

TECHNICAL NOTE

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Comparison of Gasolines Using Gas Chromatography-Mass Spectrometry and Target Ion Response

ABSTRACT: Gas chromatography-mass spectrometry was used to compare gasoline samples obtained from different sources based on the difference in amounts of certain components found in the headspace of gasoline using target response data. Many suspected arson cases involve comparing an ignitable liquid extracted from fire debris to a liquid found in a suspect's possession to determine if they could have had a common source. Various component ratios are proposed for determining if an unevaporated gasoline sample could have originated from the same source as an evaporated gasoline extracted from fire debris. Fifty and 75% evaporated gasoline samples were both found to contain similar ratios of certain components when compared with its unevaporated source gasoline. The results of the comparisons in this study demonstrate that for cases involving gasoline that has been evaporated up to 50% and extracted from pine, it is possible to eliminate comparison samples as originating from the same source. The results of the 75% comparisons suggest it may be possible to apply the same type of comparison to cases involving 75% evaporated gasoline.

KEYWORDS: forensic science, gas chromatography-mass spectrometry, gasoline comparison, ignitable liquid, arson, fire debris

In many suspected arson cases, the presence of an ignitable liquid may be detected in fire debris. Often a comparison ignitable liquid is submitted to the testing laboratory to determine if it is of the same type as that found in the fire debris. The strongest association a fire debris chemist can make regarding an ignitable liquid residue extracted from debris and the comparison ignitable liquid is based upon pattern recognition and component identification through the use of a gas chromatograph coupled with a mass spectrometer (GC-MS).

Since gasoline is the ignitable liquid detected in a large percentage of arson cases, more definitive methods of determining whether a gasoline recovered from a fire scene could have originated from a "known" source of gasoline are needed. It is widely known that different gasoline companies add patented performance markers to enhance the performance of their gasoline. These markers could potentially be used to distinguish different brands of gasoline from one another; however, because that information is proprietary and the markers are only present in minute concentrations, comparisons of this nature are not feasible for forensic work (1). However, gasoline from different sources may differ as a result of chemical conversion methods, treatment and reformulation processes, blending, and storage. Additionally, once a new shipment is sent out to a gasoline station, the new batch of gasoline is mixed with the residual gasoline still in the storage tanks, in essence creating a unique blend.

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Earlier work by Mann demonstrated the value of using gas chromatography and calculating peak-to-peak ratios for comparing one gasoline to another (2,3). In those studies, comparisons were based upon the most volatile components of gasoline; consequently it was limited to gasolines that were no more than 50% evaporated. In more recent work, Dolan and Ritacco applied the concept of using GC-MS to the sequential peak ratio method developed by Mann (4). The goal of this work is to determine if these types of methods could be applied to more highly evaporated gasoline.

Comparing gasoline found in debris to unevaporated gasoline is more complicated than analyzing gasoline alone. Fire debris does not contain an uncontaminated ignitable liquid, but rather many compounds that can contribute to and interfere with the chromatogram and make comparison to another gasoline very difficult. Materials such as synthetic carpet produce pyrolysis products that include some of the same components normally found in gasoline, which complicates the data analysis process. Wood products such as pine are also commonly found in residential fires, yet their pyrolysis products do not interfere with many of the components of gasoline, thereby making them more useful for comparison purposes (5).

In this study, using GC-MS and the sequential peak ratio method developed by Dolan and Ritacco, the headspace of evaporated gasoline extracted from fire debris is compared with the headspace of the source gasoline, which has not undergone evaporation. More highly evaporated gasoline is also compared with its source gasoline to determine if there is a potential for using these methods on more highly evaporated gasoline. Various component ratios are examined to determine if they are statistically similar to one another for the same gasoline at various stages of evaporation. The values for these selected ratios can then be compared to the corresponding

