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Comparison of Automotive Gasolines Using Capillary Gas Chromatography II: Limitations of Automotive Gasoline Comparisons in Casework

REFERENCE: Mann, D. C., "Comparison of Automotive Gasolines Using Capillary Gas Chromatography II: Limitations of Automotive Gasoline Comparisons in Casework," *Journal of Forensic Sciences*, JFSCA, Vol. 32, No. 3, May 1987, pp. 616-628.

ABSTRACT: When comparing gasoline recovered from a fire scene with a possible source, several factors must be considered, including the variability introduced by the recovery method, possible contamination of the data by pyrolysis products, distortion of the data as a result of evaporation of the gasoline, and other alterations of the recovered gasoline by chemical and physical interactions. All of these factors can contribute to a decrease in the specificity of comparisons of gasoline recovered from fire debris relative to liquid gasoline comparisons.

KEYWORDS: criminalistics, arson, gasoline, comparative analysis, chromatographic analysis

It has been shown that liquid gasoline comparisons can be made highly specific by making full use of the capabilities of temperature programmed capillary gas chromatography [1]. However, when the comparison methods are applied to the practical world of arson investigation, several additional factors must be recognized for the comparison method to remain useful. Although these additional factors decrease the specificity of the comparison, the method is still a valuable tool in arson investigation.

Recovery Methods

Before identifying gasoline in fire debris, it must first be recovered, usually by static headspace, dynamic headspace, distillation, and solvent extraction. In general, these recovery techniques are efficient at recovering the accelerant from the fire debris. The methods are reproducible enough to classify dependably the recovered product in terms of boiling point range, aromatic versus aliphatic content, and dominant component presence versus minor component presence. However, when these recovery methods are to be used for the comparison of products which are very closely related (as in Phase III of the study presented in Ref 1), the analyst is concerned about the slightest alteration of the original accelerant by the recovery method. It is desirable to use a method which can recover the accelerant in an unaltered form. At the very minimum, the recovery method used must be reproducible; that is, any changes the method causes in a product recovered from a debris sample should be reproduced in the liquid product when analyzed directly.

Received for publication 25 April 1986; revised manuscript received 14 July 1986; accepted for publication 16 July 1986.

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By extensive study of the static headspace method in this laboratory we have shown that gasoline could be recovered using a heated headspace method with essentially no alteration of the original gasoline. Variation of the gas chromatographic peak ratios of gasoline using heated headspace is of the same magnitude as the variation of the ratios of gasoline when injected neat.

Solvent extraction recovery is not compatible with the comparison method for gasoline. The solvent peak and solvent impurities (even with some nonhydrocarbon solvents) can interfere with the alkylate region of gasoline which provides most of the individualizing information.

Dynamic headspace methods have not been studied extensively in this laboratory. However, two extra steps relative to the static headspace method, the absorption and desorption of the accelerant on the solid medium, increase the chance of alteration of the original product. Volatile compounds are not held efficiently by the solid medium and can be revolatilized off the media during the trapping period. This can lead to a skewed result, with an apparent loss of the "light" end of a suspected accelerant. The portion of automotive gasoline which is most useful for comparison is volatile and may be susceptible to this revolatilization. Experience also indicates that the gasoline comparisons using samples containing extremely low levels of the alkylates are not as accurate as a result of the decreasing ability to accurately and reproducibly recover these compounds as their concentration decreases. The optimum minimum quantity required for comparison is within the range easily detectable using static headspace recovery techniques.

Steam distillation has also not been studied extensively in this laboratory. Dynamic headspace and steam distillation could possibly be used when doing comparisons if the reproducibility of the methods can be demonstrated. The time required to prepare a single sample, however, is much greater than for static headspace, and the benefits of these two recovery methods are not clear in cases where a comparison is to be performed.

Evaporation

Evaporative losses from a gasoline are present whenever it is in a fire or exposed to the environment. These losses are neither linear nor constant throughout the vapor pressure range present in gasoline. Those compounds with larger vapor pressures are lost faster than those with smaller vapor pressures. The change in the profile of gasoline with evaporation is illustrated in Fig. 1. It can be seen that the region most useful for the comparison with a second gasoline is altered before the gasoline is 40 to 60% evaporated by weight. Once this region is lost through evaporation, the comparison becomes much less specific and little can be said about possible common origin based on the hydrocarbon content. However, the loss of this region does not always prevent the determination that two samples have different origins.

Losses caused by evaporation need to be compensated for to extend the usefulness of the comparison method. This can be accomplished by dividing the alkylate region of the chromatogram into several narrow intervals. Evaporative losses within any of these now restricted intervals should be fairly constant as a result of the similarity of the vapor pressures of the compounds within any one interval. (This is true only if the elution is performed on a nonpolar column where the elution sequence reflects the differences in the boiling points of the compounds.) This principle is illustrated in Fig. 1. In the unevaporated chromatogram, Peaks A, B, C, and D are in an approximate one-to-one ratio. In the 40% evaporated chromatogram, the ratios for the same four peaks are no longer one to one. However, comparison of the ratios of peaks with approximately the same vapor pressures (in this illustration, A to B and C to D) yield results which are still approximately in the ratio of one to one. As evaporation continues, the ratios exhibit more variation relative to the unevaporated chromatogram even when considering only narrow chromatographic intervals. Eventually, there re-

