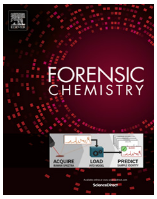
Forensic Chemistry 4 (2017) 32–40

Contents lists available at ScienceDirect

Forensic Chemistry

journal homepage: www.elsevier.com/locate/forc



Full length articles

The surprising effect of temperature on the weathering of gasoline

Heather L. Birks [a,1,2], Ashley R. Cochran [a,1], Tyler J. Williams [a,3], Glen P. Jackson [a,b,*]

[a] Department of Forensic and Investigative Science, West Virginia University, Morgantown, WV 26506-6121, USA
[b] C. Eugene Bennett Department of Chemistry, West Virginia University, Morgantown, WV 26506, USA

ARTICLE INFO

Article history:
Received 14 January 2017
Received in revised form 24 February 2017
Accepted 24 February 2017
Available online 27 February 2017

Keywords:
Gasoline
Arson
Weathering
Forensic science
Ignitable liquid residue

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_2-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.

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

---

[*] Corresponding author at: Department of Forensic and Investigative Science, West Virginia University, Morgantown, WV 26506-6121, USA.

E-mail address: glen.jackson@mail.wvu.edu (G.P. Jackson).

[1] These authors contributed equally to this work.

[2] Currently at: Department of Forensic Science, Virginia Commonwealth University, Richmond, VA, USA.

[3] Currently at: Department of Chemistry, Clemson University, Clemson, SC, USA.

http://dx.doi.org/10.1016/j.forc.2017.02.011
2468-1709/© 2017 Published by Elsevier B.V.

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

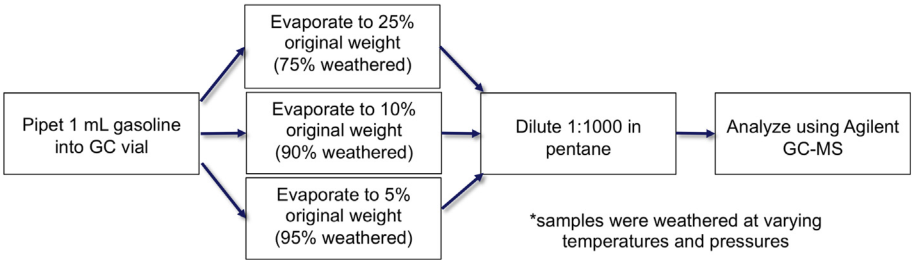


Fig. 1. Weathering and analysis procedure. Weathering was repeated: 1) under vacuum; 2) under a stream of nitrogen gas at 1 atm; 3) at three different temperatures of 25 °C, 60 °C, and 90 °C.

vials. The mass of the added gasoline was measured by difference using a 5-decimal digital balance (Mettler Toledo, Columbus, OH). The vials were then placed into a vacuum oven (Thermo Fisher) or under a nitrogen stream at the desired evaporation temperature. Evaporations were performed on at least 9 replicates at each condition to capture the experimental variance. At 25 °C, weathering times in the vacuum oven exceeded one week, so they were eliminated from the study. The extent of evaporation was monitored by mass instead of volume, being sure to cool the samples before weighing them to prevent buoyancy errors. Once weathered to the desired extent, e.g. 75, 90 or 95%, a volume of 100 µL of residue was removed and dissolved to 1 mL in pentane (1:10 dilution), followed by an additional 1:100 dilution in pentane for analysis (total 1:1000 dilution). All replicates were analyzed in triplicate.

2.2. Gas chromatography/mass spectrometry

All samples were analyzed using an HP 5977A Agilent Gas Chromatograph-Mass Spectrometer (GC/MS) with a 30 m × 0.25 mm diameter × 0.25 µm film thickness HP-5 column (Agilent). Parameters for the GC/MS were set as follows: the injection volume was 1 µL and the injector temperature was set to 250 °C with a 1:20 split ratio. The oven was set at 50 °C for 2 min, ramped to 280 °C at 15 °C/min, then held for 5 min. The carrier gas was helium with a flow rate of 1.8 mL/min and the transfer line temperature was set to 270 °C. The mass spectrometer had a solvent delay of 1.2 min, and the scan range was m/z 30–450.

A blank of pentane and an n-alkane ladder were run with all samples. Samples were run in a randomized block design. Resulting data were collected, extracted, and analyzed using Excel 2011 for Mac (Microsoft, Redmond, WA, USA) and SPSS 20 and 22 for Mac (IBM, Armonk, NY, USA).

2.3. Data collection

Before statistical analysis, compounds in the gasoline and weathered gasoline samples were divided into five categories, or bins, based on retention time. These bins were composed of the summation of TIC peak areas of all compounds within a particular time bracket: 2–3 min, which is dominated by toluene; 3–4 min, dominated by C2-alkyl benzenes; 4–5 min, dominated by C3-alkyl benzenes; 5–7 min, dominated by C4-alkyl benzenes and naphthalene; and 7–9 min, dominated by C5-alkyl benzenes and C1- & C2-alkylnaphthalenes.

2.4. Artificial gasoline

To model the evaporation of gasoline in a more precise manner, a simplified artificial version of gasoline was created, which crudely mimicked the quantity and range of a select number of components found in gasoline. The artificial mixture included toluene, octane, ethylbenzene, butylbenzene, naphthalene, hexadecane, and eicosane. This artificial mixture was weathered under the same conditions as the regular gasoline. Mathematical simulations of the artificial gasoline were completed using Excel 2011 for Mac.

3. Results and discussion

3.1. Nitrogen stream does not affect the composition of weathered residues

The use of a nitrogen stream or vacuum are two common ways to expedite the weathering of gasoline samples in a laboratory setting. Experiments were first conducted to determine whether or not the headspace factors of turbulence or pressure had a significant effect on the weathering of gasoline. To test the headspace factor, we binned the data by summing the peak areas for different retention time windows (see above) as individual variables for comparison, as shown in the histogram in Fig. 2. Statistical comparisons were made between integrated intensities for the individual retention time windows. Integrated peak areas were normalized relative to the total integrated signal (summed TIC = 1).

