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Adsorption Saturation and Chromatographic Distortion Effects on Passive Headspace Sampling with Activated Charcoal in Fire Debris Analysis*

ABSTRACT: Distortion of the chromatographic profile obtained for hydrocarbons that have been sampled by adsorption onto activated charcoal is a well-known phenomenon. The work reported here helps to better define the causes of chromatographic profile distortion and offers a potential method to avoid chromatographic distortion in some cases through a subsampling technique. The recovery of hydrocarbons from an equimolar mixture was investigated to determine the influence of hydrocarbon concentration on the molar ratios of recovered components. In a one-quart container, hydrocarbon volumes as small as 24 μL (liquid) were sufficient to saturate the surface area available for adsorption on a 99.0 mm^2 square of activated charcoal, resulting in significant distortions in the molar ratio and the chromatographic profile of the recovered hydrocarbons. Passive headspace sampling of a similarly small volume of unweathered gasoline spiked onto carpet padding resulted in a significant distortion of the chromatographic profile. The chromatographic profile of the recovered hydrocarbons closely resembled 75% weathered gasoline. Heating the container spiked with unweathered gasoline to evenly distribute the components and then removing a subsample of the carpet padding to a second container for passive headspace analysis greatly reduced the amount of distortion in the resulting chromatogram.

KEYWORDS: forensic science, fire debris, activated charcoal, passive headspace

In a study on the performance of commercial containers for evidence storage from fire debris, the passive headspace concentration of ignitable liquids was monitored by adsorption onto activated charcoal, following the ASTM E1412 standard practice (1). The recovered hydrocarbon profiles obtained by the ASTM method exhibited variations that were not readily understood based on experimental conditions. ASTM E1412 is the most commonly used method for separating ignitable liquid residues from fire debris (2). To better understand and optimize the experimental procedure used in the commercial container evidence storage study, a comprehensive investigation of the liquid-vapor-adsorbent system was undertaken. A previous study on the effects of adsorption time, temperature, charcoal size, and sample concentration on common accelerants using activated charcoal has been published along with a recommended analysis scheme (3). However, a better understanding of the system dynamics was required to establish an experimental design for investigating the performance of commercial containers.

Understanding the dynamics of the passive headspace concentration system involves characterization of the hydrocarbon vapor be-

havior within a closed system. The concentration of hydrocarbons in the system, the distribution of the hydrocarbon vapors within the system, and the hydrocarbon adsorption behavior on the activated charcoal were all studied to determine their influence on the chromatographic profile of the ignitable liquid. The data presented here demonstrates that conditions within the system (sample container) can affect the chromatographic data significantly, and may contribute to incorrect data interpretation in casework. The effects of hydrocarbon vapor concentration on passive headspace sampling with activated charcoal were thoroughly investigated to recognize problems within the system and to assist in minimizing them.

Materials and Methods

A stock solution of hydrocarbons consisting of heptane, toluene, octane, nonane, and decane was prepared in an equimolar ratio of each hydrocarbon (i.e., the mole fraction of each hydrocarbon in the mixture was 0.20). The toluene was purchased from Fisher Scientific (Pittsburgh, PA) and the alkanes were purchased from Aldrich Chemical Co (Milwaukee, WI). Low benzene carbon disulfide was also purchased from Fisher Scientific. All chemicals were used without further purification. Activated charcoal strips purchased from Albrayco (Cromwell, CT) were pressed onto 3 M double-sided tape. The strips were cut into 33.2 mm^2 area pieces using a hole-punch. In one experiment, three different size pieces of activated charcoal were cut: 12.6 mm^2 , 33.2 mm^2 , and 99.0 mm^2 . The hydrocarbon liquid container consisted of seven vial inserts (250 μL each) super-glued together on a microscope slide. A metal rod with four male quick disconnects attached every 2.5 cm and an alligator clip held the activated charcoal discs above the vial insert container, as shown in Fig. 1. The activated carbon discs and the hydrocarbon containers were placed in a 1 quart (946 mL) Ball[®] glass jar and fitted with a standard pressure-canning flat and band. After

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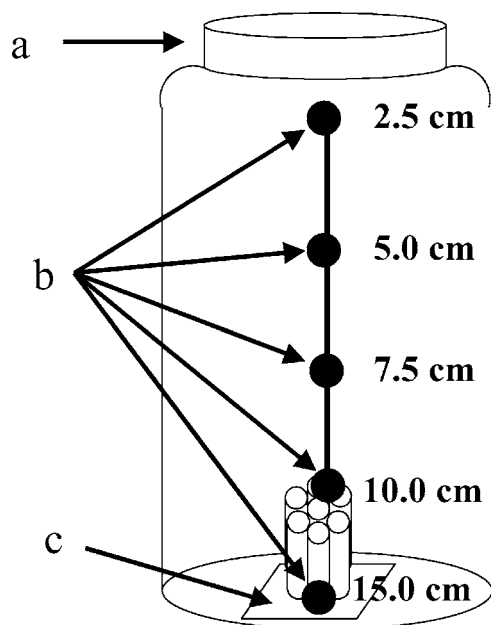


FIG. 1—Diagram showing the experimental setup including (a) Ball[®] glass container (b) positions of activated carbon discs at multiple depths in the container and (c) the glass vial inserts used to hold the hydrocarbon mix spike.

equilibration, the hydrocarbons were desorbed from the activated charcoal with carbon disulfide.

Method

The activated charcoal discs were weighed, then pressed onto the quick disconnects and the lower portion of the vial insert container (with the aid of Scotch double-sided tape to hold the carbon pieces in place). All handling of the carbon discs was done with clean metal forceps. The hydrocarbon mixture was deposited into one or more inserts depending on the volume. The volumes of hydrocarbon mix used to spike the containers were 12, 18, 24, 36, 48, 96, 120, 500, and 720 μL . Each of these volumes corresponds respectively to 1.52×10^{-5} , 2.28×10^{-5} , 3.04×10^{-5} , 4.56×10^{-5} , 6.09×10^{-5} , 1.22×10^{-4} , 1.52×10^{-4} , 6.34×10^{-4} , and 9.13×10^{-4} moles of each hydrocarbon placed in the container. The entire vial insert container and rod assembly were placed in the jar with the lid tightly secured. The jar was placed in a 66°C oven for 16 to 24 h, then removed and allowed to cool to room temperature. The activated charcoal discs were removed (along with the double-sided tape) and placed into half-dram vials with 1.0 mL of carbon disulfide. Control experiments were performed to insure that the tape did not contribute to the analytes or interfere with the analysis. An external standard method (analyte mixture at known concentrations run separately) was utilized in creating calibration curves to quantify the hydrocarbons recovered from the activated carbon.