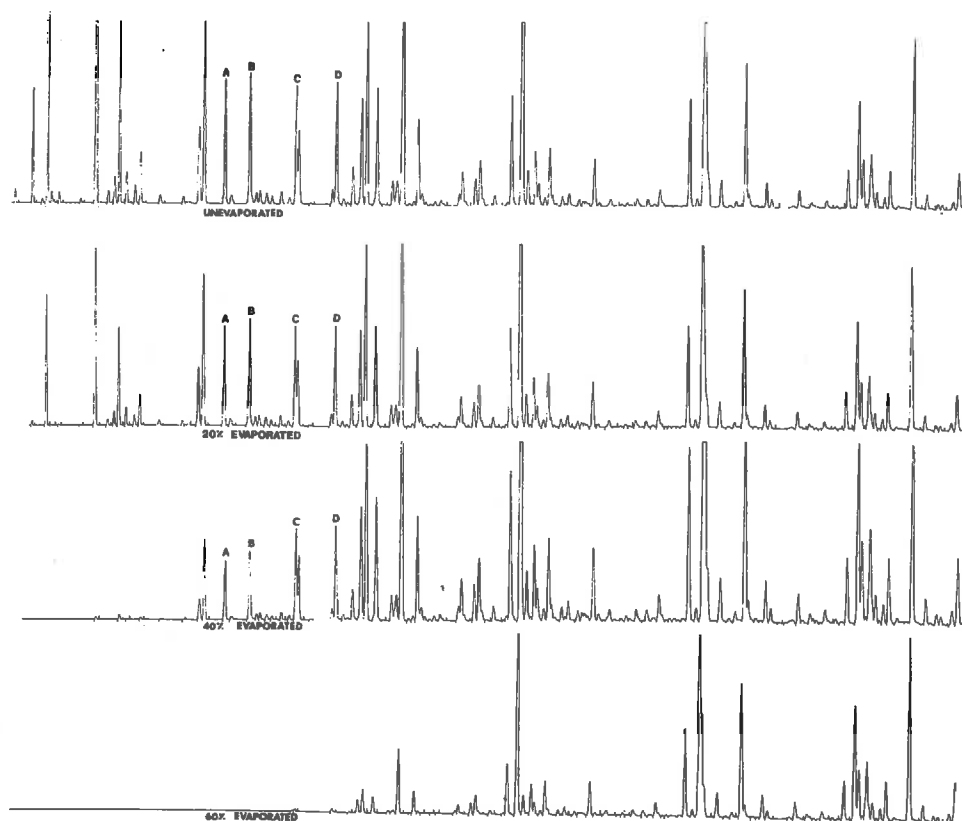


FIG. 1—Alteration of gasoline subjected to evaporation. Evaporative losses are calculated by weight. The left half of the chromatogram (the alkylate region) is the most useful region for a specific comparison.

mains insufficient information within the alkylate region to derive a meaningful conclusion regarding common origin. The graphic representation of case data in Fig. 7 shows the effects of normalizing over a restricted interval as opposed to comparing the alkylate region in two halves, as was done with liquid gasoline comparisons.

Gasolines which are less than approximately 50% evaporated can be recovered from fire debris more frequently than one might expect. Evaluation of all flammable liquid cases received in our laboratory in 1984 revealed that of the approximately 250 cases received, a gasoline suitable for comparison using the alkylate region was recovered in over 70 cases. Approximately 20% of these cases had a liquid control gasoline submitted which was independently linked to an individual through direct possession, fingerprints, or eyewitness accounts.

Pyrolysis Addition

Comparison of the relative ratios of components found in two gasoline samples is valid if the components are due only to the gasoline and not to some outside source. Figure 2 illustrates the products produced by pyrolysis of three materials commonly found in fire debris. The alkylate region of gasoline elutes in an interval free of most of these pyrolysis products. Benzene is one of two components identified within this window which is commonly associ-