Two-sample t-tests determined that, generally speaking, the use of nitrogen had an insignificant effect on weathering at the 95% confidence level. The effect of the headspace factor was tested at 75%, 90%, and 95% weathering and at three different temperatures at each percent weathering (total of nine conditions). One exception was that the stochastic detection of toluene around the threshold limit would occasionally result in a significant difference in a t-test, but these results were deemed exceptions to the general rule. Thus, when gasoline is weathered to a specific percent weathering at a specific temperature, the presence of a nitrogen stream does not have a significant effect on the general distribution of compounds in the gasoline residues.

Principal component analysis (PCA) was used to visualize the extent to which other factors influence the composition of weathered residues. Specifically, PCA was used to visualize the variance caused by the percent weathering and the temperature of weathering. The relative peak areas in each retention time window provided five variables for each experimental condition, and these variables were used for dimension reduction to visualize the factor with the biggest effect on weathering. The data points were color coded by percent weathered (Fig. 3a) and by temperature weathered (Fig. 3b). In Fig. 3a, the data naturally clustered into four distinct groups of percent weathered, whereas the data in Fig. 3b does not show any natural clustering according to the temperature weathered, with the exception of fresh gasoline, which of course has correlating factors. The PCA plots reinforce the long-held notion that the extent (percent) weathering has the most significant effect on the distribution of residues. Temperature has a much smaller effect relative to the percent weathering.

3.2. The effect of temperature

Below 90 °C, the extent (percent) of weathering has such a large effect on the distribution of components in gasoline residues that this factor needed to be fixed in order to determine any possible influence of temperature. Fig. 4 shows four chromatograms obtained when different aliquots of the same gasoline sample are exposed to the same extent of weathering (i.e. 90%), but at different temperatures. Of course, the samples took different weathering times to reach the same extent of weathering, but time is considered a dependent variable in these studies, not an independent variable.

The chromatograms in Fig. 4 show that when the extent of weathering is kept constant at 90%, the temperature of weathering does have a noticeable effect on the distribution of compounds in the chromatogram. For example, the earliest eluting, most volatile compounds, such as the C_2-alkyl benzenes, are present at obviously higher levels in the 90 °C plot (Fig. 4d) than at 25 °C (Fig. 4b). Worded another way, the chromatograms in Fig. 4b–d are all of gasoline evaporated to 10% of its original mass, but the temperature of the evaporation has a significant effect on the distribution of volatiles remaining in the residue. This result is perhaps counterintuitive because without thinking deeply about all the possible effects of temperature, it is reasonable to assume that volatiles are simply lost to the same extent at high temperatures as they are at lower temperatures.

To visualize the differences more easily, the summed peak areas for different retention time windows are plotted in Fig. 5. Unlike Fig. 4, the extent of weathering in Fig. 5 was fixed at 95%. Fig. 5

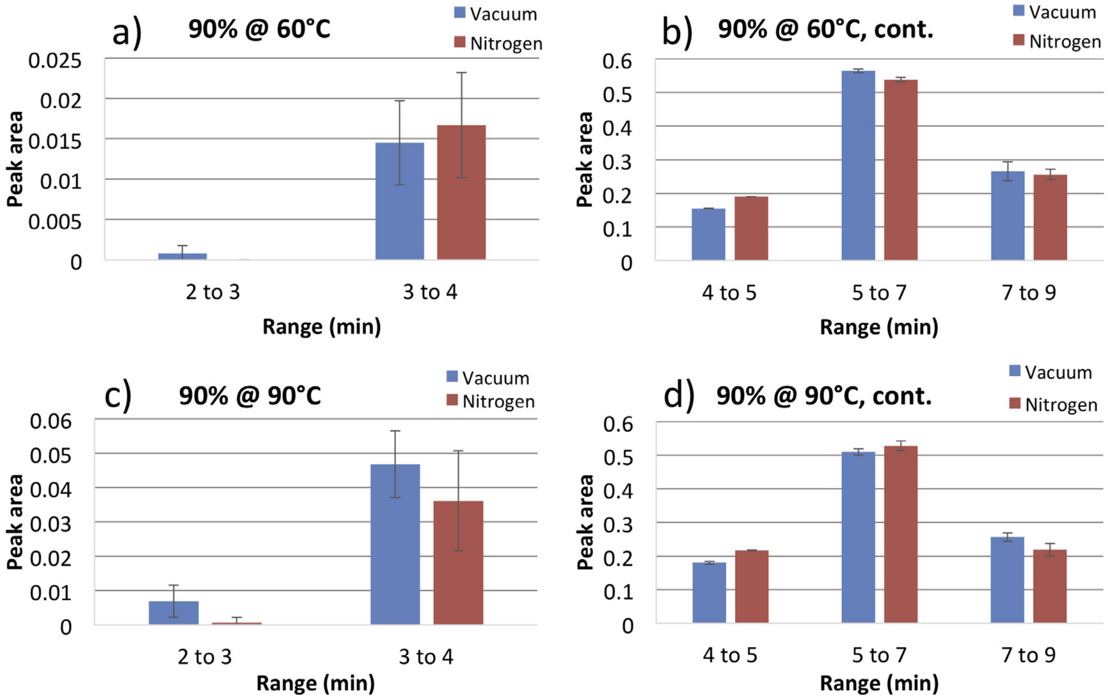


Fig. 2. Effect of headspace condition (vacuum oven or nitrogen stream) on the evaporation of gasoline. The data is split between two charts because of the magnitude difference in the relative peak areas: (a) 90% weathered at 60 °C; (b) 90% weathered at 60 °C; (c) 90% weathered at 90 °C; (d) 90% weathered at 90 °C. N = 9 for each condition. Error bars show 95% CI.

