

Dale C. Mann,¹ B.S.

Comparison of Automotive Gasolines Using Capillary Gas Chromatography I: Comparison Methodology

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ABSTRACT: Capillary gas chromatography was used to compare the relative concentrations of hydrocarbons in a variety of gasoline samples. It was found that most of the discriminating information is contained in the fraction with a volatility ranging from approximately *n*-pentane to *n*-octane. Using the described comparison method, all gasoline samples collected at random were easily distinguished. Gasolines with identical histories (from the same distributor and same lot), once added to a gasoline station residual, were also distinguishable, although not as readily as those samples obtained at random.

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

The types of physical evidence used to link a suspect to an arson scene include fingerprints, shoe impressions, toolmarks, ignition devices, glass, hairs, and fibers. However, because of the chaotic condition of fire scenes and the destructive nature of fire itself, these types of physical evidence are commonly destroyed or lost. In the experience of our laboratory, such evidence is infrequently collected by fire scene investigators.

Our laboratory began to search for additional types of physical evidence which may survive the fire scene. In most prosecuted arson cases, a flammable liquid is detected and identified in the fire debris. In addition to the debris items, a liquid control is frequently submitted with the request that the laboratory determine if it is the same type of product as that identified in the debris. In a case like this, there exists a potential two-step physical link between the fire scene and an individual. First, the link between the liquid and the individual must be established. This is usually the responsibility of the submitting agency and is accomplished by direct possession, fingerprints, and so forth. The second link, that between the liquid and the product recovered from the fire debris, is more difficult to make and is the responsibility of the laboratory. The variation of individual products within the pertinent general product classification must be determined before the attempt to establish this second link. The specificity of a proposed comparison method is demonstrated in the following studies using liquid gasolines purchased from local gasoline stations.

Gas chromatographic classification of liquid petroleum products is a well established technique [1-9]. Basic parameters used to distinguish different classes of products include

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¹Criminalist, Washington State Patrol Crime Laboratory, Seattle, WA.

boiling point range, aliphatic and aromatic hydrocarbon content, relative concentration of major versus minor components, and the presence of additives. Gas chromatography has also been used to compare liquid petroleum products within a given classification [10-13]. In these comparisons, the relative peak intensities are used to distinguish products containing the same components. Products with only a few components will not yield as much comparative information as products containing hundreds of components.

Automotive gasoline was selected as the petroleum product for comparison in this initial study for two reasons. First, evaluation of past casework and available standards revealed a larger variation and, therefore, a greater potential for differentiation among gasolines than among straight-run petroleum distillate products. Second, gasoline is the accelerant most often identified in arson casework in our laboratory. As such, a successful method of comparison for gasolines would have the greatest potential for application in casework.

Experimental Procedure

Instrumental Procedure

All analyses were performed on a Hewlett-Packard 5840A gas chromatograph operated at 50/1 or 250/1 split ratios. The column used was a nonpolar fused silica quartz column (J&W DB-1), 60 m long, 0.25-mm inside diameter and 1.0- μ m film thickness. Hydrogen was used as carrier gas at a linear velocity of approximately 45 cm/s. The oven was temperature programmed from 35° (2 min) to 260°C at 8°C/min. This combination of column and conditions allows good separation for hydrocarbons (permitting baseline separation of methane and ethane) while still permitting a short (approximately 25-min) analysis time for automotive gasoline. A fast chart speed (5 cm/min) was used to "spread" the data out for easier visual evaluation of the peaks heights and shapes (Fig. 1).

Comparison Mechanics

Evaluation of randomly acquired gasolines showed that different segments of the chromatogram produce different degrees of gasoline-to-gasoline variation (Fig. 2). The early eluting portion of gasoline (from *n*-butane to *n*-octane) shows much more variation than the latter portion (*n*-octane to *n*-dodecane). This difference in variation is due to the relative sensitivities of the types of compounds in the two regions to subtle changes in the refining parameters and blending processes² [14, 15]. Since the comparison of the gasolines in these studies was to be done manually, the number of components actually used for the comparison had to be reasonably small. Based on this initial evaluation, the chromatogram segment from approximately *n*-pentane to *n*-heptane was selected as the basis for the gasoline comparisons. This chromatogram segment contains approximately 22 major components, which makes the manual comparison feasible.