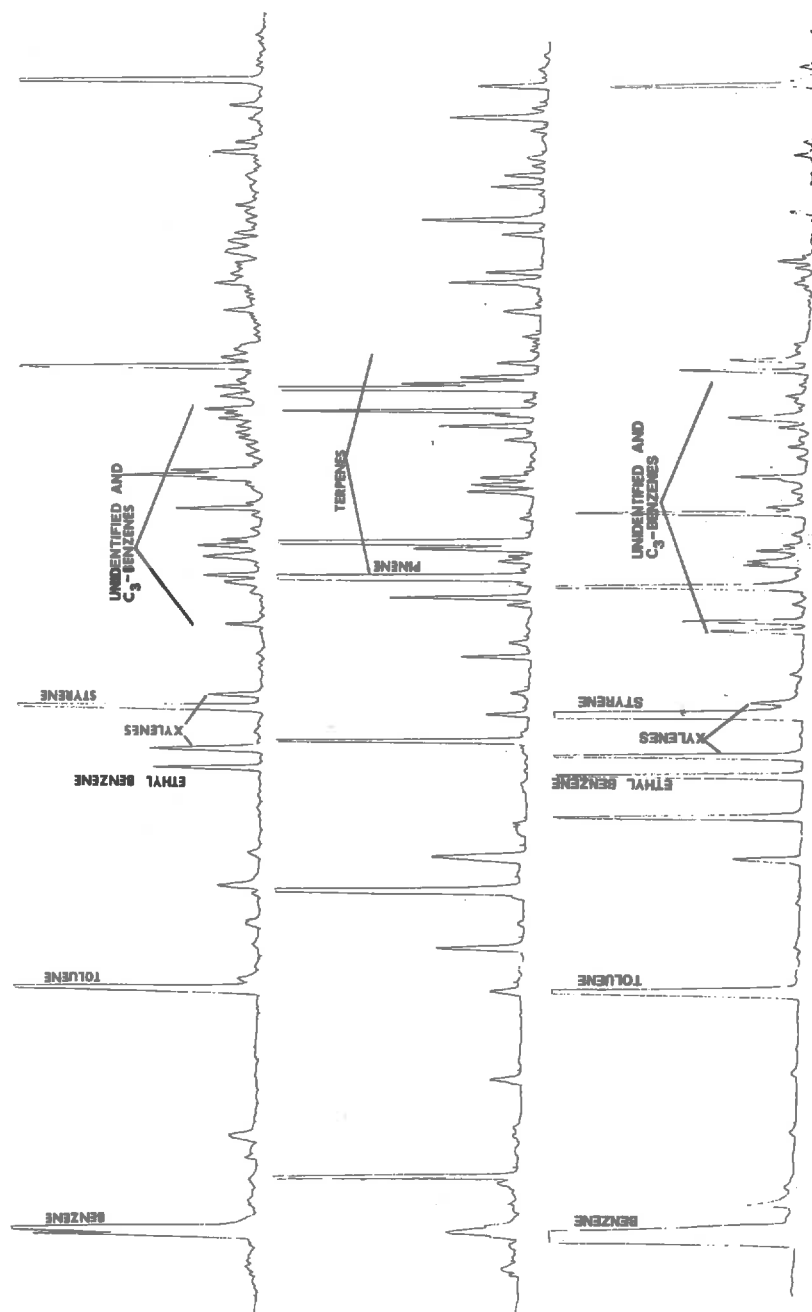


FIG. 2.—Comparison of common products of pyrolysis from nylon carpet (a), fir wood (b), and polystyrene (c). Note relative lack of products eluting before toluene (in the alkylate region).

ated with pyrolysis. For this reason, benzene is never used when comparing a gasoline recovered from fire debris to a control gasoline.

Many of the pyrolysis products from synthetic carpets and polystyrene (as well as numerous other synthetic materials) are the same aromatic compounds found in gasoline [2]. Therefore, aromatic compounds in general should not be used in the comparison except perhaps when two liquid gasolines are compared. Styrene is not present in appreciable quantities in uncontaminated gasolines, but is a major product produced in the pyrolysis of many synthetic materials. Its presence can be used as a flag to indicate pyrolysis addition in fire debris.

Other materials, wood in particular, produce nonhydrocarbon pyrolysis products which elute in the *n*-octane to *n*-decane region of gasoline. This potential pyrolytic interference does not eliminate the comparison potential of recovered gasolines since most individualizing information is contained in the relatively contaminant-free alkylate region (*n*-pentane to *n*-octane).

Microbial Degradation

Soil has been shown to be a very good retentive media for gasoline relative to wood and carpet [3]. However, bacteria in the soil may use available hydrocarbons as a food source [4,5]. It has been demonstrated in our laboratory that gasoline can be quickly altered when added to garden soil with a high organic content. Preliminary results have shown that the aromatics and straight chain paraffins are consumed first by the bacteria. The last and least affected compounds are the highly branched, saturated hydrocarbons (Fig. 3). Gasoline recovered from soils (and other media with a potential for high concentrations of bacteria) should be examined closely before an attempt is made to compare it to a control gasoline.

Case Examples

Case I

A fire was discovered in an abandoned house and was quickly extinguished. Fire investigators determined the origin of the fire and collected a carpet sample from that location. Investigation outside yielded a gas can laying on its side in the yard. The can, soil under the can, and the carpet samples were submitted to the laboratory for analysis. Figure 4 illustrates the results of the heated headspace analysis. The gasoline recovered from the can shows little evaporation. The gasoline recovered from the carpet is approximately 30 to 40% evaporated; therefore, comparison of the liquid control to the carpet sample should be done in small increments throughout the alkylate range. Good agreement can be seen between the two samples with the exception that Peak "A" in the carpet sample is larger relative to the same peak in the gasoline control. This peak is benzene and is an expected pyrolysis addition product from the burned carpet. The degree of similarity between these samples leads to the conclusion that the gasoline recovered from the carpet could have come from the can.

The gasoline recovered from the soil is presumably the same gas as in the can. However, the gasoline in the soil sample shows evaporative alteration as well as probable microbial degradation. The gasoline recovered from the soil has been so severely altered that little can be concluded regarding possible origin based solely on the volatile hydrocarbon composition.