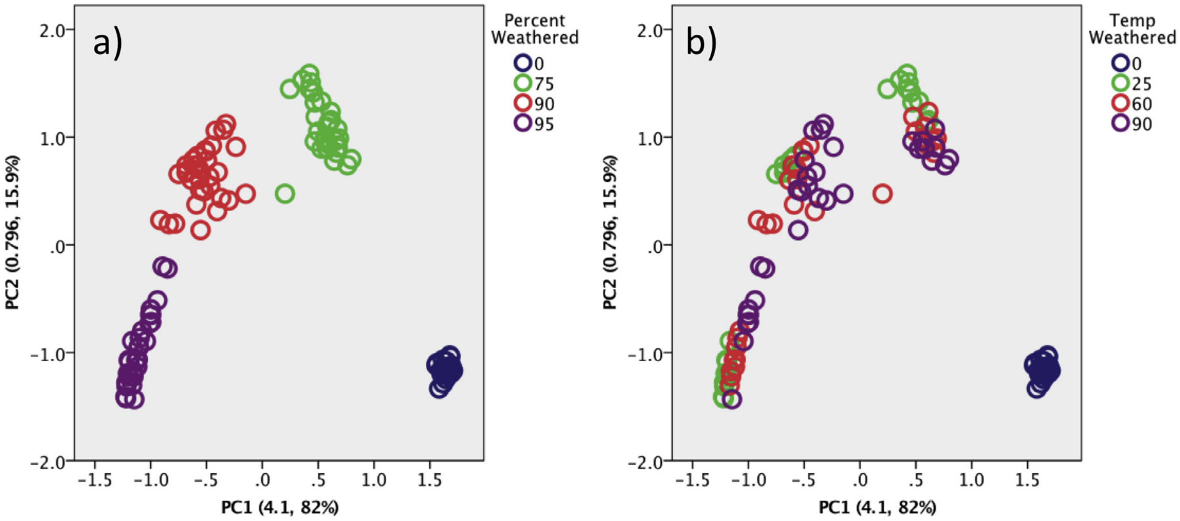


Fig. 3. Principal Component Analysis (PCA) showing the natural clustering of the data. Plots are color coded differently to represent: (a) data colored by percent weathering, regardless of weathering temperature; (b) data colored by temperature weathered, regardless of percent weathering.

shows that at 95% weathering, samples weathered at 90 °C had toluene and C_2-alkyl benzene peaks that were 3–4 times more abundant than samples weathered at room temperature ($\alpha \sim 1 \times 10^{-7}$, N = 10 at each temperature). At 90% and 95% weathering, the same peaks were typically below threshold when weathered at 25 °C and 60 °C, but were typically above threshold when weathered at 90 °C.

Because of the major differences in peak areas between the time bins, the data in Fig. 5 is split between two charts with different y-axis magnitudes. Comparisons within time bins are shown at a 95% confidence interval (CI). The main components of the 7–9 min time bin include the C5-alkyl benzenes and the C1 and C2-alkylnaphthalenes. In this bin, there are significant differences in gasoline samples weathered at 25 °C and 90 °C ($p < 0.01$) as well as 60 °C and 90 °C ($p < 0.01$), but there are no significant differences between samples weathered at 25 °C and 60 °C in this time bin. Based on these results, it is clear that temperature does have a measureable impact on weathering.

3.3. Simulations

To simplify quantitation and provide a basis for simulations, an artificial mixture of seven compounds was created to mimic the distribution of compounds in gasoline. These seven compounds included toluene, octane, ethylbenzene, butylbenzene, naphthalene, hexadecane, and eicosane. These compounds have

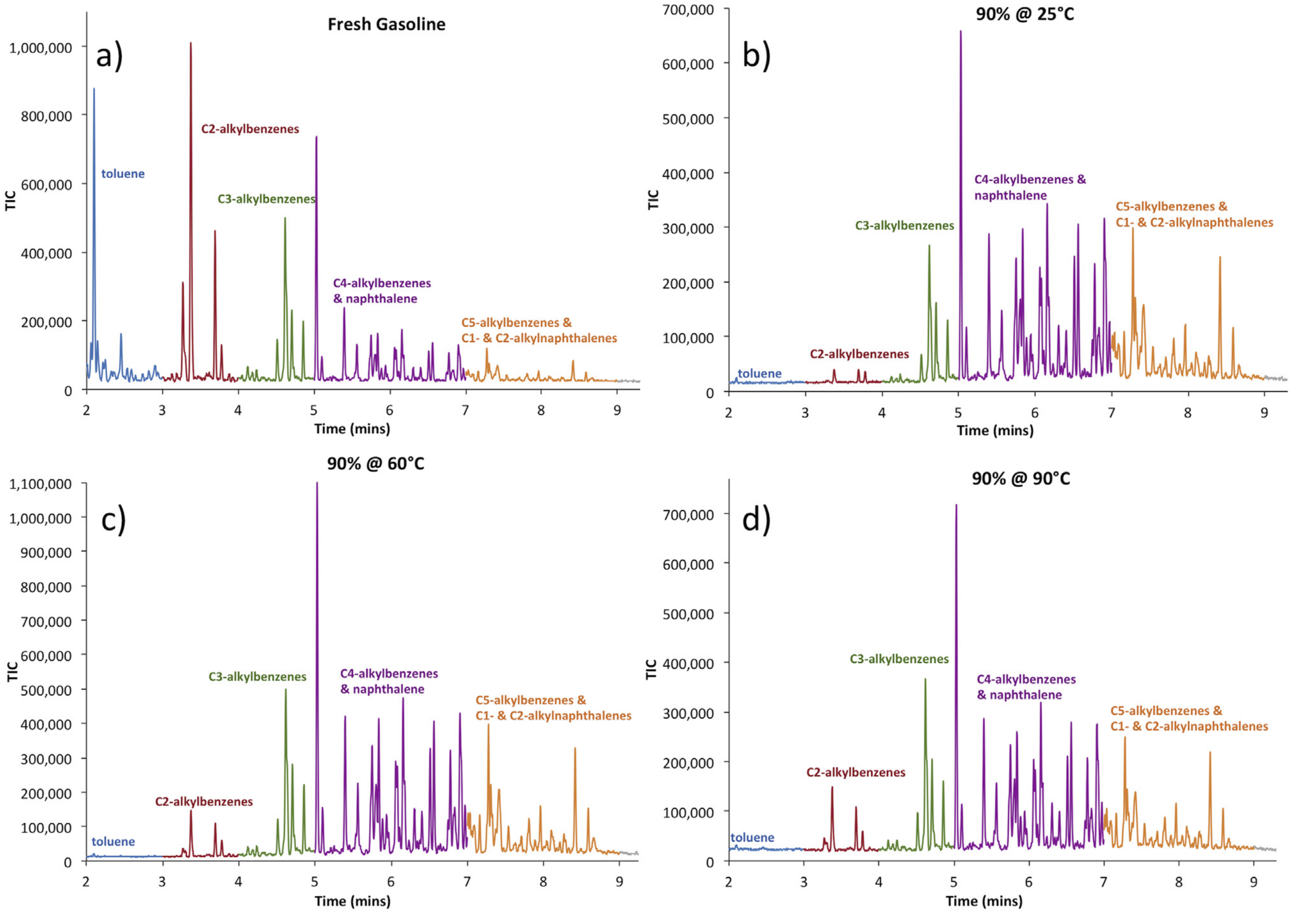


Fig. 4. Chromatograms produced at different weathering temperatures. (a) fresh gasoline, (b) gasoline weathered to 90% at 25 °C, (c) gasoline weathered to 90% at 60 °C, (d) gasoline weathered to 90% at 90 °C. Labels show the dominant compounds in each region.

