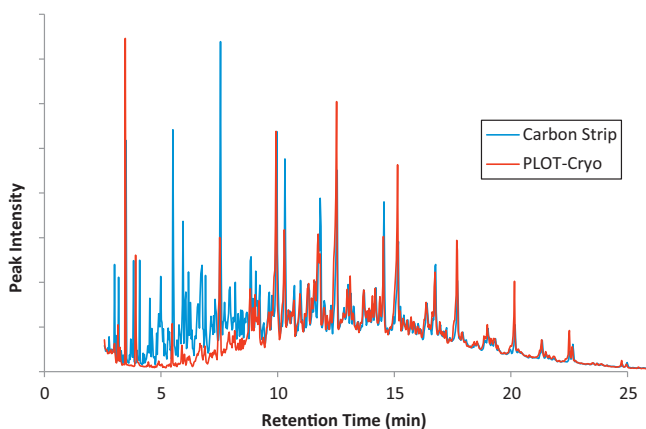


**Fig. 8.** An overlay of chromatograms of vapor collected from fire debris collected from diesel fuel on PY ignited after a 10 min latency, comparing PLOT-cryo with the usual carbon strip technique.

the carbon strip collected a larger quantity of the most volatile constituents, and that after the 2 h collection period, the PLOT capillary was overloaded. It is clear that PLOT-cryo is more suited for smaller samples. We also note that the usual solvent used with the carbon strip is carbon disulfide rather than the acetone that was used here. Several comparison experiments were done with both solvents and with the diesel fuel fire debris used here, no difference in performance of the two solvents could be discerned.

## 4. Conclusions

In this work we have applied the PLOT-cryo approach to the study of fire debris in an effort to (1) identify the IL that was used, (2) assess the limitations of the method and (3) compare the approach with other common techniques. We can draw the following conclusions from this work:

1. The PLOT-cryo method performs better than the traditional dynamic purge and trap approach. It provides more efficient, faster collections; more chromatographic peaks can be identified, the measured raw areas are higher, and the volume of headspace required for collection is smaller than typical purge and trap methods. This conclusion is necessarily limited to the application of the bed of porous polymer that was used in the comparison, as well as the solvents used for elution; other adsorbents and solvents might provide different results.

2. For the collection of vapor samples above fire debris by use of PLOT-cryo, we were able to employ very small sample sizes and collect vapor from as many as 8 sample vials, simultaneously. This allows for the measurement of many replicates and makes it practical to set up a grid investigatory pattern in the investigation of a fire scene. It also allows for multiple replicate samples to be easily collected from each location at a fire scene. Moreover, the analyst is able to simultaneously collect vapor from standards while collecting fire debris vapor from collected samples. In all cases we were able to identify the IL from the resulting chromatogram.

   The relatively smaller sample that can be measured by PLOT-cryo is amenable to round robin studies among different laboratories, for example, in research and quality control exercises. In such instances, the samples must be smaller than those typically collected at a fire scene [68].

3. Despite the application to small samples, it is nevertheless possible to apply PLOT-cryo to larger samples, including the more typical paint can presentations of 1–2 kg of fire debris. This was demonstrated with the septum vials applied to the soil samples. Moreover, current work with much larger samples will be reported in the near future.

4. The PLOT-cryo method allowed for very rapid vapor collections. While most of the work presented here was done with collection periods of 30 min, we have demonstrated that collection periods as short as 3 min allowed the IL to be identified readily. The high throughput characteristic of the PLOT-cryo method, and the low cost and durability of the capillaries, has the potential of lowering the cost of individual analyses.

5. We were able to study the effect of IL latency on the recovered vapor. We found that lighter or more volatile components were present in higher concentrations at lower latencies than at higher latencies. Heavier or less volatile components were present in lower concentrations at lower latencies than at higher latencies.

6. Because of the high throughput of the method, we were able to study the variability of different, independent samples of the vapor recovered from fire debris. We found that, based on the relatively small separate sample population (i.e., six separate

measurements), the combined coefficient of variation of chromatographic areas averaged 44%.

7. In an effort to determine the limits of PLOT-cryo for the hydrocarbon vapors studied here, we were able to obtain satisfactory results with PLOT capillaries as short as 20 cm. Vapor collections from these short capillaries still allowed for the identification of the IL. The shortest capillaries did prove to be awkward to handle in the laboratory, however, so some intermediate length might be the most convenient while optimizing economy.

8. We compared the performance of PLOT-cryo with the common carbon strip method. While the carbon strip performs admirably, it is outperformed by the PLOT-cryo method. The carbon strip collected a larger quantity of the most volatile constituents, and after the 2 h collection period, the PLOT capillary was overloaded. It is clear that PLOT-cryo is more suited for smaller samples, yet it also works very well for larger samples (such as those employed with the soil samples discussed above). Indeed, in our prior work (cited earlier), we used the metrology for the detection of grave soil above buried animals. In current work, we are using PLOT-cryo to sample vapors present in large paint cans and pieces of luggage.

9. While not explicitly discussed above, we observed that among the liquids we tested, the most effective fuel for initiating and sustaining a fire on the substrates we considered in our experiments was diesel fuel. This fluid provided what appears to be good trade-offs between ease of ignition, sustained burning and heat release. We also observed that the most effective substrate that we tested was plywood; the more porous grain allowed greater depth of penetration for the IL, and a longer sustained flame. It is likely, although we have not experimentally explored this possibility, that the mixture of gasoline and diesel fuel known as dieseline might perform in a similar manner and might be more easily ignited [69,70]. Criminalists will need to anticipate this potential.

## Acknowledgements

## Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at http://dx.doi.org/10.1016/j.chroma.2014.01.080.

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