Case II

The fire started at 2 a.m. in the garage and spread quickly to the adjoining house where a family of five was asleep. There were no injuries, but approximately \$200 000 in damage was

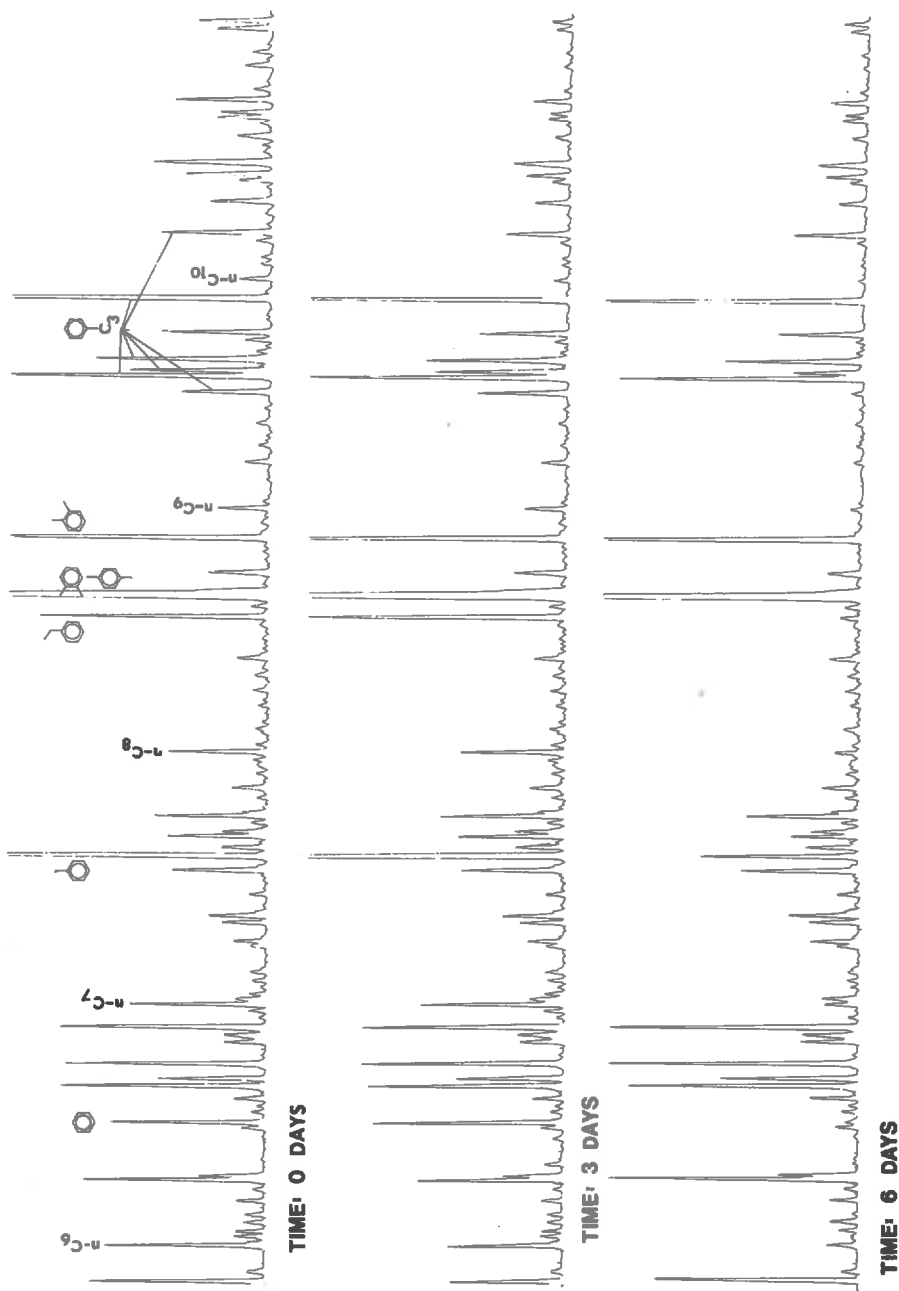


FIG. 3—Effect of bacterial action on gasoline added to a soil with a high organic content.