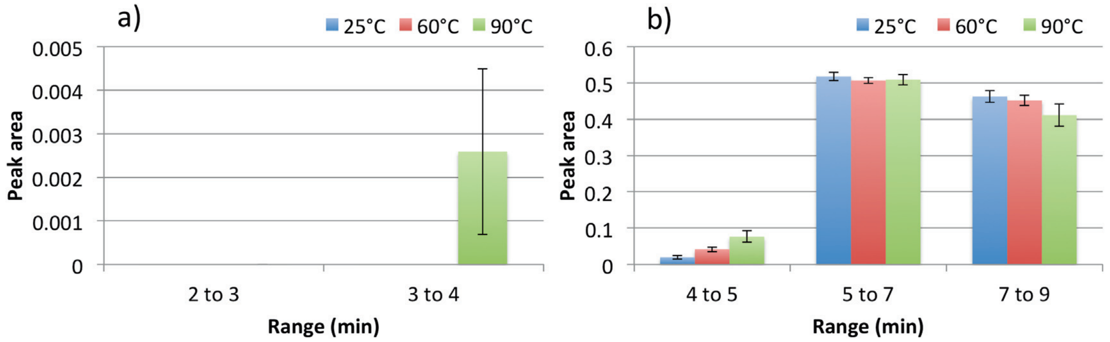


Fig. 5. Bar graphs showing the effect of temperature on weathering gasoline 95%: (a) summed peaks for components eluting between 2–3 and 3–4 min, (b) summed peaks for components eluting between 4–5, 5–7 and 7–9 min. N = 10 for each condition. Error bars show 95% CI. An asterisk (*) denotes significant difference at $p < 0.01$ when compared to 25 °C. A double dagger (‡) denotes $p < 0.01$ when compared to 60 °C.

well-characterized Antoine coefficients [39–42], which can be used to model the vapor pressures and weathering at different temperatures.

The relative vapor pressures for each of the seven selected components of the artificial mixture were calculated from Antoine constants from a common source [42], and are listed in Table 1. Primary references were also considered (toluene, octane, ethyl benzene [43]; butyl benzene [40]; naphthalene [41]; hexadecane [39]), which contained slightly different Antoine constants than the values in reference [42], but the resulting simulations were not meaningfully different than when using the values provided in reference [42]. Table 1 shows the absolute equilibrium vapor pressures at 25 °C and the vapor pressures relative to 25 °C at six additional temperatures. In several cases, the calculations were conducted at temperatures well beyond the range over which the Antoine constants were intended for use, which means that the vapor pressures are likely to contain some error or uncertainty. The upper temperature limits recommended for use are provided in the section titled “elevated temperature simulations”.

At 25 °C, toluene, which elutes earliest of the listed compounds, has the highest vapor pressure of 6.8×10^{-5} bar. Eicosane, which elutes last, has the lowest vapor pressure at 25 °C of

Table 1
Calculated vapor pressures of each compound in the artificial gasoline mixture relative to 25 °C (and absolute vapor pressure in bar at 25 °C).

Temp (°C)	Toluene	Octane	Ethyl benzene	Butyl benzene	Naphthalene	Hexadecane	Eicosane
25	1 (6.8×10^{-5})	1 (3.3×10^{-5})	1 (2.3×10^{-5})	1 (2.5×10^{-6})	1 (6.1×10^{-7})	1 (2.2×10^{-9})	1 (7.2×10^{-12})
60	3.8	4.3	4.4	6.1	7.2	24	91
90	11	14	15	26	34	270	2400
120	27	35	38	82	120	1800	3.0×10^4
150	57	77	87	220	350	8200	2.2×10^5
230	250	380	440	1500	2900	1.5×10^5	8.4×10^6
500	3300	5600	7200	3.8×10^4	1.0×10^5	1.3×10^7	2.1×10^9

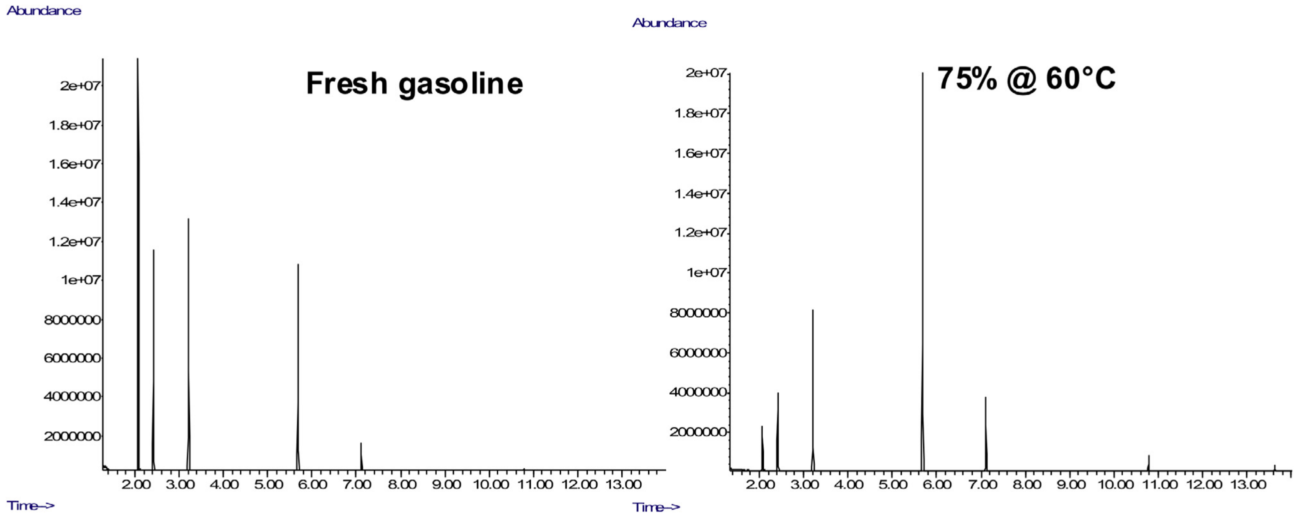


Fig. 6. Examples of experimentally obtained chromatograms of an artificial mixture of seven compounds found in gasoline: a) unweathered artificial gasoline, b) artificial gasoline weathered 75% at 60 °C.