Two comparison mechanisms were employed in these exercises. The first was a simple qualitative method. In this method, two chromatograms, with the relevant peaks on scale and approximately the same size, are simply superimposed on a light box. Large to moderate differences between peak ratios in the two chromatograms are readily visible. Peak ratios which are more similar may be difficult to compare visually. Extra care should be taken when comparing sets of peaks which do not separate completely. A slight increase in separation can cause a significant decrease in peak height. The overlay method provides a rapid screening procedure to determine if it is necessary to proceed to the more precise quantitative comparison.

The peak areas (provided automatically by the HP-5840A) were used to perform the quan-

²E. Brown, personal correspondence, supervising chemist, Shell Oil Company, Anacortes, WA, 1984.

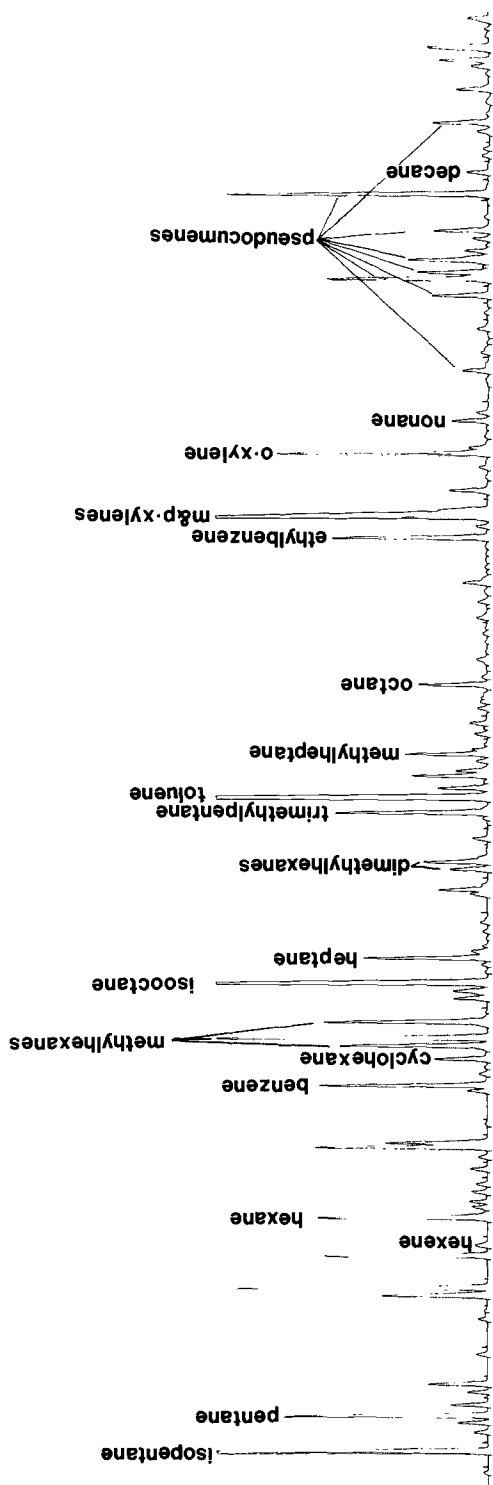


FIG. 1—A portion of a typical gas chromatogram for a liquid gasoline (neat injection). This portion represents greater than 95% of gasoline by volume.