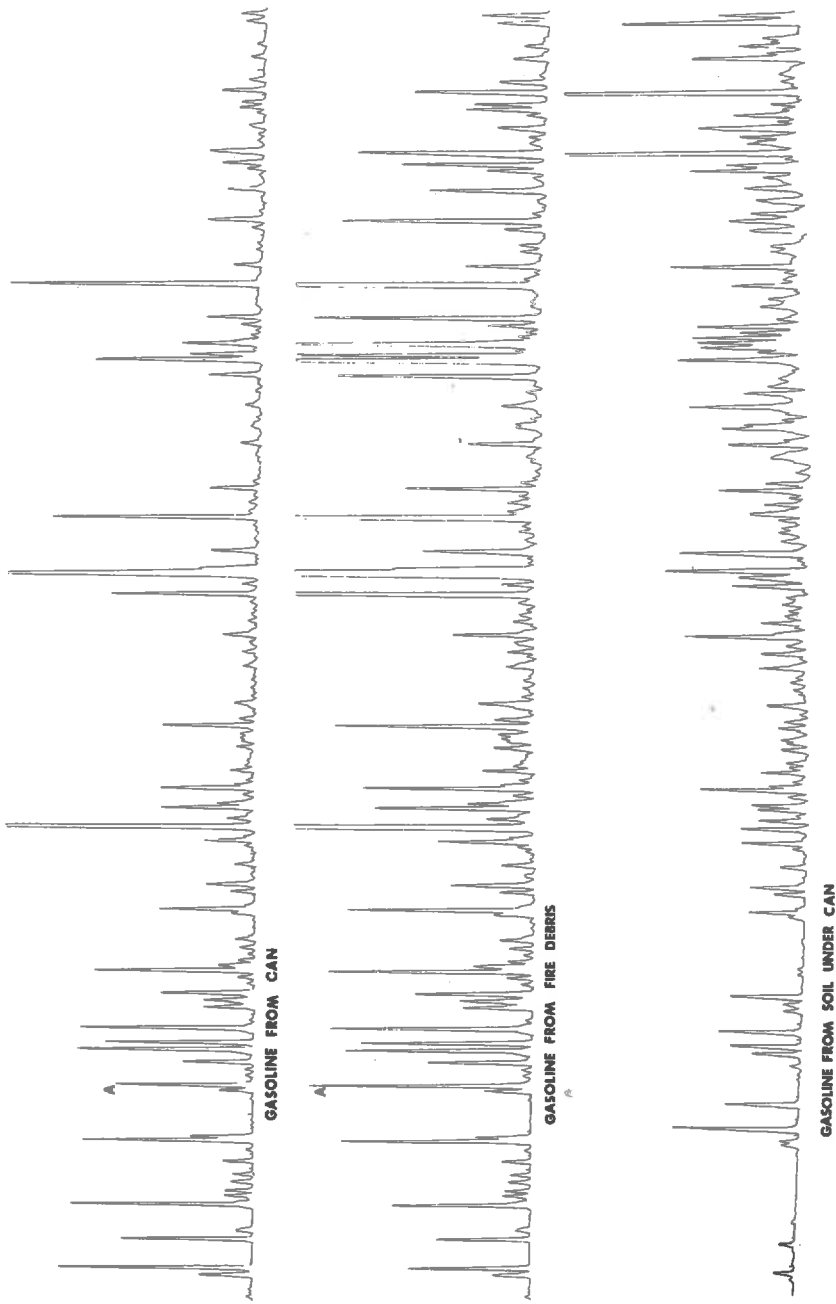


FIG. 4—Comparison of gasolines recovered at the scene of an arson fire. Note distortion of the gasoline recovered from the soil sample relative to what was in the can. All were recovered using heated headspace methods.

done to the structure. The fire investigation unit pinpointed the origin of the blaze in a bundle of gasoline soaked newspapers. Samples from the interior of this bundle were taken as evidence. Gasoline from the Alfa Romeo parked in the garage was also collected. A suspect was almost immediately developed. The trunk of his automobile was searched the next morning and two partially filled gasoline cans and an "empty" jar with an attached lid were collected as evidence.

Heated headspace test results for the four samples involved in this case are illustrated in Figs. 5 and 6. It is apparent that the three liquid gasolines are different from each other and that two of the liquid gasolines can be easily distinguished from the gasoline recovered from the newspapers. The gasoline recovered from the interior of the bundle of newspapers has undergone little evaporation and there is no pyrolysis addition. The gasoline in the 1-gal (4-L) can from the trunk of the suspect's automobile is very similar to the gasoline recovered from the newspaper bundle.

The "empty" glass jar contained traces of a partially evaporated gasoline. This gasoline is compared with the gasoline recovered from the bundle of newspapers and to the liquid gasoline from the 1-gal (4-L) can in Fig. 7. The top graph depicts the comparison of the three samples using one reference compound (Peak 9). The effects of evaporation are readily visible in the gasolines from the jar and newspapers relative to the gasoline in the 1-gal (4-L) can. (The gasoline remaining in the jar is more evaporated than in the newspapers, and both are evaporated relative to the liquid gasoline.) As the vapor pressures of the individual normalized components increase to approximate the vapor pressure of the first reference compound (Peak 9), the comparison becomes more accurate.

The bottom graph depicts the same samples after compensating as much as possible for evaporation. In this comparison, the area of each peak in the alkylate region was divided by the area of the next eluting peak (sequential peak normalization). Since the vapor pressures of the normalized component and the "floating" reference compound are very similar, the degree of evaporation of the two compounds should also be very similar. When compensation is made for evaporation in this manner, a strong correlation emerges between the gasolines in the three items.

In this case, one can conclude that the gasoline in the Alfa Romeo and in the 2.5-gal (9.5-L) can are definitely not the source for the gasoline recovered from the newspapers. The test results lead to the conclusion that the gasoline from the newspapers could have originated from the 1-gal (4-L) can. Additional knowledge of the history of the gasoline in the can (for example, was the can empty before filling, what was the source of the gasoline in the can, and so forth) can help to make the "could have" statement more specific.

Case III

The fire totally engulfed the home in which a family of eight was sleeping. Two of the children died in the fire; the remaining six suffered a variety of burns. The fire originated in the hallway in front of the bedrooms. Several layers of debris were isolated and sampled from this location. The next day, a search was made of the residence and automobile of the suspect. The search yielded a 2-gal (7.5-L) gas can containing a small amount of gasoline. The samples submitted to the laboratory included numerous fire debris samples, the 2-gal (7.5-L) gas can, gasoline samples from the victim's car and the suspect's car, and the three grades of gasoline available at three different stations from which the suspect regularly purchased gasoline.