7.2×10^{-12} bar. The relative increase in vapor pressure of each compound as the temperature increases is provided at several elevated temperatures.

At 90 °C, eicosane is 2400 times more volatile than it was at 25 °C, whereas toluene is only 11 times more volatile over the same temperature change. The other values in the table show that the less-volatile compounds have a greater relative increase in vapor pressure than the volatile compounds as the temperature increases. Described another way, at room temperature, the vapor pressure of eicosane is calculated to be about 10,000,000 times less than the vapor pressure of toluene. However, at 90 °C, the vapor pressure of eicosane is only 44,000 times less than toluene. The vapor pressures are therefore closer by more than a factor of 200 at the elevated temperature. At 230 °C, which is still within the temperature range of many of the experimentally-derived Antoine constants, the vapor pressure of eicosane is predicted to be within a factor of 300 of toluene, a change of more than four orders of magnitude. This different rate of change of vapor pressure as a function of temperature for each compound helps explain the shifts in the chromatograms of gasoline weathered at different temperatures shown in Fig. 2.

When the artificial gasoline was weathered, the observed trend in evaporative losses reflected the trends observed for real gasoline. Fig. 6 shows that in the fresh gasoline, the more volatile components are in a higher relative abundance compared to the less volatile components. In the gasoline that was weathered at 60 °C, for example, the more volatile components like toluene have evaporated to a larger extent than the less volatile components. As described below, the advantage of the simpler artificial mixture shown in Fig. 6 is that each component in the mixture can be mathematically simulated based on its precise physical and chemical properties, such as using the vapor pressures in Table 1, but adjusted for temperature changes.

3.4. Mathematical simulations

The vapor pressures of each compound above the liquid mixture were calculated using a combination of Raoult's law and Dalton's law [44]. Raoult's law states that the partial vapor pressure P_A of A, is proportional to the product of the mole fractionx_A. and the vapor pressure of the pure liquid P_A^* [44],

$$P_A = x_A P_A^* \qquad (1)$$

This law assumes that the intermolecular interactions between unlike compounds are equal to those between like compounds. Dalton's law applies similar logic to the vapor phase and states that partial pressures are simply additive. The measured molar fraction of the artificial gasoline mixture was used as the starting values for the molar fraction in the weathering simulations. The measured fractions are simply the fractional peak areas in the total ion chromatogram (TIC) and have not been corrected for ionization efficiency.

The first step of the simulation involved using Raoult's Law and Dalton's Law at a given temperature to calculate the equilibrium partial and total pressure for the headspace above the artificial mixture. Then, a small fractional volume, e.g. 5%, of the vapor phase was subtracted from the initial vapor phase to simulate an irreversible evaporative loss. The same fractional loss of vapor phase composition was applied to each compound, which resulted in a different absolute loss because of their different partial pressures. After subtracting the small vapor loss, new equilibrium partial and total vapor pressures were then calculated from the