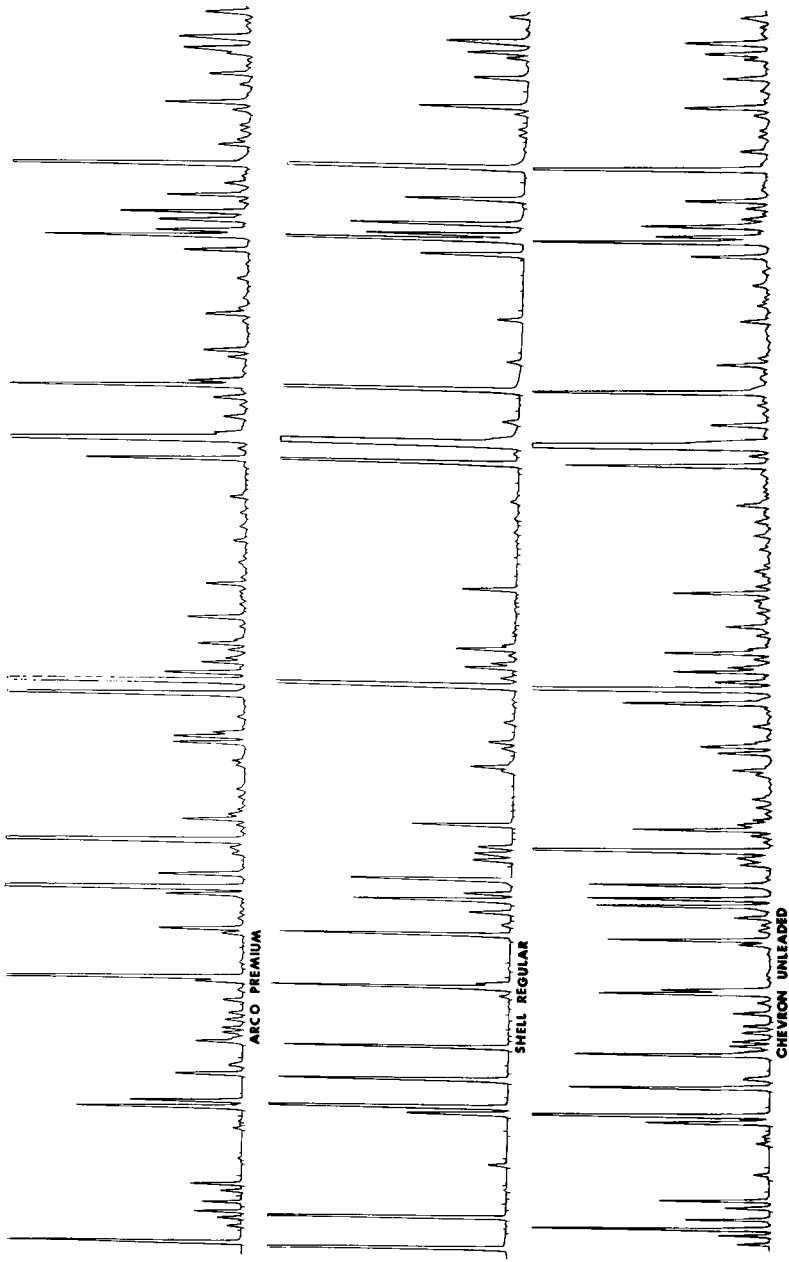


FIG. 2.—Gas chromatographic comparison of three gasolines acquired at random. Note the greater variation between gasolines when comparing the first half of each chromatogram than when comparing the second half.

titative comparisons in this study. Two of the integrated peaks (designated in Fig. 3) were selected as reference compounds. Each area of the remaining peaks was divided by the area of the closest reference compound to obtain two sets of normalized areas. A table of normalized areas thus was constructed for each sample in the study.

Tables of normalized areas representing individual gasolines are compared directly to determine the degree of similarity. Gasolines unchanged by evaporation and so forth, which have a common origin will yield normalized areas within the range of variation inherent in the gas chromatographic analysis. Unrelated gasolines should yield ratios which vary much more.

Reproducibility

The selection of the reference compounds is critical to the reproducibility and specificity of the comparison. Components with potential for greater variation in their integrated areas (such as those not completely resolved from adjacent peaks) should not be used as reference compounds because of potential variability in the normalized areas on a run-to-run basis. The larger the range of variability, the greater the chance of two different gasolines yielding results which fall within the range.

Triplicate analyses of neat gasolines yielded an average coefficient of variation of less than 1% for the normalized peaks of interest (Fig. 5). This small coefficient of variation allows the discrimination of gasolines whose marketing histories indicate they should be very similar.

Sampling

Phase I of the study involved sampling twelve Chevron unleaded regular gasolines from locations throughout the State of Washington. Over a one-week period, eight samples were taken in the greater Seattle area and four from Eastern Washington.

Phase II of the study involved sampling at a single Chevron station after six sequential shipments of unleaded regular gasoline. This was done to see what sort of shipment-to-shipment variation exists at a single outlet.