Figure 8 illustrates the range of results obtained with the gasoline recovered from three of the debris samples, which were sampled in a layer fashion, as well as the gasoline from the 2-gal (7.5-L) can. Each was analyzed in duplicate. The range of the results for the debris

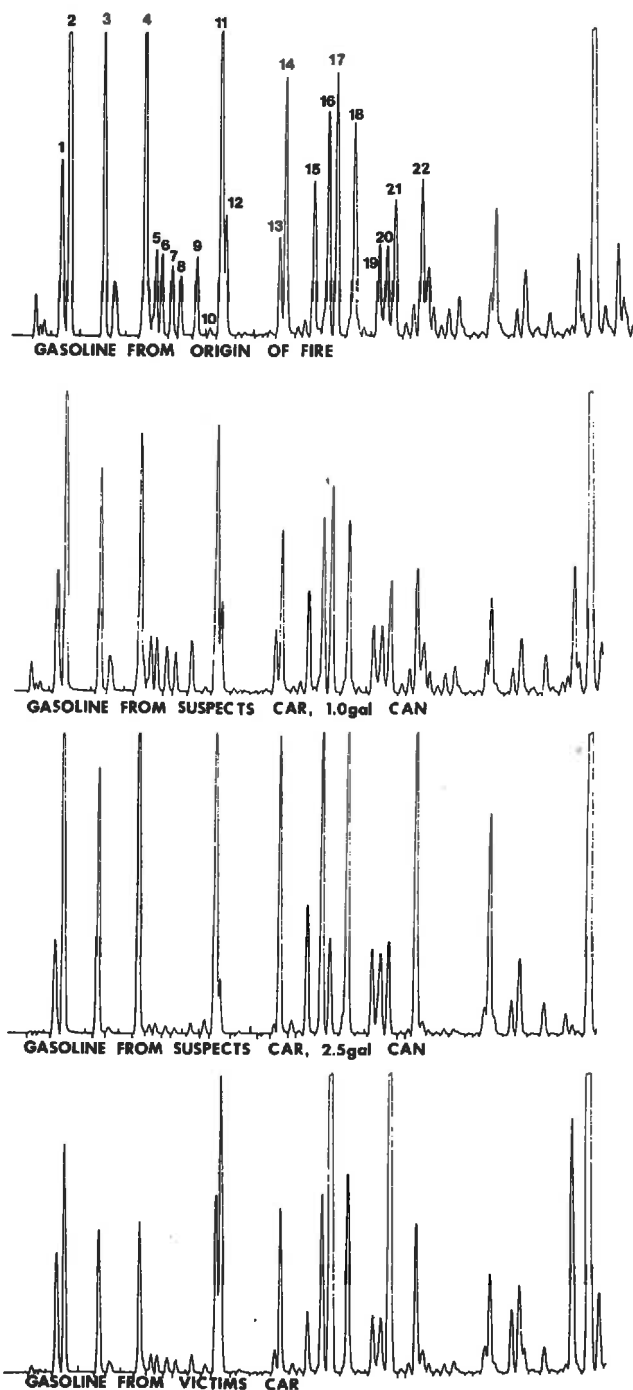


FIG. 5—Comparison of alkylate region of three liquid gasolines to gasoline recovered from fire debris. All were recovered using heated headspace methods.

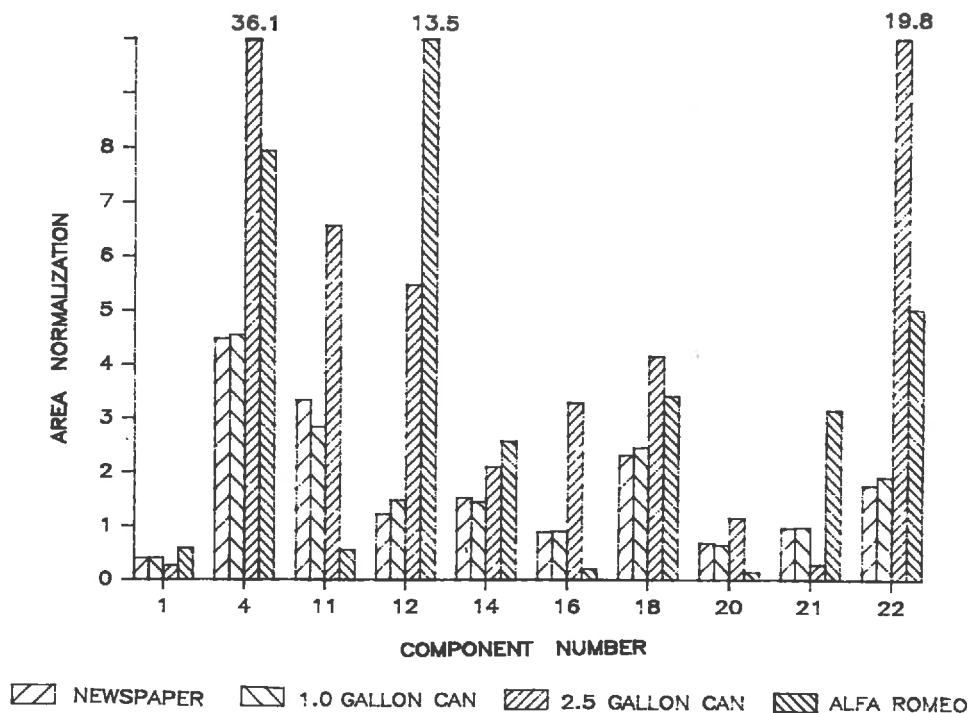


FIG. 6—Graphic representation of the gasolines illustrated in Fig. 5. Normalization is via a sequential peak ("floating") reference compound method (see text). Similar gasolines become readily apparent using this technique.