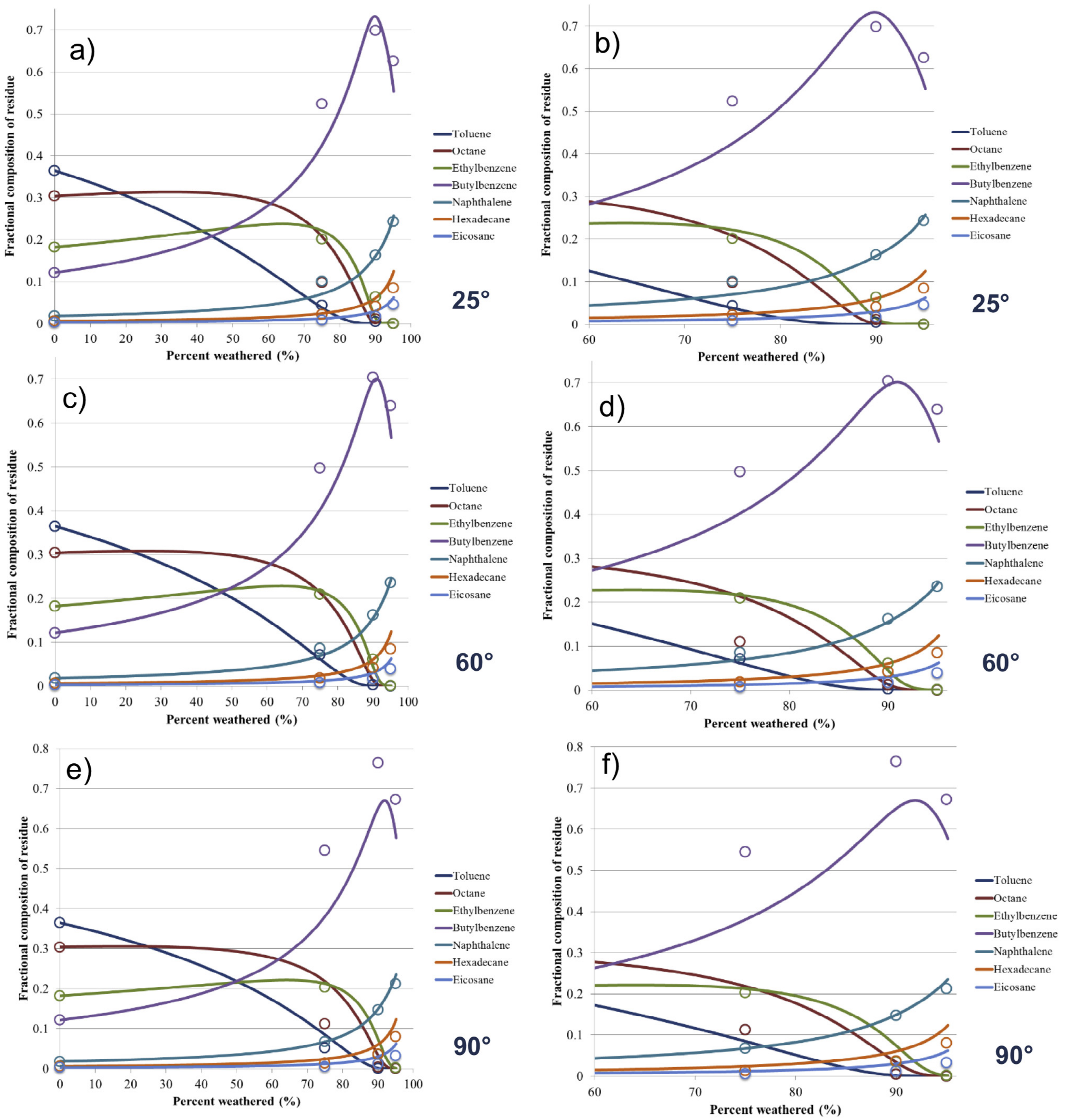


Fig. 7. Mathematically simulated weathering of artificial gasoline (solid line) versus experimentally simulated weathering of artificial gasoline (open circles). Full plots (a, c, e) show weathering simulation from start to finish. Expanded plots (b, d, f) show end of simulation only for visualization purposes. (a) 25° plot, (b) 25 °C zoom plot, (c) 60 °C plot, (d) 60 °C zoom plot, (e) 90 °C plot, (f) 90 °C zoom plot.

remaining molar ratios before another 5% loss was taken into account. This iterative process, representing an exponential decay in the amount of liquid residue as a function of steps, was repeated until the amount of residue remaining matched the desired percent weathering (e.g. 95%). Simulations were repeated with different step sizes, e.g. 2%, and the simulations were not meaningfully different than the 5% step size, thereby verifying that the step size was sufficiently small to represent a gradual evaporation. We also repeated the simulations using Antoine constants derived from other sources, measured over different temperature ranges, and although the exact fractional compositions were slightly different, the overall results were not meaningfully different.

Fig. 7 shows the mathematically simulated weathering data plotted against the experimentally measured weathering data for the artificial gasoline. The simulated data fits the measured data rather well at all three temperatures, especially given the fundamental assumptions that are made when calculating the mathematical model: 1) that there are no differences in intermolecular interactions between like and unlike compounds, either in the condensed phase or the gas phase, and 2) that the gas phase and condensed phase are in equilibrium.

An important feature of the simulations in Fig. 7b, d and f is the relative quantity of toluene remaining beyond 80% weathering. At 25 °C, the mathematical simulations predict that the toluene drops

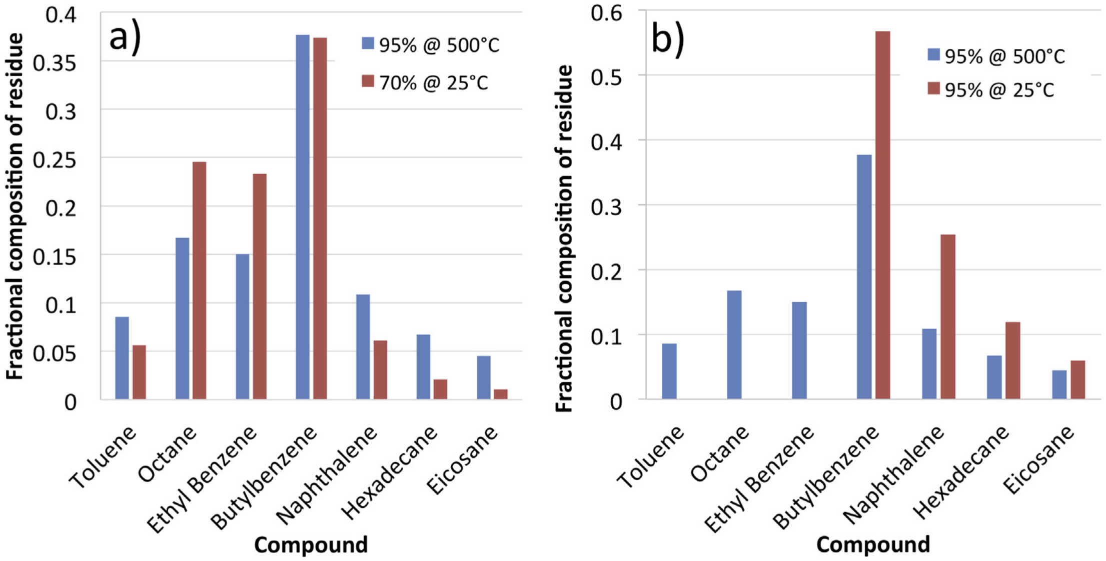


Fig. 8. 500 °C weathering simulation (mathematical only). (a) gasoline 95% weathered at 500 °C vs. 70% weathered at 25 °C, (b) gasoline 95% weathered at 500 °C vs. 95% weathered at 25 °C.

off to baseline at around 83% weathering, which is supported by the experimental weathering. At 90 °C, the simulations predict that toluene doesn't drop off until around 90% weathering, which is again supported by the experimental measurements. Similarly, at 25 °C, ethylbenzene is predicted to decrease to baseline around 90% weathering, but at 90 °C, it doesn't reach the baseline until ~94% weathering. At low weathering temperatures, the theory and experimental observations result in a naphthalene composition close to 0.25 (25%) at 95% weathering, but at 90 degrees, the theory and experimental observations result in a naphthalene composition closer to 0.21 (21%) at 95% weathering. In short, these mathematical models, derived from first principles, predict the experimental weathering observations of artificial gasoline remarkably well, and help explain the observations for real gasoline shown in Fig. 4.

