

Volatiles from carpet: a source of frequent misinterpretation in arson analysis

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Abstract

Carpet and carpet padding are frequently submitted to laboratories for the analysis of residual accelerant in suspect arson cases. Charring and pyrolysis of the above matrixes produces volatiles that can cause interferences with some accelerants, most notably gasoline. A study was conducted to evaluate the interference potential of pyrolysis products obtained from simulated fire debris samples and from samples collected in the field. It was found that variable amounts of alkylbenzenes and naphthalenes are produced, along with large quantities of styrene and alkylstyrenes. Small amounts of higher-molecular-mass aromatic hydrocarbons are also generated but no alkanes or alkenes appeared.

Since aromatic hydrocarbons are the major diagnostic components in gasoline, a potential interference is indicated. Careful observation of patterns within each group of isomers is required to rule out interferences. The distribution of alkylbenzenes in gasoline is quite different from the patterns produced by pyrolysis. Guidelines are proposed to distinguish between petroleum-based aromatic hydrocarbons and those derived from the pyrolysis of carpet/carpet padding. Mass fragmentography was found to be particularly useful toward the discrimination of interferences.

1. Introduction

Chemical analysis of residual accelerant in fire debris is an important investigative tool to determine whether a fire loss can be attributed to natural causes, such as malfunctioning electrical circuits, or is incendiary in nature [1]. One of the tasks of an arson investigator is to examine burn patterns at the fire scene and secure debris samples for later chemical analysis [2]. Among the many materials that can be collected for testing, carpet and carpet padding represent an almost ideal choice from an arson investigator's point of view. Carpet is widely encountered at the fire scene because most modern homes are furnished with carpeting. It is common practice in the building industry to install carpet on

padding to provide additional insulation and improve comfort. Since most incendiary fires are started by pouring a petroleum-based liquid along the walls of a structure, there is a good possibility of locating a burn pattern on carpet. The favorable adsorptive properties of carpet and carpet padding make them good candidates for the preservation of residual accelerant. One needs to keep in mind that combustion under such conditions is a gas-phase process that only involves the vapor above the solid. A trace of an accelerant that has deeply penetrated into the matrix may remain in recoverable quantities, even after a severe fire.

It is not surprising that approximately two-thirds of all samples submitted for chemical analysis consist of carpet/carpet padding or, at

least, contain some of these matrixes [3]. From a chemist's point of view, carpet/carpet padding has a number of disadvantages. Modern carpets generally are composed of synthetic fibers, such as nylon, that are attached to a support consisting of a polypropylene copolymer. Carpet padding is usually composed of a synthetic rubber that sometimes contains fiber for added strength. When heated to a temperature where pyrolysis takes place, a variety of products are generated from the polymers. In contrast to other building materials such as sheet rock, wood and tile, carpet and carpet padding produce copious amounts of volatiles. Combustion studies indicate that carpet padding does not generate hydrocarbons that can be confused with petroleum-based products [4]. The fiber in carpet does not produce significant amounts of hydrocarbons but the carpet backing is a rich source for alkylbenzenes and similar compounds. Aromatic hydrocarbons, including benzene, toluene, ethylbenzene, styrene, and alkylstyrenes have been identified in charred carpet [5–7].

Accelerant analysis is commonly carried out by comparing the gas chromatographic (GC) profile from a sample to chromatograms from standards [8]. Most laboratory analysts keep a library of chromatograms from petroleum-based fuels at hand. Results from round robin tests involving charred carpet show that isolation of residual accelerant and separation of isolated volatiles by GC do not seem to present problems. Serious errors however may occur in the interpretation of chromatographic data. Approximately 10% of all laboratories participating in a large-scale study reported an accelerant in charred carpet which did not contain a flammable substance [9]. In most cases gasoline was reported. This is obviously a very serious error. The situation is compounded because gasoline is the most frequently used accelerant in incendiary fires [10,11].

Gasoline is relatively difficult to recognize in a chromatogram. In contrast to many other accelerant types such as kerosene, gasoline does not produce a pattern of equidistant peaks. A further complication arises from exposure to heat and other environmental factors. While the effects of partial evaporation are easily compen-

sated for in accelerants that are dominated by *n*-alkanes, chromatographic patterns for highly evaporated gasoline are much more difficult to recognize [12]. Only 70% of some 120 laboratories supplied with a 95% evaporated gasoline were able to correctly interpret the chromatographic profile [9]. The variable contribution from different matrixes make analysis of petroleum-based accelerants particularly difficult. In most laboratories, capillary column GC with flame ionization detection is the standard method. This will probably change in the not too distant future. With the large scale introduction of benchtop mass spectrometers, GC-MS is becoming increasingly accepted, even in small laboratories.