The analyses were performed on an Agilent 6890 gas chromatograph with a 5973 mass selective detector and a 7683 auto-sampler. Samples were chromatographed on a 25 m HP-1 methylsiloxane column with a 0.2 mm ID and 0.50 μm film thickness. Sample volumes of 1 μL were injected through a 250°C split/splitless injector with a 50:1 split ratio. The sample passed onto the chromatographic column at an initial temperature of 50°C . The initial temperature was held constant for 3 min and then increased at a rate of $10^\circ\text{C}/\text{min}$ to a final temperature of 280°C and held at the final temperature for 4 min. The mass spectrometer was tuned according to the man-

ufacturer's specification at a source temperature of 250°C . Spectra were scanned over a range of 30–350 m/z units.

The surface area occupied by each hydrocarbon, adsorbed onto activated carbon in an extended conformation, was calculated based on the molecular van der Waals surface. The van der Waals surface was calculated with Hyperchem 7 (HyperCube Inc. Gainesville, FL) molecular modeling software.

Results

Hydrocarbon Depth Profile

The standard deviation in the mole fractions of each hydrocarbon recovered from the activated charcoal at different depths within a container varied by approximately 1% in the lowest concentration samples (spiking volume of 12 μL of hydrocarbon mix). The mole fraction of each recovered hydrocarbon was close to 0.20, which corresponds to the mole fraction composition in the starting hydrocarbon mix. The mole fractions of the recovered hydrocarbons from a 12 μL volume spike are plotted in Fig. 2a. At the higher spiking volume of 96 μL , the variability of the mole fraction of each hydrocarbon recovered from the activated charcoal discs at different depths within the jar remained low, as shown in Fig. 2b.

It is important to note that in the 96 μL loading, the mole fraction of decane in the hydrocarbons recovered from the activated carbon increased to near 0.40, almost double the mole fraction of decane in the original hydrocarbon mix. Additionally, the mole fraction of recovered heptane in the experiment decreased to 0.02–0.03. The mole fractions of the recovered hydrocarbons from activated charcoal discs spiked with 24, 36, 48, 120, 500, and 720 μL varied from the composition of the initial mix. Hydrocarbon displacement on the activated charcoal and distortion of the hydrocarbon profile under GC-MS analysis are discussed below.

Moles Adsorbed

The number of moles of total hydrocarbon extracted from the activated charcoal increased significantly as the total amount of hydrocarbon in the container was varied from the lower volume of 12 μL up to 18 μL ; however, further significant increases in the quantity of moles adsorbed were not observed, even though the volume of liquid added to the system was increased considerably. The molar distribution of recovered hydrocarbons per gram of activated carbon varied as a function of the total volume of hydrocarbon mix spiked into each container, for volumes of 24 μL through 720 μL ; however, the total surface area available for adsorption (on a per gram basis) is constant. An estimate of the activated charcoal surface area accessible for adsorption was made based on the moles of each hydrocarbon adsorbed and one half of the van der Waals surface area for each hydrocarbon molecule. Each hydrocarbon was assumed to adsorb onto the activated charcoal surface in an extended conformation. The calculated van der Waals surface is an over-estimate of the surface area occupied by an adsorbed hydrocarbon. To a first approximation, only one side of the molecule lies on the surface and the opposite side is exposed to the vapor phase. The surface area occupied by each adsorbed hydrocarbon was estimated as one half of the total van der Waals surface area. The total van der Waals surface areas calculated for heptane, toluene, octane, nonane, and decane were 173.26, 128.56, 194.00, 214.97, and 235.69 $\text{\AA}^2/\text{molecule}$ respectively. The average activated charcoal surface area was calculated for each spike volume 24 μL –720 μL , and an overall average of $1128 \pm 197 \text{ m}^2/\text{g}$ was determined. A plot of the adsorption surface area corresponding to the recovered hydrocarbon mixture at each spiking volume is shown in Fig. 3. The