3.5. Elevated temperature simulations

Mathematical simulations were conducted at temperatures that exceeded our experimental weathering temperatures. In the interest of safety, we did not evaporate gasoline or the artificial gasoline at temperatures above 90 °C. Simulations were conducted at 120 °C, 150 °C, 230 °C and 500 °C to investigate the distribution of residues expected to remain in more realistic fire conditions. These simulations assume that it is reasonable to extrapolate the use of the tabulated Antoine constants to 500 °C, when in reality many of the curves have only been measured up to temperatures well below this; e.g. 136 °C for toluene, 152 °C for octane, 163 °C for ethylbenzene, 213 °C for butylbenzene, 250 °C for naphthalene, 320 °C for hexadecane, and 379 °C for eicosane [41]. For this reason, the accuracy of the vapor pressures cannot be assured. However, it is nonetheless helpful to assess the general expectations of evaporation at elevated temperatures.

The simulation results in Fig. 8 show that temperature has a considerable effect at high temperatures and that gasoline weathered 95% at 500 °C more closely resembles gasoline weathered 70% at 25 °C than it does gasoline weathered 95% at 25 °C (Fig. 8). The mixtures weathered 95% at 500 °C and 70% at 25 °C both contain significantly more of the volatile components in the residue than the same solution weathered 95% at 25 °C.

At high temperatures (>200 °C), the temperature of weathering has a much larger influence than at low temperatures, and the effect on the distribution of compounds remaining in the fire debris could be as- or more-significant than the extent of weathering. Again, the reason is that at room temperature, the vapor pressures of the various compounds are different by more than 6 orders of magnitude. At elevated temperatures, the vapor pressures of the different compounds are thousands of times closer together, which leads to a much more uniform evaporation at high temperatures. These simulations provide an alternative, or additional, explanation as to why gasoline recovered from fire scenes appears to be less weathered than one might expect after exposure to such high temperatures.

Regarding the applicability of these results to other work, the current work suggests that the evaporation curves demonstrated by Smith et al. [16] as a function of GC retention time would have different, and less-steep, sigmoidal curves at elevated temperatures. These results do not contradict the recent work of Smith et al. [16], but they do offer a fundamental basis with which to extend the existing model to evaporation at significantly elevated temperatures.

4. Conclusions

Three factors are known to influence the relative distribution of residues in weathered ignitable liquids. They are; percent weathered > temperature > nitrogen gas (convection), in order of magnitude of effect. The influence of a vacuum or a nitrogen stream to assist with the weathering process is negligible and over small temperature ranges, the extent (percent) of weathering is the dominant of the three factors. However, when liquids are evaporated at significantly elevated temperatures, e.g. hundreds of degrees Celsius, the temperature becomes a very important factor such that a liquid that is heavily (95%) weathered at high temperature (500 °C) will be almost indistinguishable from a liquid that is weathered to a lesser extent (70%) at room temperature. These results are derived from fundamental properties of matter, using the known relationships between vapor pressure and temperature, and they provide an alternative or additional explanation as to why gasoline recovered from arson scenes does not appear to be as weathered as one would expect.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.forc.2017.02.011.

References

[1] J.R. Almirall, K.G. Furton, Characterization of background and pyrolysis products that may interfere with the forensic analysis of fire debris, J. Anal. Appl. Pyrol. 71 (2004) 51–67.

[2] M. Sandercock, Fire investigation and ignitable liquid residue analysis: a review: 2001–2007, Forens. Sci. Int. 176 (2008) 93–110.

[3] J.R. Almirall, K.G. Furton, Analysis and Interpretation of Fire Scene Evidence, Forensic Science Techniques, CRC Press, New York, NY, 2004.

[4] R. Chandler, Fire Investigation, Delmar, Cengage Learning, Clifton Park, NY, 2009.

[5] M. Ferreiro-González, J. Ayuso, J.A. Álvarez, M. Palma, C.G. Barroso, Application of an hs–MS for the detection of ignitable liquids from fire debris, Talanta 142 (2015) 150–156.

[6] D.T. Sheppard, Analysis and Interpretation of Fire Scene Evidence, CRC Press LLC, Boca Raton, FL, 2004.

[7] G. Frysinger, R. Gaines, Forensic analysis of ignitable liquids in fire debris by comprehensive two-dimensional gas chromatography, J. Forens. Sci. 47 (2002) 471–482.

[8] E1618-14 Standard Test Method for Ignitable Liquid Residues in Extracts From Fire Debris Samples by Gas Chromatography-mass Spectrometry, ASTM international, 2014.

[9] P.M.L. Sandercock, E. Du Pasquier, Chemical fingerprinting of gasoline: 2. Comparison of unevaporated and evaporated automotive gasoline samples, Forens. Sci. Int. 140 (2004) 43–59.

[10] J.M. Baerncopf, V.L. McGuffin, R.W. Smith, Association of ignitable liquid residues to neat ignitable liquids in the presence of matrix interferences using chemometric procedures, J. Forens. Sci. 56 (2011) 70–81.

[11] D.A. Turner, J.V. Goodpaster, Comparing the effects of weathering and microbial degradation on gasoline using principal components analysis, J. Forens. Sci. 57 (2012) 64–69.

[12] D.A. Turner, J.V. Goodpaster, The effects of microbial degradation on ignitable liquids, Anal. Bioanal. Chem. 394 (2009) 363–371.

[13] D.A. Turner, J.V. Goodpaster, The effect of microbial degradation on the chromatographic profiles of tiki torch fuel, lamp oil, and turpentine, J. Forens. Sci. 56 (2011) 984–987.

[14] M. Lopatka, M.E. Sigman, M.J. Sjerps, M.R. Williams, G. Vivó-Truyols, Class-conditional feature modeling for ignitable liquid classification with substantial substrate contribution in fire debris analysis, Forens. Sci. Int. 252 (2015) 177–186.

[15] T.J. Bruno, T.M. Lovestead, M.L. Huber, Prediction and preliminary standardization of fire debris constituents with the advanced distillation curve method, J. Forens. Sci. 56 (2011) S192–S202.

[16] R.W. Smith, R.J. Brehe, J.W. McIlroy, V.L. McGuffin, Mathematically modeling chromatograms of evaporated ignitable liquids for fire debris applications, Forens. Chem. 2 (2016) 37–45.

[17] W.N.S.M. Desa, N.N. Daeid, D. Ismail, K. Savage, Application of unsupervised chemometric analysis and self-organizing feature map (SOFM) for the classification of lighter fuels, Anal. Chem. 82 (2010) 6395–6400.