Mass fragmentography is an effective method for the reduction of chemical interferences [13]. Petroleum-based fuels contain a large number of individual compounds. Fortunately, the bulk of these substances falls into only a few categories [14–16]. Mass fragments can be assigned that are common to individual categories, *i.e.*, *m/z* 57, 71, etc. represent alkanes. Examination of mass fragmentograms representing alkylbenzenes shows that carpets produce several of the compounds that are diagnostic indicators for petroleum-based fluids, in particular of gasoline.

In this study, we report on the generation of some alkylbenzene isomers originating from the combustion of carpet/carpet padding. Results from simulated arson samples and from samples obtained in the field are presented. Guidelines are proposed to distinguish alkylbenzenes originating from the pyrolysis of carpet/carpet padding to those found in petroleum-based fluids.

2. Experimental

Carpet and carpet padding for the control experiments were obtained from local sources. Actual arson samples were also processed [17]. The carpet and carpet padding in the control experiments were placed in one-gallon (*ca.* 3.6 l) paint cans and charred on a Bunsen burner under a variety of conditions. In some experiments, charring was extensive to simulate the

effects of a burnout. In others, fires were extinguished by dousing with water or by oxygen starvation. Unburned carpets, both used and fresh from the shelf, were also investigated. Volatiles were collected by a heated headspace method using a scaled down version of conventional charcoal adsorption/ CS_2 extraction [18]. Sample extracts were analyzed by GC–MS on a standard benchtop instrument (MSD 5970A, Hewlett-Packard, Avondale, PA, USA). A standard fused-silica capillary, 25 m \times 0.21 mm, coated with a 0.33- μm film of methylpolysiloxane was used under temperature-programmed conditions. Data were examined after manual extraction of ion chromatograms as well as by automated data processing [8,13].

3. Results and discussion

Interpretation of chromatographic data from fire debris remains one of the most difficult and ill-defined steps in the analysis of accelerants from suspect arson samples. Interpretation is commonly carried out by visual inspection of chromatograms. The analyst attempts to visually extract an accelerant pattern from the target sample. This is a manual process in which the chromatographic profile from the sample is compared to profiles from a series of accelerant standards. The major difficulties in interpretation originate from the contributions of extraneous components and from changes in accelerant profiles due to environmental factors. Chromatographic resolution, ratio of interferences to accelerant, and methods of chromatogram comparison influence the outcome, to various degrees [12]. A mass spectrometer can be used as a tunable detector to suppress chemical noise from the matrix. The combination of retention data and mass spectral selectivity greatly improves the level of confidence but it can only work if the components generated from pyrolysis differ in mass spectral response characteristics from those produced from the analyte. It is a manual process where the analyst attempts to visually extract an accelerant pattern from a suspect sample and correlate it to a standard. The major difficulties in interpretation originate from the contribu-

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Fig. 1 shows the total ion chromatograms of charred carpet/carpet padding before and after spiking with a small amount of partially evaporated gasoline. The corresponding gasoline standard is also shown. It is evident that charred carpet contains only a few of the substances found in gasoline. Due to the high level of interferences from pyrolysis products, it is quite impossible to recognize a gasoline pattern in the simulated arson sample. Large amounts of styrene and methylstyrenes suppress the chromatogram scale and many of the substances from the background coelute with the compounds of

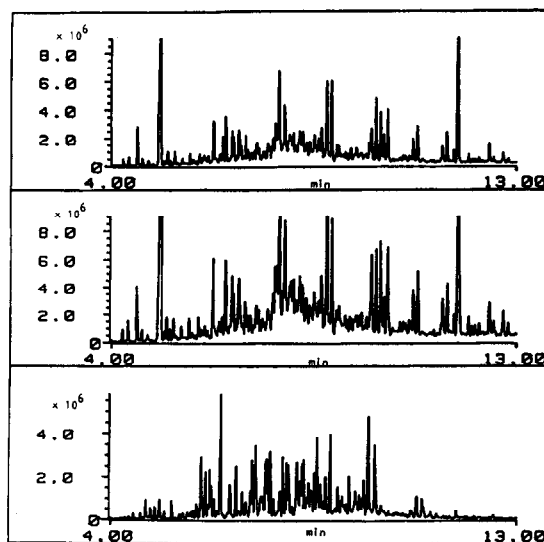


Fig. 1. Total ion chromatograms. Bottom: 50% evaporated gasoline standard; middle: burned carpet/carpet padding, spiked with a small amount of the evaporated gasoline standard; top: burned carpet/carpet padding matrix.