Phase III of the study involved sampling gasolines which were as closely related to each other as possible. To accomplish this, ten Chevron gas stations were identified which received deliveries regularly from one distributor and were scheduled to receive a shipment the same day. The unleaded regular gasoline at these ten stations was sampled the day after this delivery. Delivered volumes of gasoline ranged from 2100 to 4800 gal (7950 to 18 170 L). Residual volumes (in storage at the gas station before delivery) ranged from 980 to 6600 gal (3710 to 24 980 L).

In all phases, the gasoline comparisons were made using the visual overlay method and the quantitative method.

Results

Phase I

The twelve gasolines sampled in Phase I of this study were readily distinguished using either the visual overlay method (Fig. 3) or the more precise quantitative comparison method (Fig. 4). No effort was made to determine the origin of the gasoline at these stations. The sources of three samples selected from among these twelve gasolines was correctly identified in a blind test.

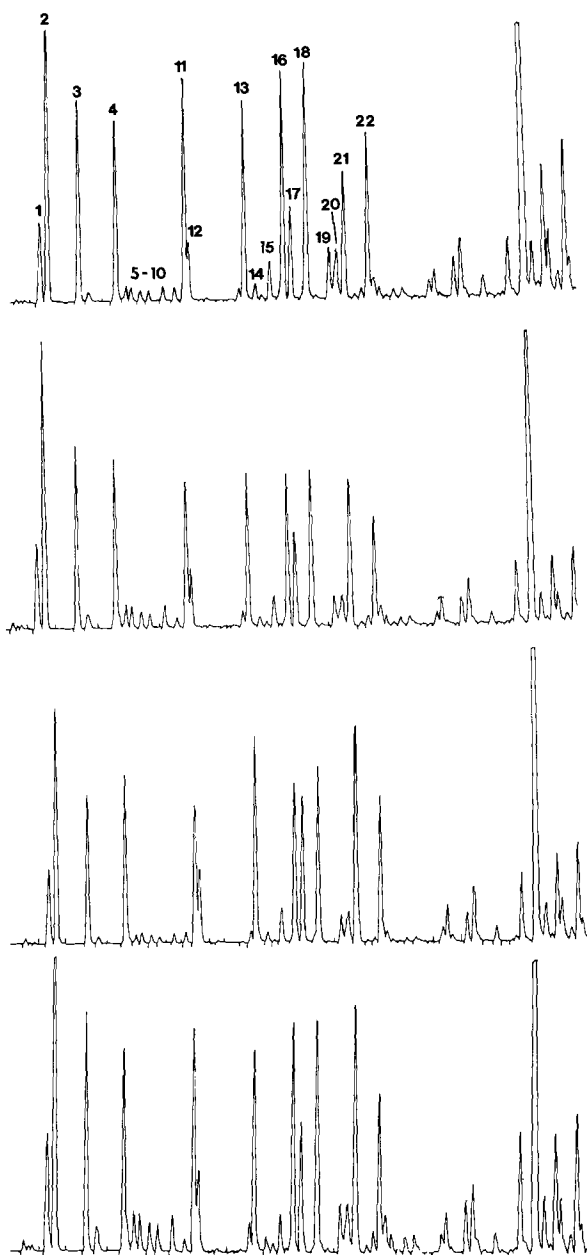


FIG. 3—Gas chromatographic comparison of the alkylate region of four of the eight Chevron unleaded regular gasolines obtained at random from the Seattle area (Phase I). Numbered peaks denote those used in the quantitative comparison technique. Peaks numbered 9 and 17 were used as reference compounds for the normalization process.