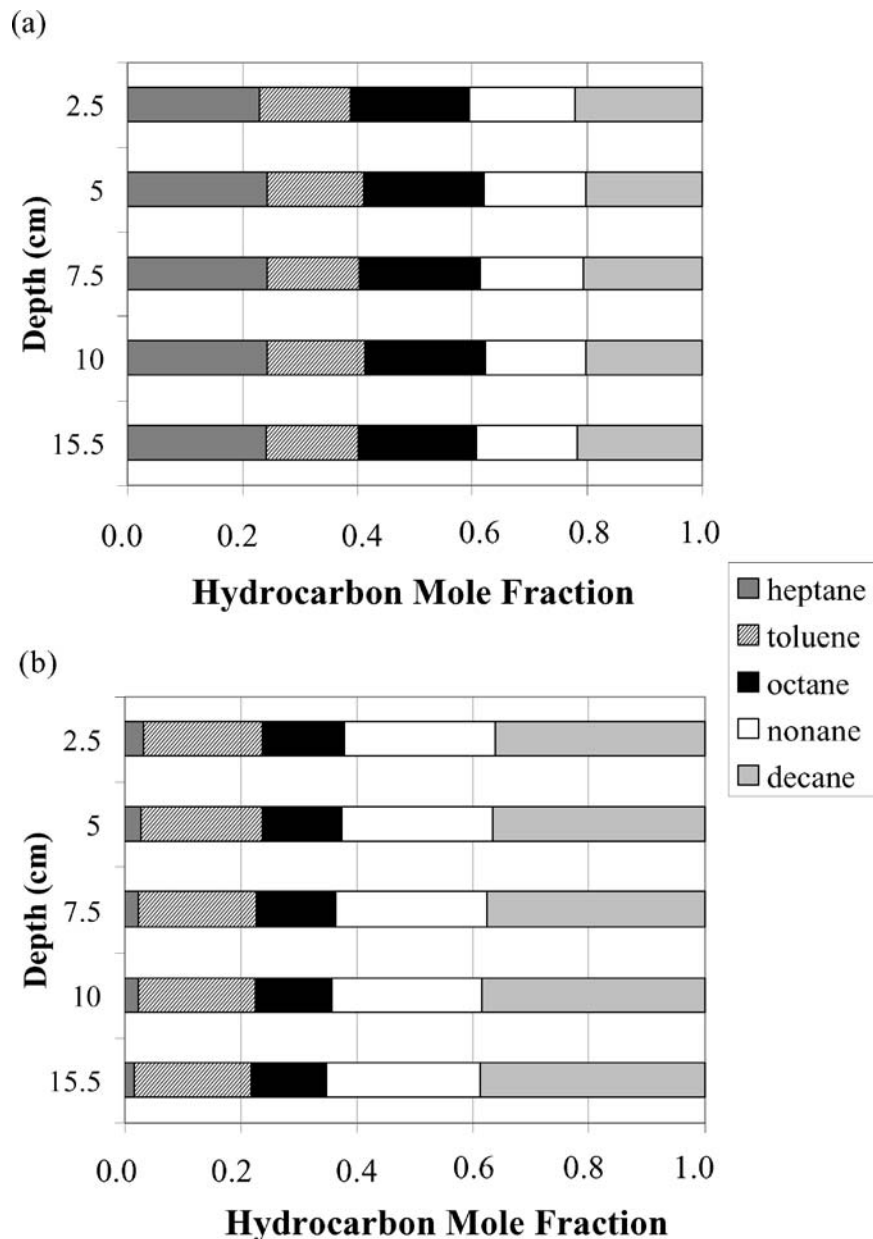


FIG. 2—(a) Mole fraction of hydrocarbons recovered from the activated carbon at a container loading of 12 μL of hydrocarbon mix. (b) Mole fraction of hydrocarbons recovered from the activated carbon at a container loading of 96 μL of hydrocarbon mix.

surface area determined in these experiments is similar to the surface area of 1,100–1,200 m^2/g that has been measured by nitrogen adsorption for Sorbonorit B (Norit Co.) activated carbon (4).

Effects of Activated Charcoal Size

ASTM Method E1412-00 makes reference to the physical “size” of activated carbon strip to be used for ignitable liquid sampling. It is important to distinguish between the physical “size” (typically measured in mm^2), and the surface area available for adsorption (typically measured in m^2/g). As the physical size and weight of the carbon strip increases, so will the total surface area, which is available for adsorption. The amount of surface area available for adsorption is one factor that can significantly impact the recovered hydrocarbon chromatographic profile. In order to retain a point of reference to the ASTM protocol (1), a series of experiments were carried out by spiking the hydrocarbon mix into containers that each contained

activated carbon strips of differing physical “size.” Three sizes of activated charcoal strips (12.6 mm^2 , 33.2 mm^2 , and 99.0 mm^2) were used in these experiments. The corresponding surface areas available for adsorption were 6.8 m^2 , 22.6 m^2 and 68.8 m^2 , as calculated based on the mass of the activated carbon strip and the average surface area determined here of 1128 m^2/g . At the lowest spiking volume of 12 μL , a significant deviation of the recovered hydrocarbon mole fractions from 0.20 was observed only on the 12.6 mm^2 area activated charcoal, as shown in Fig. 4a. At a spiking volume of 18 μL , a significant deviation of the recovered hydrocarbon mole fractions from 0.20 was observed for both the 12.6 mm^2 and 33.2 mm^2 activated charcoal sizes, but no distortion was observed for the 99.0 mm^2 size, as shown in Fig. 4b. Spiking volumes of 24 μL and higher resulted in deviation of the recovered hydrocarbon mole fractions away from the composition of the original hydrocarbon mix on the 99 mm^2 size activated charcoal, as shown in Fig. 4c. Figure 4c also shows that the distribution of hydrocarbons

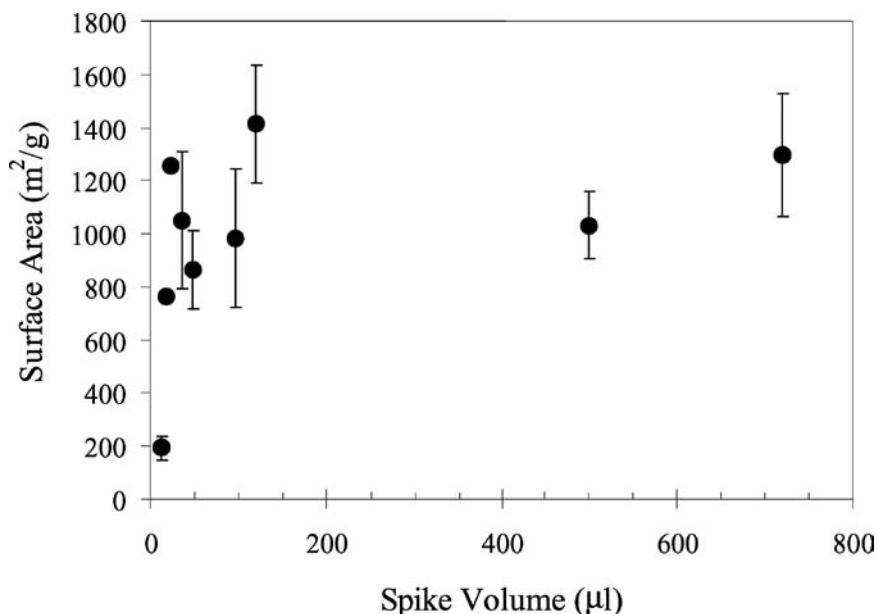


FIG. 3—Activated charcoal surface area covered by adsorbed hydrocarbon as calculated from the molecular van der Waals areas of each hydrocarbon and composition of recovered hydrocarbon mixture at each spiking volume.

recovered from the 12.6 mm², 33.2 mm² and 99.0 mm² size charcoal were the same.

Displacement of Hydrocarbons on Activated Charcoal

The mole fraction of each hydrocarbon recovered from the activated charcoal pieces at 7.5 cm depth for each container spiked with increasing volumes of the original equimolar hydrocarbon mix is shown in Fig. 5. The mole fraction of each hydrocarbon recovered from activated carbon in the container spiked with 12 µL volume was similar to that of the original hydrocarbon mix, which contained 20% of each hydrocarbon. As the volume of hydrocarbon mix was increased, a higher mole fraction of decane and a lower mole fraction of heptane were observed for the hydrocarbons recovered from the activated carbon discs. A maximum enhancement in the mole fraction of decane occurred in containers spiked with 96 µL and 120 µL of hydrocarbon mix. For the container loading volumes of 500 µL and 720 µL, the mole fractions of the hydrocarbons recovered from the activated carbon discs return to levels approximating the composition of the original mixture, with the exceptions of toluene and heptane, which returned to values of 0.32 and 0.11 respectively. These results reflect data obtained from heating the sample at 66°C for 16–24 h. The effects of time and temperature on hydrocarbon displacement and chromatographic distortion have previously been addressed (3).