items is due to several factors, including the inherent variability of the comparison method, the variability as a result of the headspace recovery method, and the inability to compensate totally for the evaporation of the gasoline. Despite these limiting factors, a workable narrow range of results was developed. Test results from the 2-gal (7.5-L) can fall within the range established by the debris items. Of the eleven other liquid gasoline controls submitted for comparison, only one fell within the range of the debris samples and the gasoline in the 2-gal (7.5-L) can. (This gasoline is also depicted in Fig. 8.) The suspect claimed independently (without knowing the laboratory results) that he purchased the empty can the day before the fire and filled it with gasoline that same day because his car had run out of gas. He volunteered the source of the gasoline as an unleaded regular from a U.S.A. station, which was the one found to be similar.

Additional investigation of the distribution pattern of gasoline in the geographic area revealed that the gasoline from the U.S.A. station originated from a distributor approximately 150 miles (240 km) away and that that station was the only one in the area to use this distributor. Therefore, the gasoline was quite "rare" in the town and would not be expected to be duplicated as a random event.

The U.S.A. station received sequential shipments of unleaded gasoline the day before the purchase of gasoline by the suspect and the day after the fire. These unleaded gasolines were both provided by the same distributor from a single lot. The gasoline at the station was sampled two days after the fire by the detective. Although not indistinguishable (Fig. 8), the similarities between the two gasolines (from the suspect's can and from the U.S.A. station)

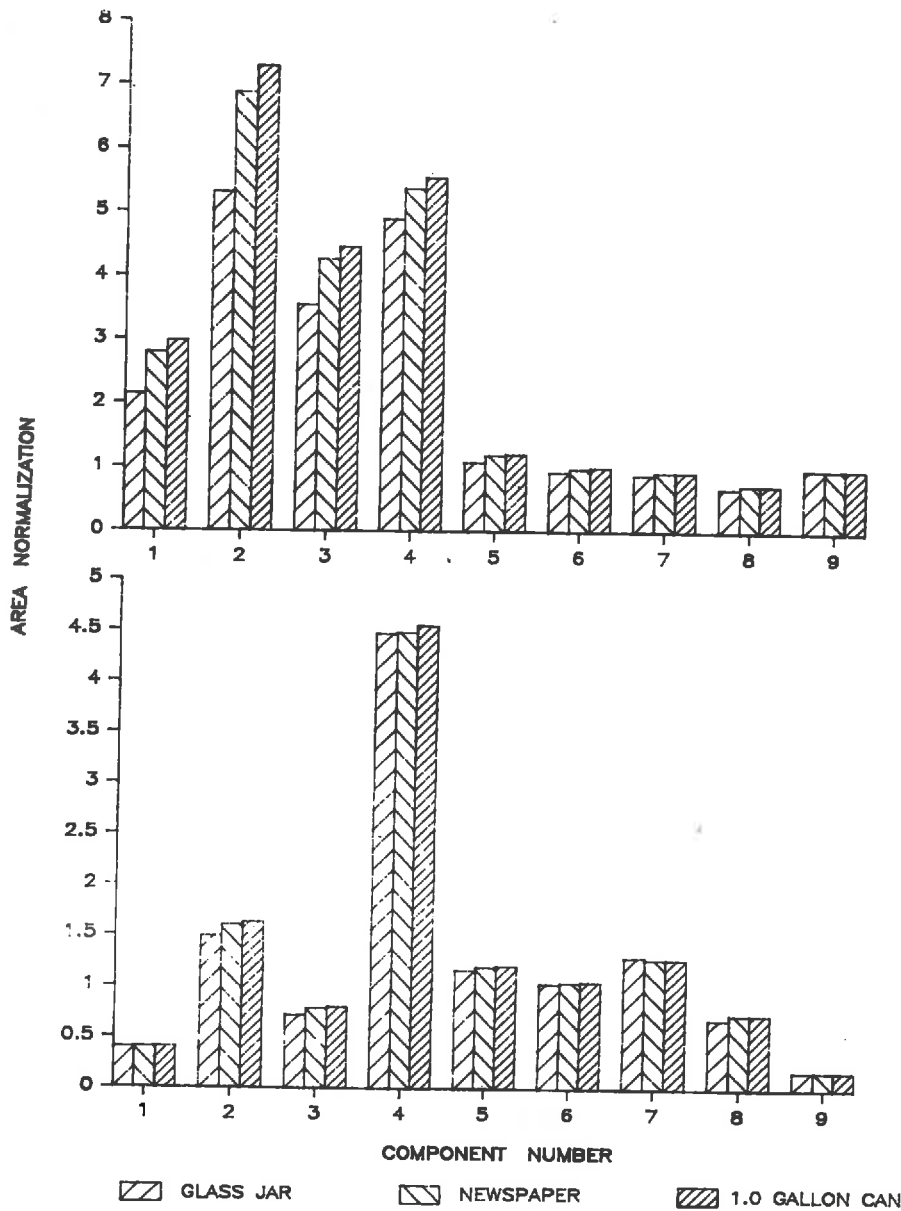


FIG. 7—Graphic comparison of gasolines recovered from the glass jar, the bundle of newspapers, and the 1-gal (4-L) can. (a) Two internal standards (the normalization to only one of these internal standards, Peak 9, is shown). (b) Sequential peak ("floating") normalization method.

correlate well with their histories. The same phenomenon was demonstrated in the study of sequential shipments of gasoline to a single station in [1].