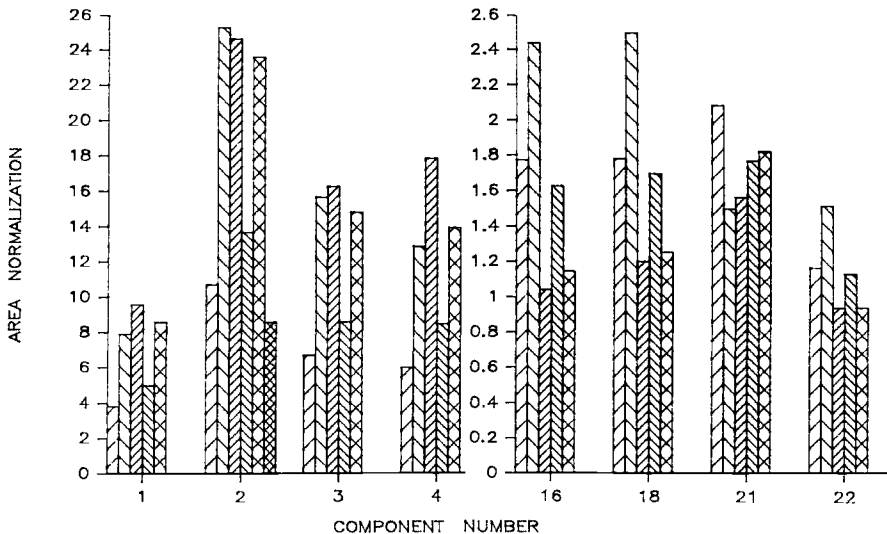


FIG. 4—Quantitative comparison of eight selected peaks from five (of the eight) Chevron unleaded regular gasolines obtained at random from the Seattle area (Phase I). Components 1-4 were normalized to Component 9; Components 16, 18, 21, and 22 were normalized to Component 17. (These five gasolines do not include all four gasolines depicted in Fig. 3.)

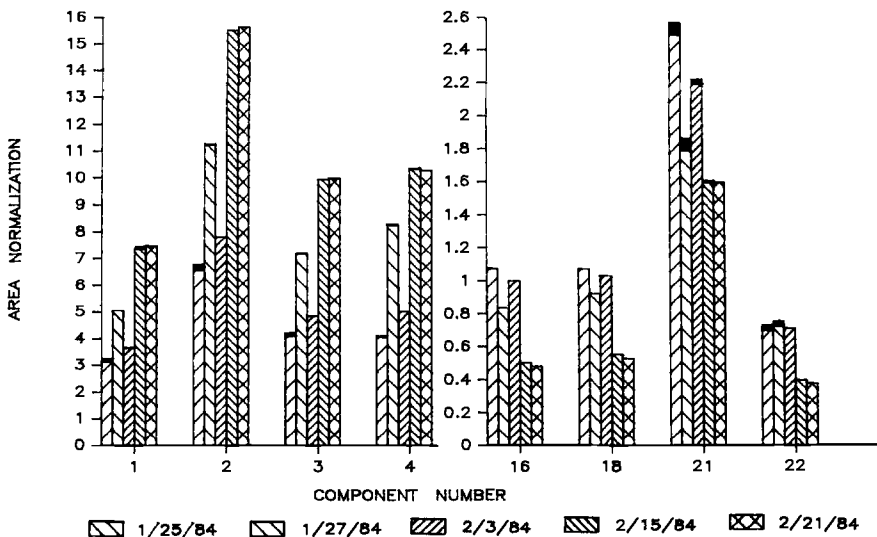


FIG. 5—Quantitative comparison of eight selected components from five sequential shipments of unleaded regular gasoline to a single Chevron station (Phase II). Note the variation of the analytical technique ($n = 2$ or 3) represented by the solid tops of the individual bars. The sample purchased 21 Feb. 1984 was analyzed once only.

Phase II

Shipment-to-shipment differences in the regular unleaded gasoline delivered to the single gas station in Phase II of this study are shown in Fig 5. It should be noted that the gas shipment delivered between 3 Feb. 1984 and 15 Feb. 1984 was not sampled. Hence, the large difference in the test results between these dates.

Comparisons of these six gasolines yielded results which were distinguishable with the exception of the two purchased on 15 Feb. 1984 and 22 Feb. 1984. The differences for most of the individual peak ratios for these two gasolines fall within the range of variation for the analytical method. Subsequent investigation showed that the distributor had not received a new supply of gasoline between the dates of these shipments to the station. In other words, the same gasoline was delivered twice in a row (on 15 Feb. 1984 and 22 Feb. 1984) to this station. Given this situation, it is reasonable to expect a high degree of similarity between the two samples. This unexpected circumstance provided a true blind test of the comparison technique.