Liquid Hydrocarbon Recovery

Liquid hydrocarbon mix was recovered from the vial inserts of the 120, 500, and 720 µL spiking volumes for containers that had been heated to 66°C, indicating that the vapor phase was saturated with hydrocarbon at the elevated temperature. The recovered liquid volumes were 15, 160, and 300 µL respectively. The fact that significant quantities of hydrocarbon mix were recovered in the insert where the mixture was originally placed demonstrates that all of the liquid did not go into the vapor phase at 66°C. If the hydrocarbon liquid had all gone into the vapor phase at 66°C, when condensate formed inside the container upon cooling, the amount inside the insert would have been miniscule (i.e., in proportion to the fraction

TABLE 1—Mole fractions of hydrocarbons in the vapor phase at 66°C and in the liquid hydrocarbon mix recovered from the glass inserts (see Fig. 1).

Spike Volume (µL)	Vapor Phase							Recovered Liquid		
	12	36	48	96	120*	500*	720*	120	500	720
Heptane	0.20	0.20	0.20	0.20	0.22	0.26	0.28	0.01	0.04	0.05
Toluene	0.20	0.20	0.20	0.20	0.22	0.27	0.30	0.01	0.02	0.03
Octane	0.20	0.20	0.20	0.20	0.22	0.24	0.25	0.02	0.10	0.11
Nonane	0.20	0.20	0.20	0.20	0.20	0.18	0.16	0.19	0.26	0.27
Decane	0.20	0.20	0.20	0.20	0.13	0.06	0.01	0.77	0.58	0.54

* Calculated from recovered liquid composition.

of the container volume occupied by the insert). The mole fractions of each hydrocarbon in the recovered liquid from the 120, 500, and 720 µL spikes are given in Table 1, along with the vapor phase mole fractions for each hydrocarbon at all spiking volumes.

Gasoline

Unweathered gasoline volumes of 12, 96, and 720 µL were used in place of the equimolar hydrocarbon mixture to investigate the effects described above on the chromatographic profiles of an ignitable liquid that is commonly found in fire investigations. The chromatogram of the recovered hydrocarbons from a 12 µL spike volume is shown in Fig. 6a, along with the chromatographic profile of the unweathered gasoline in Fig. 6b. The chromatogram of the recovered hydrocarbons from a 96 µL spike volume of the same gasoline sample is shown in Fig. 7a, and the chromatograph of a 75% weathered sample of the gasoline is shown in Fig. 7b. The data in Figs. 6 and 7 were obtained using 33.2 mm² carbon discs.

In a second experiment, 96 µL of unweathered gasoline was placed at the center of each of two 3.8 cm × 7.6 cm pieces of carpet, backed by carpet padding, in quart jars. A 99.0 mm² activated charcoal strip was placed in one of the jars, and both jars were closed and heated at 66°C for 16 h. The carbon strip was removed from the one jar and eluted with 1 mL of CS₂. The chromatographic profile resulting from the sample is shown in Fig. 8a. In an attempt

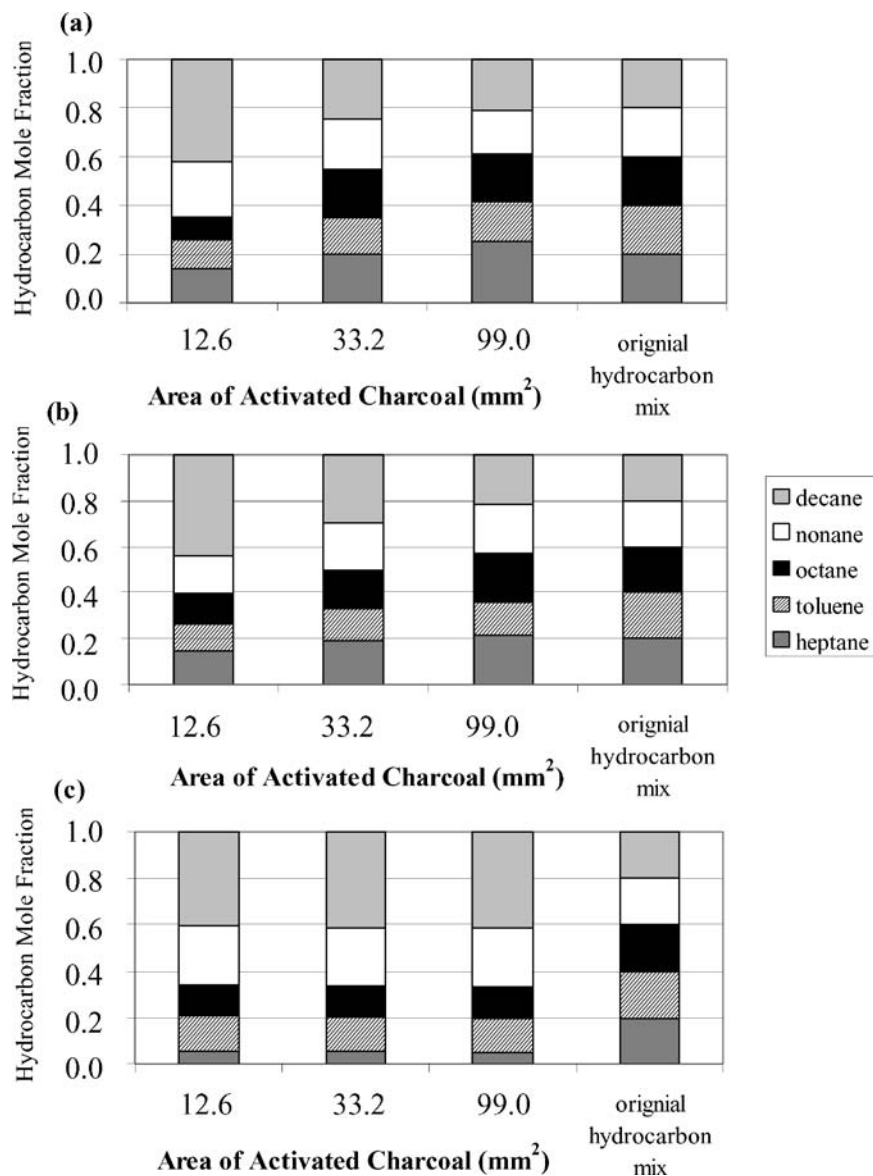


FIG. 4—The mole fraction of hydrocarbons recovered from activated carbon strips of differing physical “size” are shown for hydrocarbon mix spiking volumes of (a) 12 (b) 18 and (c) 24 μL .

