



## Full length articles

## The surprising effect of temperature on the weathering of gasoline

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## ABSTRACT

During the identification of ignitable liquid residues in fire debris, it is well known that evaporative losses result in a general increase in the abundance of non-volatile residues relative to volatile residues. However, previous work has provided an incomplete understanding of weathering such that we cannot adequately relate weathered residues to un-weathered pristine samples. Here, we studied various factors that influence the relative abundance of weathered residues.

Real gasoline samples were weathered to varying extents, at different temperatures, and under conditions of a vacuum or a nitrogen stream. Analysis of the liquid residues was performed using gas chromatography mass spectrometry (GC/MS), which showed that, as expected, the extent of weathering has the largest effect on the abundance of different residues. However, the results also showed that at a constant extent of weathering, the earliest eluting compounds—like toluene and the C<sub>2</sub>-alkyl benzenes—tend to remain at significantly higher levels ( $\alpha < 0.05$ ) at higher temperatures than at lower temperatures.

Experimental weathering and mathematical simulations were also performed on a simpler seven-component mixture. Weathering simulations closely follow the experimental data below 100 °C, even up to 95% weathering. The model was extrapolated to significantly elevated temperatures, which showed that heavily weathered (95%) gasoline at high temperature (500 °C) would be almost indistinguishable from a liquid that is weathered to a lesser extent (70%) at room temperature. These results provide an alternative or additional explanation for why gasoline recovered from arson scenes does not appear to be as weathered as one would expect.

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## 1. Introduction

Arson investigations often involve the identification and characterization of ignitable liquid residues (ILR) in fire debris. Crimes involving fires are particularly challenging to investigate because of the damage to, or lack of, physical evidence at the scene. Fire debris analysts therefore rely on the trace chemical analysis of the fire debris [1–3]. Arson is referred to as intentionally and willfully setting a fire with malice [4], and such intent can often be supported if fire debris can be found to contain an elevated level of an ignitable liquid relative to control samples. Gasoline is the most commonly used ignitable liquid for intentionally set fires because it is so readily available and because it is particularly

effective. Less-common ignitable liquids include kerosene, diesel, charcoal lighter fluid, alcohols, and paint thinners [2,5].

When ignitable liquids are stored in vessels that are not hermetically sealed, or when they are exposed to high temperatures, they are known to undergo evaporative losses, called weathering, which alters the distribution of compounds in the remaining liquid because of the difference in evaporation rates of the different components. Weathering can therefore occur at temperatures ranging from room temperature to the elevated temperatures of a fire, which often exceeds 1000 °C [6]. Weathering is a well-known phenomenon in which the most volatile components of a mixture evaporate more quickly than non-volatile components, and may even evaporate to levels below the limits of detection of the analysis method. On the other hand, compounds of lower volatility and with lower vapor pressures will undergo slower evaporation and thus appear more concentrated relative to the original liquid [7].

Standard practices for the interpretation of ignitable liquid residues stipulate that ignitable liquid residues are more likely to resemble weathered versions rather than pristine version of liquid samples [8]. For this reason, laboratories will often weather

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reference or control samples of gasoline to different extents in an attempt to replicate the extent of evaporation in the fire debris [9]. Identification of ignitable liquid residues becomes challenging or impossible when comparisons are attempted between ignitable liquids that are pristine (un-evaporated) and ignitable liquids that are weathered (partially evaporated) to different extents. In addition to the complexities of weathering, microbial degradation of ignitable liquids and the presence of matrix interferences, such as pyrolysis products, can also obscure the identification or comparison of ignitable liquids [10–14].

Previous research has investigated the weathering characteristics of gasoline under a variety of experimental conditions, but to date this research has been somewhat limited to general trends in chromatograms rather than a rigorous mathematical description of evaporation. There are two notable exceptions. Bruno and Allen have described a method involving the advanced distillation curve approach, which can help predict the extent of evaporation as a function of temperature [15]. However, this approach measures distillate fractions recovered under equilibrium conditions and is not suitable to describe the distribution of compounds remaining after short (i.e. non-equilibrium) periods of evaporation at elevated temperatures. Smith's group has recently made some interesting progress towards a mathematical description of weathering at a constant temperature [16]. The model uses an empirically determined relationship between evaporation rate and retention time on the GC—which is closely related to boiling point—to model evaporation. This approach enables the unique ability to make chromatographic predictions between pristine liquids and evaporated residues [16]. However, more work needs to be completed to incorporate the influence of evaporation temperature on weathering, as it may not be appropriate to assume that the weathering pattern is independent of temperature.