Phase III

Variations were much smaller among the ten gasolines sampled in Phase III of this study (Fig. 6). Since the same source gasoline was supplied to all ten stations, differences in these gasolines after delivery were due only to the residual gasoline in the storage tank at the station before the new shipment. In general, the smaller the volume of gasoline delivered relative to what was on hand, the greater the difference between the chromatographic results for the gas station sample and the source sample. As expected, those stations which had the greatest proportions of gasoline delivered (relative to the residual volume) yielded results which exhibited the greatest similarity. However, all ten gasolines were distinguishable from each other and from the source gasoline. The sources of three samples selected from among the eleven (ten stations and distributor) were correctly identified in a blind test.

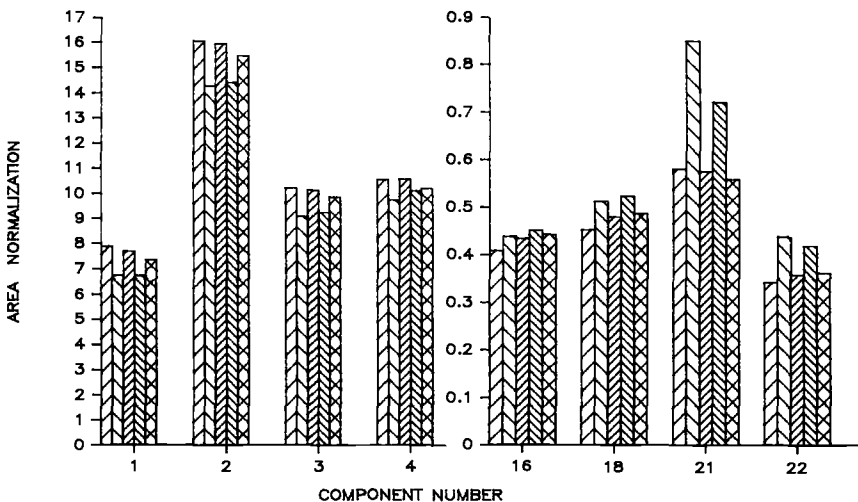


FIG. 6—Quantitative comparison of eight selected components from five Chevron unleaded regular gasolines originating from one lot of gasoline from a single distributor (Phase III). Note the narrow range of results of a single component relative to that obtained with randomly acquired Chevron gasoline (Fig. 4).

Discussion

Although these studies were limited to a small population, they demonstrate the variability that exists among gasolines available on the market. The studies also indicate how difficult it is to find gasolines from different sources which cannot be distinguished.

The size of the theoretical population of source gasolines should be considered when drawing a conclusion based solely on this comparison method. The conclusion resulting from the comparison of gasolines chosen from the small population of ten can be much more specific than if the number of possible sources included all those stations to which the distributor delivered that lot of gasoline. It is not possible to make a conclusive determination unless every possible source gasoline is used in the comparison.

Conclusions

The comparison of neat, unevaporated automotive gasolines using capillary gas chromatography can be highly discriminating. The potential for discrimination relies on resolution in the *n*-butane to *n*-octane region of the chromatogram and on good analytical reproducibility. The method is ideal to formulate a negative conclusion: for example, the two gasolines studied definitely do not share a common origin. The method is also useful to determine if two gasolines could have or probably have a common origin. The comparison method should not be used to formulate a conclusive link between two samples unless a closed system exists and all possible sources have been tested.

The use of a computer could increase the specificity of the comparison by allowing more components to be compared in a larger number of gasolines. A computer would also allow the use of a sophisticated statistical method of comparison instead of the somewhat subjective comparison of the normalized areas as performed in this study.

A variation of this comparison method may also be applied to straight-run petroleum products. However, as a result of the relative lack of variation manufactured into these products, and the manner in which they are marketed, the comparison would not be expected to yield the degree of specificity that is possible when comparing automotive gasolines, although a strong negative conclusion would still be possible.

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Address requests for reprints or additional information to
Dale C. Mann, Criminalist
Washington State Patrol Crime Laboratory
610 3rd Ave.
Public Safety Bldg., 2nd Fl.
Seattle, WA 98104-1820