to obtain homogeneous and representative subsamples from the second jar, the contents were cooled to room temperature, the jar was opened, and 1.9 cm \times 1.9 cm sections of carpet and padding were removed from the outer edges of the sample, away from the site of the original spike. Each of the subsamples was placed in a clean quart jar, along with a 99.0 mm² piece of activated charcoal. The jars containing the subsamples were closed and heated to 66°C for 16 h before they were opened and the carbon strips eluted with 1 mL of CS₂. The chromatographic profiles from the two subsamples were very similar; however, they differed significantly from the profile shown in Fig. 8a. The chromatogram resulting from the analysis of the carpet padding is shown in Fig. 8b.

Discussion

The vapor density of each hydrocarbon used in these experiments range from 3.5 (heptane) to 4.9 (decane) times the density of air. The data in Fig. 2 does not reveal evidence of hydrocarbon vapor stratification in the closed containers heated at 66°C for

16 h. Similarly, the mole fraction of hydrocarbon recovered from the activated charcoal discs at each of the five depths within a container show minimal variation for all of the spiking volumes. This data demonstrates that the hydrocarbon molecules are evenly distributed throughout the system for hydrocarbons in the narrow range of C7–C10. A set of hydrocarbons that spanned a much larger range in molecular size could be expected to display unequal distributions within the container. Denser-than-air vapor stratification is a well-known behavior that is a complicating factor in areas ranging from modeling the dispersion of explosive vapor clouds (5), to the analysis of fuel distribution within combustion chambers (6).

Although variations in the adsorbed hydrocarbon distribution were not observed as a function of sampling location within a single container, a significant variation in mole fraction distribution was observed as the spike volume of the equimolar hydrocarbon mix was varied. It is interesting to note that the moles of hydrocarbon adsorbed per gram of activated charcoal remain moderately constant on a 33.2 mm² carbon disc at spiking volumes greater than 24 μL , as shown in Fig. 3. An estimate of the activated charcoal surface area

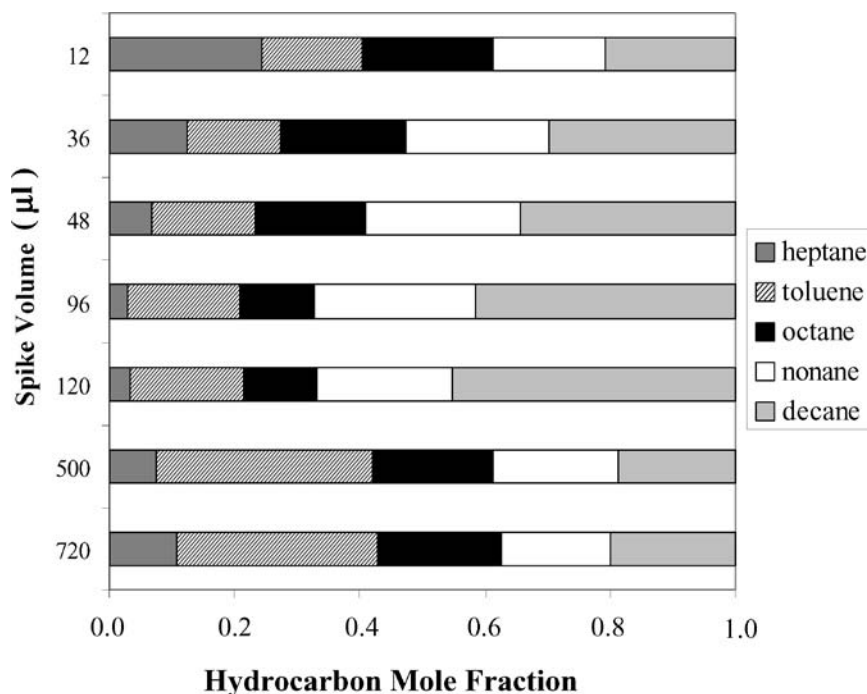


FIG. 5—The mole fraction distribution for hydrocarbons recovered from activated charcoal strips of 33.18 mm^2 .

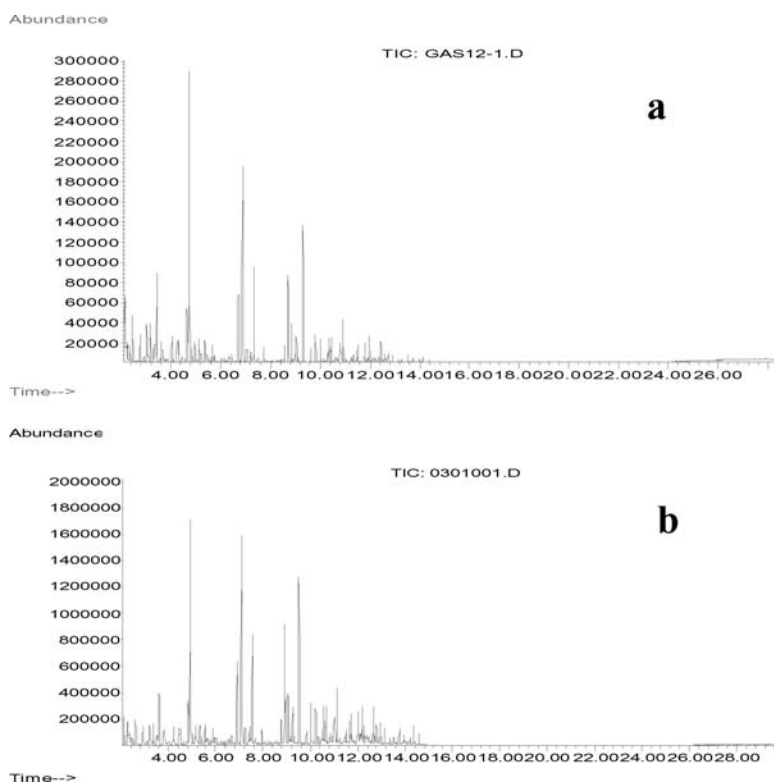


FIG. 6—(a) Total ion chromatogram for the hydrocarbons recovered from activated charcoal monitoring of the headspace in a container spiked with $12 \mu\text{L}$ of the gasoline sample. The gasoline was spiked into the container insert. (b) Total ion chromatogram of an unweathered gasoline sample.