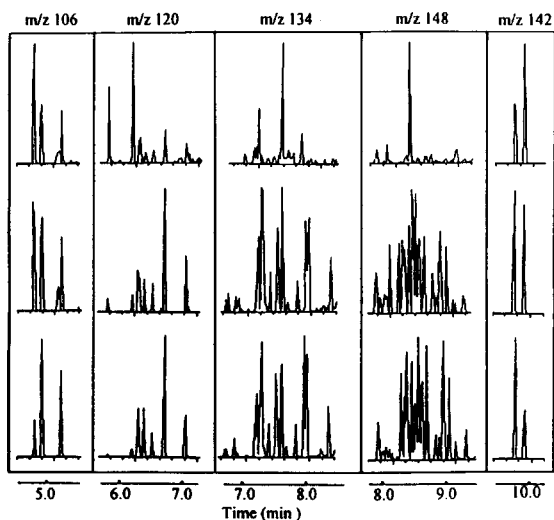


Fig. 2. Selected ion chromatograms of the samples from Fig. 1. m/z 106, 120, 134 and 148 are C_2 – C_5 alkylbenzenes, and m/z 142 are methylnaphthalenes.

interest. The major peak at the beginning of the matrix and spiked matrix chromatograms represents styrene. Fig. 2 represents several extracted ion chromatograms from Fig. 1. For brevity, only a few of the target components are shown. The sequence of chromatograms is the same as in Fig. 1. Gasoline contains only small amounts of styrenes whereas this substance class constitutes the major compounds in charred carpet. Fragments m/z 106, 120, 134, 148 and 142 are indicative of C_2 – C_5 alkylbenzenes and of the two methylnaphthalene isomers. These substances are considered primary indicators of highly evaporated gasoline. Examination of the fragments shows that the ion profiles between gasoline and charred carpet differ significantly. It can be seen that the matrix contains small amounts of aromatic hydrocarbons. In the charred carpet, one isomer usually dominates in each group. In some cases, more than one isomer may be generated during combustion but the ratio of isomers within a group is always distorted and different from gasoline. Distortions are particularly noticeable in the xylene isomer group where ethylbenzene is often larger than the other isomer. The spiked ion chromatograms show that the characteristic ions for gasoline are pres-

ent but additional peaks have appeared. Different carpets do not always produce the same interferences. The number of isomers generated by pyrolysis is relatively small. Carpets also produce naphthalene and methylnaphthalenes. The generation of naphthalene is particularly noteworthy. It seems to be correlated to styrene. When styrene is present in large amounts, a large naphthalene peak usually is also visible. The 2-methylnaphthalene isomers are also affected. The ratio between the two methylnaphthalene isomers is about 1:0.5 in favor of the 2-methylnaphthalene isomer which elutes first on a non-polar column. In carpet pyrolysate, these ratios are often reversed and the 1-methylnaphthalene peak is often larger than the 2-methylnaphthalene peak. In contrast, isomer distributions in petroleum-based products are highly reproducible. It should be noted that the diagnostic components of gasoline are also contained in small amounts in straight-run distillates, such as mineral spirits, kerosene and fuel oils. Even though these fuels have significantly different boiling point ranges and physical properties, chromatographic patterns of alkylbenzenes are highly reproducible and resemble those found in gasoline [13]. Peak ratios among each isomer group vary little, even for partially evaporated fuels. A pattern recognition process can, therefore, be instituted that takes into consideration the contributions from pyrolysis products.

The question of “false positives” in accelerant analysis is a matter of continuous discussion in the community of laboratory analysts. The data from this study indicate that some accelerant type compounds can be generated from pyrolysis of carpet/carpet padding but profiles consistent with accelerants are not produced unless the accelerant is already present in the matrix or is adsorbed on the matrix. Under conditions of very high sensitivity, virgin carpet can produce a discernable amount of petroleum-type hydrocarbons. These are likely left over from production or are simply absorbed on the surface [19]. The chemist should always be cautious when the fire debris contains newly manufactured materials. Extraneous contributions from petroleum-based products are a very serious source of interfer-

ences. Treatment of carpets with materials containing a petroleum base, such as a water-proofing agent or an insect spray can generate profiles consistent with gasoline. Interferences due to adsorption from air can easily be dealt with by adjustment of a proper threshold level. Unfortunately, it is far more difficult to eliminate potential artifacts from the second source. It is not possible to reproduce the pyrolysis conditions of a fire in the laboratory. So called control samples are meaningless for background evaluation [20]. Only vigilance on part of both the fire investigator and chemist can minimize such problems.

4. Conclusions

Data from simulated arson samples and from a field study show that the pyrolysis of carpet/carpet padding generates a small number of aromatic hydrocarbons. Even in the presence of these interferences, gasoline can be recognized by setting thresholds for the ratios of the components constituting the various isomer groups. The presence of large amounts of styrene and methylstyrenes always indicates pyrolysis and special caution must be exercised in data interpretation of such cases.

5. References

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