Given the excellent correspondence between the gasolines, the uniqueness of this gasoline to the area, and the knowledge of the gasoline delivery schedule, the following conclusions were made. The gasolines from the fire scene and from the 2-gal (7.5-L) can probably originated from a single source; and the gasoline in the can could very well have come from the unleaded regular gasoline from the U.S.A. station.

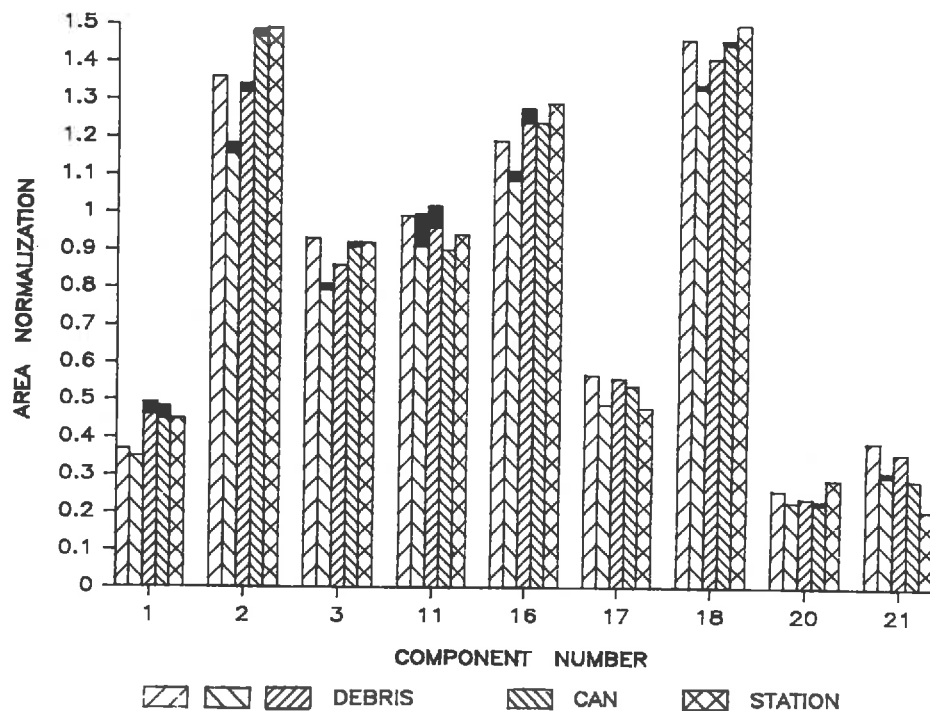


FIG. 8—Graphic representation of gasolines recovered from debris in a double homicide/fire scene (sampled in a layer fashion), and two control gasolines. Heated headspace was used to recover all samples. Solid tips on the individual bars represent the range calculated from duplicate analyses. Visually, the gasoline from the can falls within the range established by the debris items for all components except Number 2. Statistically, these cannot be distinguished at a level of significance of 0.05 [6]. The liquid gasolines from the can and from the U.S.A. station can be distinguished but resemble each other closely, as their histories suggest they should. None of the other liquid gasoline controls collected in this case resembled these two.

Conclusion

It was found that when properly modified, the gasoline comparison method outlined previously [1] is applicable to general casework. The primary detrimental factors to the comparison are evaporation and pyrolysis addition; however, recognition and compensation for both of these processes is possible. The method of recovery from the debris should also be carefully considered.

The comparison method is extremely useful in eliminating the possibility of common origin between two samples. It is much more difficult to determine conclusively that two samples have a common origin; this conclusion is beyond the ability of the comparison method by itself. It is very useful to have some idea of the variability of the population of gasolines potentially involved in the case, as this can increase the specificity of a comparison.

Experience shows that it is very effective to teach the jury (using a slide show) how the comparisons are made and demonstrate the results of studies and experiments using the comparison methods. The difficulty of obtaining a good correlation between two different gasolines as a random event is thus effectively illustrated. When the case results are shown, the jury can readily grasp the significance of the correlation and are able to understand the conclusions of the criminalist. Since the comparison method is somewhat subjective, a probability statement is not appropriate. This teaching method provides a mechanism whereby a probability statement is not necessary.

Acknowledgments

The author wishes to thank Dr. William Gresham, Ms. Robin Bussoletti, and Mr. Raymond Kasumi of the Washington State Patrol Crime Laboratory for their assistance and encouragement during the project. The author acknowledges L.E.A.A. for the grant enabling the purchase of the instruments used in this project.

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