



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



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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 (<sup>1</sup>H and <sup>13</sup>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

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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-diphenylphenylene 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

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