[18] P. Doble, M. Sandercock, E. Du Pasquier, P. Petocz, C. Roux, M. Dawson, Classification of premium and regular gasoline by gas chromatography/mass spectrometry, principal component analysis and artificial neural networks, Forens. Sci. Int. 132 (2003) 26–39.

[19] W.Y. Lu, J.G. Rankin, A. Bondra, C. Trader, A. Heeren, P.D. Harrington, Ignitable liquid identification using gas chromatography/mass spectrometry data by projected difference resolution mapping and fuzzy rule-building expert system classification, Forens. Sci. Int. 220 (2012) 210–218.

[20] Y. Lu, P. Chen, P.B. Harrington, Comparison of differential mobility spectrometry and mass spectrometry for gas chromatographic detection of ignitable liquids from fire debris using projected difference resolution, Anal. Bioanal. Chem. 394 (2009) 2061–2067.

[21] M.E. Sigman, M.R. Williams, Covariance mapping in the analysis of ignitable liquids by gas chromatography/mass spectrometry, Anal. Chem. 78 (2006) 1713–1718.

[22] M.E. Sigman, M.R. Williams, R.G. Ivy, Individualization of gasoline samples by covariance mapping and gas chromatography/mass spectrometry, Anal. Chem. 79 (2007) 3462–3468.

[23] M.E. Sigman, M.R. Williams, J.A. Castelbuono, J.G. Colca, C.D. Clark, Ignitable liquid classification and identification using the summed-ion mass spectrum, Instrum Sci. Technol. 36 (2008) 375–393.

[24] M.R. Williams, M.E. Sigman, J. Lewis, K.M. Pitan, Combined target factor analysis and bayesian soft-classification of interference-contaminated samples: forensic fire debris analysis, Forensic Sci. Int. 222 (2012) 373–386.

[25] J. Jasper, J. Edwards, L. Ford, A novel method for arson accelerant analysis: gas chromatography/isotope ratio mass spectrometry, Molecular Isotope Technologies LLC, 2001, pp. 1–8, Accessed at http://www.naturesfingerprint.com/pdfs/ArsonStable Isotope Analysis.pdf, October 2016.

[26] J. Jasper, J. Edwards, L. Ford, R. Corry, Putting the arsonist at the scene "DNA" for the fire investigator? Gas chromatography/isotope ratio mass spectrometry, Fire Arson Inv. 51 (2002) 30–34.

[27] B.J. Smallwood, R.P. Philp, J.D. Allen, Stable carbon isotopic composition of gasolines determined by isotope ratio monitoring gas chromatography mass spectrometry, Org. Geochem. 33 (2002) 149–159.

[28] C. Gauchotte, G. O'Sullivan, S. Davis, R.M. Kalin, Development of an advanced on-line position-specific stable carbon isotope system and application to methyl tert-butyl ether, Rapid Commun. Mass Spectrom. 23 (2009) 3183–3193.

[29] G. O'Sullivan, R.M. Kalin, Investigation of the range of carbon and hydrogen isotopes within a global set of gasolines, Environ. Forensics 9 (2008) 166–176.

[30] Y. Li, Y.Q. Xiong, C.C. Fang, Q.Y. Liang, J.R. Zhang, P.A. Peng, A new application of headspace single-drop microextraction technique for compound specific carbon isotopic determination of gasoline range hydrocarbons, Org. Geochem. 42 (2011) 559–565.

[31] S.D. Harvey, K.H. Jarman, J.J. Moran, C.M. Sorensen, B.W. Wright, Characterization of diesel fuel by chemical separation combined with capillary gas chromatography (GC) isotope ratio mass spectrometry (IRMS), Talanta 99 (2012) 262–269.

[32] Z. Schwartz, Y. An, K.I. Konstantynova, G.P. Jackson, Analysis of household ignitable liquids and their post-combustion weathered residues using compound-specific gas chromatography-combustion-isotope ratio mass spectrometry, Forens. Sci. Int. 233 (2013) 365–373.

[33] S.A. Harris, M.J. Whiticar, M.K. Eek, Molecular and isotopic analysis of oils by solid phase microextraction of gasoline range hydrocarbons, Org. Geochem. 30 (1999) 721–737.

[34] C. Martin-Alberca, F.E. Ortega-Ojeda, C. Garcia-Ruiz, Analytical tools for the analysis of fire debris. A review: 2008–2015, Anal. Chim. Acta 928 (2016) 1–19.

[35] B.M. Zorzetti, J.M. Shaver, J.J. Harynuk, Estimation of the age of a weathered mixture of volatile organic compounds, Anal. Chim. Acta 694 (2011) 31–37.

[36] E. Stauffer, J.A. Dolan, R. Newman, Fire Debris Analysis, Elsevier Inc, Burlington, MA, 2008.

[37] D. Mann, Comparison of Automotive Gasolines Using Capillary Gas Chromatography ii: Limitations of Automotive Gasoline Comparisons in Casework, 1987.

[38] T.J. Bruno, S. Allen, Weathering patterns of ignitable liquids with the advanced distillation curve method, J. Res. Natl. Stand. 118 (2013) 29–51.

[39] D.L. Camin, A.F. Forziati, F.D. Rossini, Physical properties of n-hexadecane, n-decylcyclopentane, n-decylcyclohexane, 1-hexadecene and n-decylbenzene, J. Phys. Chem. 58 (1954) 440–442.

[40] A.F. Forziati, W.R. Norris, F.D. Rossini, Vapor pressures and boiling points of sixty API-NBS hydrocarbons, J. Res. Natl. Bur. Stand. (U.S.) 43 (1949) 555–563.

[41] L. Fowler, W.N. Trump, C.E. Vogler, Vapor pressure of naphthalene. Measurements between 40 and 180, J. Chem. Eng. Data 13 (1968) 209–210.

[42] B.R. Poling, J.M. Prausnitz, J.P. O'Connell, Properties of Gases and Liquids, 5th ed., McGraw-Hill, New York, NY, 2001.

[43] C.B. Willingham, W.J. Taylor, J.M. Pignocco, F.D. Rossini, Vapor pressures and boiling points of some paraffin, alkylcyclopentane, alkylcyclohexane, and alkylbenzene hydrocarbons, J. Res. Natl. Stand. 35 (1945) 219–244.

[44] P. Atkins, J. dePaula, Physical Chemistry, ninth ed., W.H. Freeman and Company, New York, NY, 2009.