available for adsorption was made based on the hydrocarbon mole fraction distribution and the van der Waals surface area for each hydrocarbon molecule, assuming that each hydrocarbon adsorbed in an extended conformation. The average carbon surface area calculated from the 33.2 mm^2 activated charcoal disc data at spiking volumes exceeding $24 \mu\text{L}$, was $1128 \pm 197 \text{ m}^2/\text{g}$. The surface area

determined from the adsorption data is not dramatically different from surface areas determined by nitrogen adsorption for other activated carbons and represent the surface area available for adsorption of hydrocarbons (4). At higher vapor concentrations, equilibrium is established between hydrocarbons in the vapor phase and the adsorbed hydrocarbons on the activated carbon surface. After the

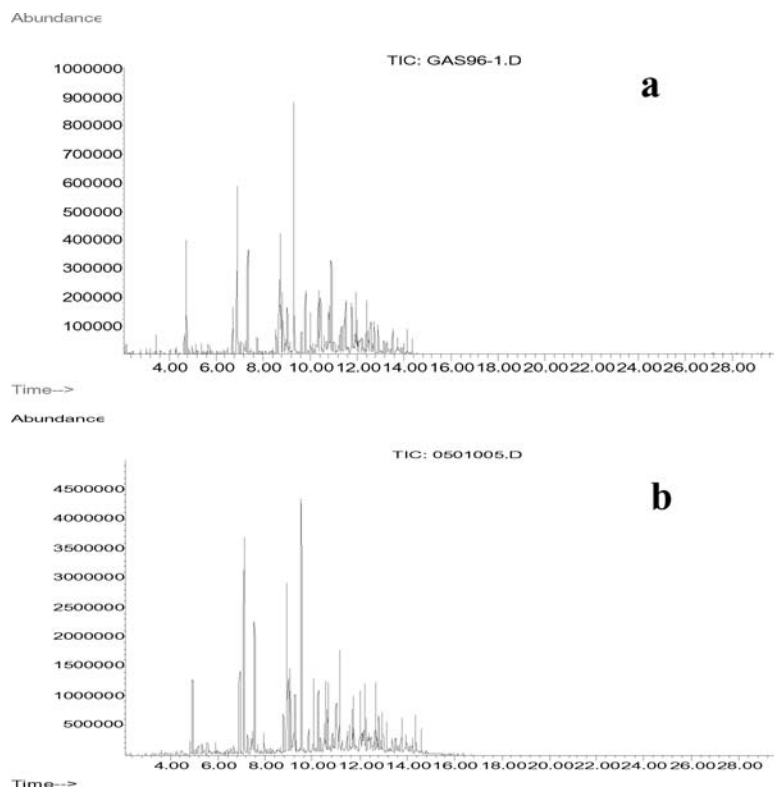


FIG. 7—(a) Total ion chromatogram for the hydrocarbons recovered from activated charcoal monitoring of the headspace in a container spiked with 96 μL of the gasoline sample. The gasoline was spiked into the container insert. (b) Total ion chromatogram of an 75% weathered gasoline sample.

adsorption capacity of the activated charcoal has been reached, the distribution of adsorbed hydrocarbons will be modified by equilibration in response to the concentration of hydrocarbons in the vapor phase. The distribution of recovered hydrocarbons and the resulting chromatographic profile for the mixture will reflect these changes, even though the adsorption capacity does not change.

Until the activated charcoal surface area is saturated with hydrocarbon, equilibrium-driven displacement and chromatographic distortion are not observed. The size of the activated charcoal therefore plays an important role in determining the molar ratio of the recovered hydrocarbons. Smaller sizes/weights of activated carbon have less available surface area for adsorption and are therefore saturated at lower vapor concentrations. Once the surface is saturated, hydrocarbon displacement begins to occur, changing the recovered hydrocarbon mole fractions and resulting in a chromatographic profile that can differ significantly from the profile of the original hydrocarbon mix. In the experiments reported here, hydrocarbon distortion was observed on a 99.0 mm^2 size carbon strip at spiking volumes exceeding 24 μL . The ASTM E1412-recommended carbon strip size for ignitable liquid residue sampling from fire debris is 100 mm^2 . This result demonstrates that even the ASTM-recommended size of activated carbon can be saturated by a very small volume of ignitable liquid. The degree of chromatographic distortion that results from activated charcoal surface saturation and hydrocarbon displacement depends on the equilibrated vapor concentrations and the relative strengths of adsorption for each hydrocarbon.

In the samples used in this study, hydrocarbon displacement from the 33.2 mm^2 size activated charcoal began to be observed at a spiking volume of 18 μL of the equimolar hydrocarbon mix, when the activated charcoal had reached its absorption capacity. These results directly demonstrate how displacement is related to the capacity of the activated charcoal (3). The displacement of the lower molecular

weight hydrocarbons by the higher molecular weight hydrocarbons reached a maximum at a 96 μL spiking volume. A 96 μL aliquot of the equimolar hydrocarbon mix contained a quantity of decane slightly exceeding the amount required to saturate the vapor phase with decane at 25°C, thus leaving a small quantity of condensed liquid. In traditional notation, P/P_0 for decane reached a limiting value of 1. An estimation of the vapor pressure of the individual hydrocarbon components at 66°C based on their heats of vaporization and the Clausius-Clapeyron equation predicts vapor pressures at the elevated temperature that would allow complete vaporization of all hydrocarbons at each spiking level, except for 720 μL , where a trace of decane would remain in the liquid phase. In the experiments reported here, liquid hydrocarbon mix was recovered from within the inserts at spiking volumes of 120 μL and larger, after the container had been heated to 66°C. This result indicates that the vapor phase had been saturated at 66°C and all of the liquid did not evaporate from the insert. This behavior represents a strong negative deviation from ideality (i.e., lowering of the expected individual vapor pressures) for the hydrocarbon components. The 96 μL spiking volume was the largest spike for which a condensed phase was not observed in the inserts at 66°C. The corresponding vapor phase concentrations for heptane, toluene, octane, nonane and decane at the 96 μL spiking level were 13 ppm, 12 ppm, 15 ppm, 17 ppm and 18 ppm.