Chemometric approaches are proving to be particularly effective for the classification and discrimination of pristine ignitable liquids [10,17–20], even in the presence of a confounding matrix or background. Sigman and coworkers have shown that a summed mass spectrum approach, which is not influenced by GC retention times, can effectively classify ignitable liquids according to the widely accepted ASTM classification scheme [21–24]. Generally speaking, most chemometric approaches fail to have the same success in associating weathered residues with pristine versions of the same ignitable liquids. In this regard, Smith's group is perhaps the closest to making predictions about a pristine liquid from a weathered residue [16].

Isotope ratio mass spectrometry (IRMS) has been proposed to be a potential solution to linking pristine and evaporated ignitable liquid residues [25,26]. Similar to chemometric approaches, IRMS works well for linking pristine ignitable liquids to other pristine ignitable liquids [27–31], and although slow evaporation at low temperatures provides little or no fractionation, weathering has been found to have an unpredictable influence on isotope ratios following more-realistic—i.e. higher temperature—weathering conditions [32,33].

Several studies have illustrated how weathering conditions, such as temperature, light, pressure, and convection, affect the relative distribution of chemical residues [34], but these studies tend to be described in terms of general trends rather than quantitative calculations. For example, some methods utilize a nitrogen stream and a heat bath to help expedite the weathering process, whereas others utilize an oven under vacuum [34]. Complex chambers have also been built for weathering studies so that conditions can be altered and closely controlled [35]. Simply leaving the gasoline to weather under a hood has also been used [36]. The extent of weathering can be measured by either weight or volume, but weathering by volume is the more popular approach. Weathering by weight allows for a more accurate assessment of weathering, especially with small quantities [36].

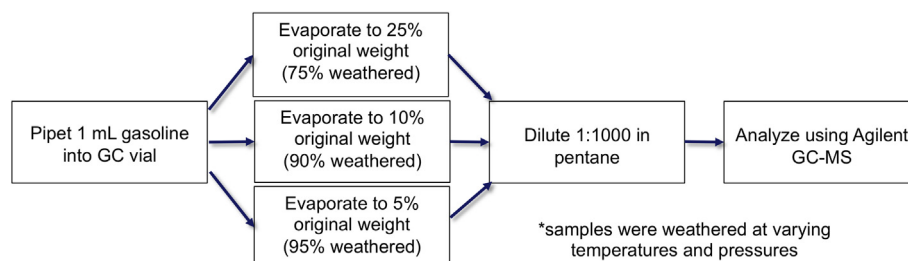
Ignitable liquids that are recovered from arson scenes are almost always compared to weathered samples because they have already been exposed to the elements and undergone evaporation to some extent. These residues are often compared to samples that have been 50–70% weathered [3,8,36]. To a chemist without specialized training, it might seem somewhat intriguing that ignitable liquids encountered in casework that have been exposed to extreme temperatures of a fire, and oftentimes for extended durations, often have the appearance of being weathered only 50–70% [37]. One explanation for the moderate weathering at extreme temperatures is the concept of entrapment, in which ignitable liquids are said to penetrate quite deep into a porous substrate (i.e. carpet) and are thus less susceptible to evaporation. However, distillation curves of gasoline spiked on wood chips and carpet suggest that entrapment or absorption has a very minor effect on evaporative losses [38], and this explanation is therefore not always sufficient to explain the apparent lack of weathering of casework samples exposed to high temperatures [37].

In an attempt to provide an explanation for the apparent lack of weathering in casework samples, and in an attempt to provide a first-principles approach to predicting evaporative changes in the composition of ignitable liquids, we hereby present an explanation based on the kinetics of evaporation of different components of gasoline at different temperatures. In short, when the temperature of evaporation is increased, the rate of change in vapor pressure with respect to temperature is greater for non-volatile compounds than it is for volatile compounds. The ramifications of this fact are that relative to evaporation at room temperature, evaporation at higher temperatures will provide increased evaporation of non-volatiles—when the extent of evaporation is kept constant. Higher evaporation temperatures will therefore contain a larger relative proportion of volatile components respective to low temperature evaporation.

## 2. Methods

### 2.1. Weathered gasoline sample preparation

Sample preparation is summarized in Fig. 1. Replicate 1 mL aliquots of a gasoline sample were pipetted into different 1.5-mL GC



**Fig. 1.** Weathering and analysis procedure. Weathering was repeated: 1) under vacuum; 2) under a stream of nitrogen gas at 1 atm; 3) at three different temperatures of 25 °C, 60 °C, and 90 °C.

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