When a condensed phase is present, the behavior of the vapor and liquid can become complicated and deviations from ideal behavior are observed, as discussed in the previous paragraph. It is interesting to note that a simple ideal treatment of the hydrocarbon components in these experiments as non-interacting species leads to predicted hydrocarbon liquid volumes of 8, 14, 179 and 314 μL at 25°C, resulting from spike volumes of 96, 120, 500 and 720 μL respectively. The predicted volumes compare well with the experimentally recovered volumes of 15, 160, and 300 μL recovered from

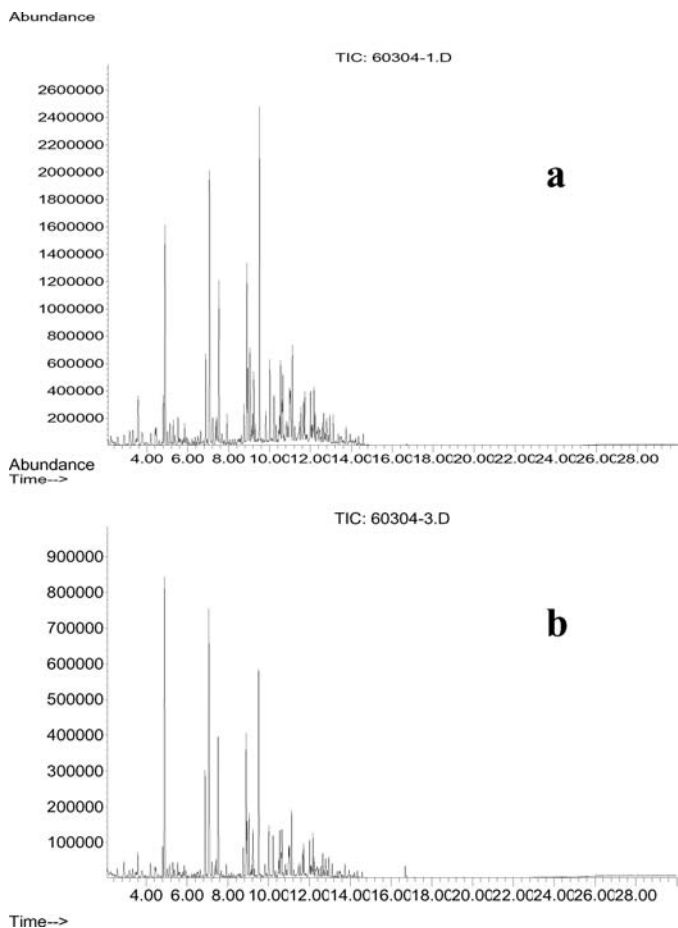


FIG. 8—(a) Total ion chromatogram of hydrocarbons recovered from a 96 mL spike of unweathered gasoline. The gasoline was spiked onto carpet backed with carpet-padding. (b) Total ion chromatogram of hydrocarbons recovered from a subsample of carpet-padding spiked with unweathered gasoline after equilibration of the original sample at 66°C.

120, 500 and 720 μL spike volumes respectively. The experimental uncertainties for recovered volumes as small as 15 μL are estimated to be as large as 20%.

Once the vapor phase is saturated for any one component in the mix, the composition of the vapor phase will begin to become enriched in the more volatile hydrocarbons, as the less volatile components are left in the condensed phase, as demonstrated in Table 1 and Fig. 9. The data in Table 1 shows, for example, that the recovered hydrocarbon mix from the 720 μL spike contained heptane, toluene, octane, nonane and decane mole fractions of 0.04, 0.03, 0.11, 0.27 and 0.55 respectively. By assuming that all liquid missing from the insert was in the vapor phase at 66°C, the gas phase for the 720 μL spike would contain heptane, toluene, octane, nonane and decane at mole fractions of 0.29, 0.30, 0.25, 0.16 and less than 0.01 respectively. The associated vapor phase concentrations of each hydrocarbon are 89 ppm, 84 ppm, 88 ppm, 64 ppm and 2 ppm respectively. Again it is interesting to note that the hydrocarbon mole fractions in the vapor phase, calculated for ideal behavior at 25°C and resulting from a 720 μL spike volume, would be 0.32, 0.32, 0.25, 0.08 and 0.03 for heptane, toluene, octane, nonane and decane respectively. The similarity of the experimental results and the ideal behavior at 25°C suggests that the hydrocarbon mixture is demonstrating significant negative deviation from ideal behavior (vapor pressure lowering) and that all constituent compounds are

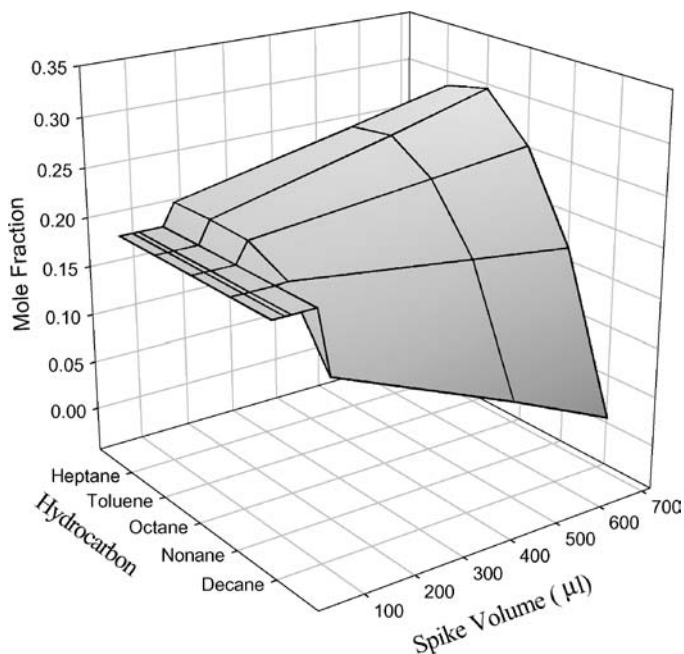


FIG. 9—The mole fractions of each hydrocarbon in the vapor phase at 66°C are shown for each of the spike volumes.

affected similarly. The mole fraction distribution calculated for the vapor phase at 66°C, based on the recovered liquid composition, differs significantly from a value of 0.20 for each of the five components in the equimolar mixture. As the vapor phase composition becomes enriched in the volatile hydrocarbons, the equilibrium with the activated carbon surface shifts to reflect the vapor phase composition. The recovered hydrocarbon mole fraction and the resulting chromatographic profile reflect the change, as seen in Fig. 5.

Toluene comprised the largest recovered mole fraction (off activated carbon) from the 720 μL spiking volume experiments, as shown in Fig. 5. Toluene and other aromatics are known to be retained on activated charcoal more effectively than the aliphatic hydrocarbons (7). The extent of distortion of the molar distribution of adsorbed hydrocarbons is controlled by the strength of interaction of each hydrocarbon with the surface upon physical adsorption, as expressed in Polanyi's theory of adsorption (8–10). The hydrocarbon molecules are physically adsorbed to the activated charcoal primarily through London dispersion forces (11). The strength of dispersion interactions is proportional to the square of the molecular polarizability, α^2 . The molecular polarizability has been used in several quantitative structure-activity relationships for the prediction of hydrocarbon adsorption properties on activated carbon (12–14). The data in Fig. 4c demonstrates that the distribution of hydrocarbons recovered from 12.6 mm², 33.2 mm² and 99.0 mm² size activated charcoal strips in a container spiked with 24 μL of equimolar hydrocarbon mix were the same for each size carbon strip. Under the experimental conditions, there is sufficient hydrocarbon present to saturate each piece of carbon, and the entire 24 μL container spike is in the vapor phase. The molar quantities adsorbed are a small fraction of the total hydrocarbon load and therefore the molar ratios of the vapor phase hydrocarbons remain approximately equimolar. Under these conditions, the adsorbed mole fraction of each hydrocarbon becomes a linear function of the square of the molecular polarizability, as shown in Fig. 10 ($n = 9$, $r = 0.998$).

The profound effects of vapor phase concentration and adsorbent saturation on the resulting chromatographic profile is demonstrated

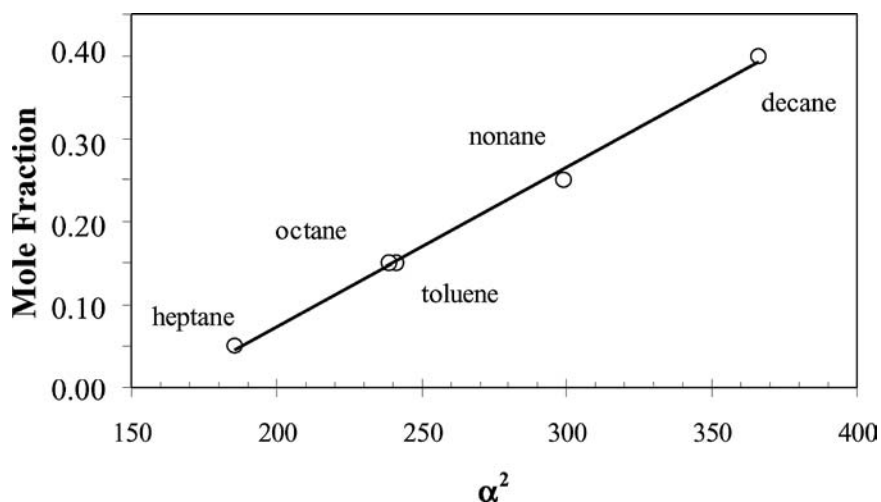


FIG. 10—The mole fraction of adsorbed hydrocarbon on activated charcoal is plotted as a function of the square of the molecular polarizability (α^2) for a 24 μL spike volume, sampled on a 99 mm^2 carbon strip (data from Fig. 4c).

in Figs. 6 and 7 for a sample of gasoline spiked in volumes of 12, 96, and 720 μL in place of the hydrocarbon mix. When the spiked volume of gasoline was very low, the activated charcoal surface was not saturated and no distortion was observed. However, when the concentration was raised to the point where the carbon was saturated, significant distortion occurred and the resulting chromatogram resembled that of a 75% weathered gasoline sample.

The volume of ignitable liquid contained in a fire debris sample is an uncontrolled parameter. Although the effect of hydrocarbon adsorption on the debris is not well studied, results from preliminary experiments with an unweathered gasoline sample spiked onto carpet padding are shown in Fig. 8a. The 99.0 mm^2 activated charcoal strip was saturated with hydrocarbon, resulting in displacement of the less volatile components to yield a chromatographic profile resembling that of 75% weathered gasoline (see Fig. 8a). The result is identical to results acquired by placing the spike into the container insert (see Fig. 7a for comparison). In the case of a carpet/carpet-padding debris sample, the presence of the debris in the container did not significantly influence the chromatographic profile.

The results presented in this paper suggest two possible approaches for overcoming the inherent problem of distortion in activated charcoal sampling: (1) maximize the carbon strip size or (2) limit the sample size. The approach of increasing the carbon strip size appears to be an unworkable solution given the high cost of activated charcoal strips and the indeterminate amount of hydrocarbon in the total sample. Despite the high surface area of the activated charcoal, a 99.0 mm^2 size piece is readily saturated at a very low hydrocarbon load in the container (see Fig. 6b). The alternative approach of limiting the sample size is complicated by the heterogeneous nature of a fire debris sample. Figure 8b demonstrates that this problem may be overcome by first heating the sample, to achieve an even distribution of hydrocarbons in the container, before a sub-sample is removed. The two sub-samples taken from the sample of gasoline on carpet and carpet-padding yielded chromatographic profiles that resemble the unweathered gasoline used to spike the container. By heating the container and cooling it back to room temperature prior to taking a sub-sample, the hydrocarbon components were uniformly distributed in the container. The sub-sample contained a representative fraction of the original sample, in a quantity that did not saturate the activated carbon, and therefore resulting in an undistorted chromatographic profile. Fur-

ther work in our laboratory is focused on determining the recovery of hydrocarbons from common building materials for the purpose of sub-sample collection from fire debris evidence.

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