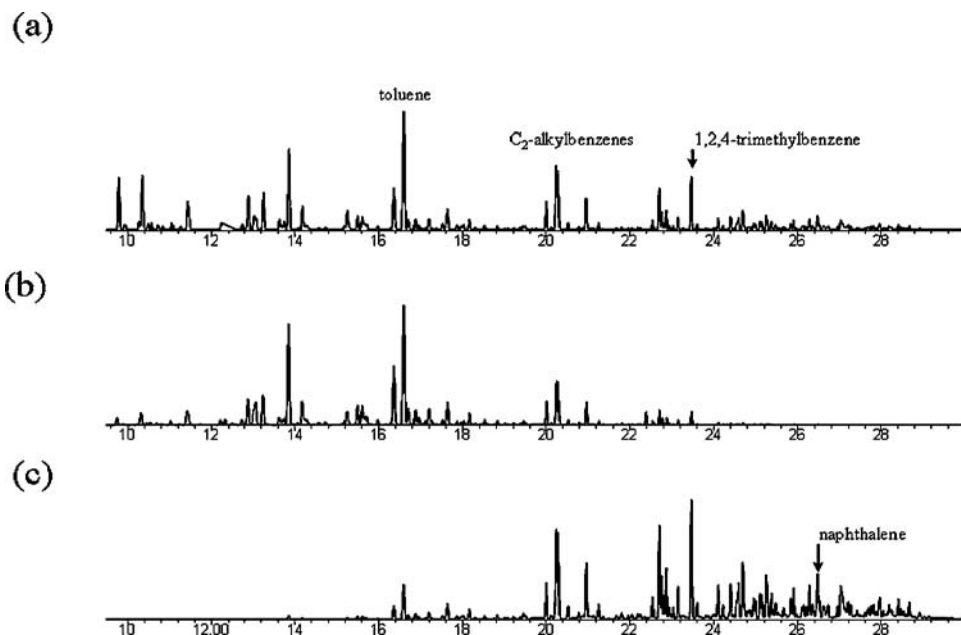


FIG. 1—Full sample chromatograms from GC-MS of: (a) unevaporated gasoline using passive headspace concentration; (b) 50% evaporated gasoline from fire debris using headspace sampling; and (c) 75% evaporated gasoline using passive headspace concentration.

values obtained from different sources of gasoline in order to determine if discrimination is possible.

Materials and Methods

All analyses were performed on an Agilent 6890 gas chromatograph coupled to a 5973 mass spectrometer. The GC-MS was equipped with a 60 m DB-1 column with a 0.25 mm internal diameter and 1 μ m film thickness. Helium was used as the carrier gas with a 20:1 split ratio. The oven temperature program was as follows: 35°C for 2 min followed by a temperature ramp of 5°C/min to 110°C (no hold time), then at 12°C/min to 250°C. The scanning mode for the MS was 29 to 200 amu's.

Target Compound Analysis was used to identify components in gasoline based on user-supplied data. Parameters were entered into the software so that it would provide target response data for the base peak for all components eluting in the isobutane to methylnaphthalene region of a typical gasoline chromatogram.

The gasoline used for the experiment was collected from several different gasoline stations throughout the Washington, DC metropolitan area and stored in Quorpack® 4 oz bottles with Teflon®-lined lids to prevent evaporation. For each sample of gasoline collected, an aliquot was removed as an unevaporated sample and the rest was divided into two samples, which were evaporated to 50% and 75% of their original volumes. Gasoline from the same source refers to gasoline collected from the same station and derived from the same bottle for the study. Sixteen different sources of gasoline were used for the 50% comparisons and ten different sources were used for the 75% comparisons. Different methods were used for the 50% comparison study and the 75% comparison study. While simple headspace sampling is the preferred means for recovering gasoline residues for comparison, it would not be effective at higher stages of evaporation.

Part I—50% Comparisons

To simulate fire debris where gasoline was used as an accelerant, a 6 \times 6 cm piece of pine was charred using a propane torch and sealed

in an unlined quart can. After 30 min 100 μ L of 50% evaporated gasoline was injected through a hole in the lid and covered with tape. Three cans were prepared in this way, and each was allowed to sit for 24 h at room temperature before headspace sampling.

Because the method of sampling will affect the data, it was necessary to obtain data for unevaporated samples via headspace as well. To do this, three cans were prepared by placing a single Kimwipe® in each, then adding 50 μ L of unevaporated gasoline to each can, and then immediately sealing the lid. These cans were also allowed to sit 24 h at room temperature before any headspace samples were analyzed via a hole placed in the lid.

A 2 mL headspace sample was introduced into the GC-MS in accordance with ASTM E 1388-00 (6). Three samples were taken from each can, resulting in nine sets of data for both the 50% evaporated gasoline and the unevaporated gasoline from the same source.

Part II—75% Comparisons

A single Kimwipe® was placed in two different cans, and then 10 μ L of 75% evaporated gasoline were placed on each Kimwipe®. This process was repeated for the unevaporated gasoline from the same source. The four cans were allowed to sit for 24 h and then passive headspace concentration was used to recover the sample in accordance with ASTM E 1412-00 (7). Each sample was extracted by placing an 8 \times 10 mm section of charcoal strip into the can, and heating the sample at 65°C for 16 h. The strip was then removed, and eluted with 250 μ L of carbon disulfide. A system blank was included in the analytical scheme to ensure no contamination occurred. Three injections per extract were performed, resulting in six sets of data for both the 75% evaporated gasoline and the unevaporated gasoline from the same source.

Data Analysis

The data acquired from each injection were analyzed using a target compound program, which selected the peaks of interest based on retention time and the presence of target and qualifier ions. Figure 1a-c illustrates typical chromatograms for unevaporated,

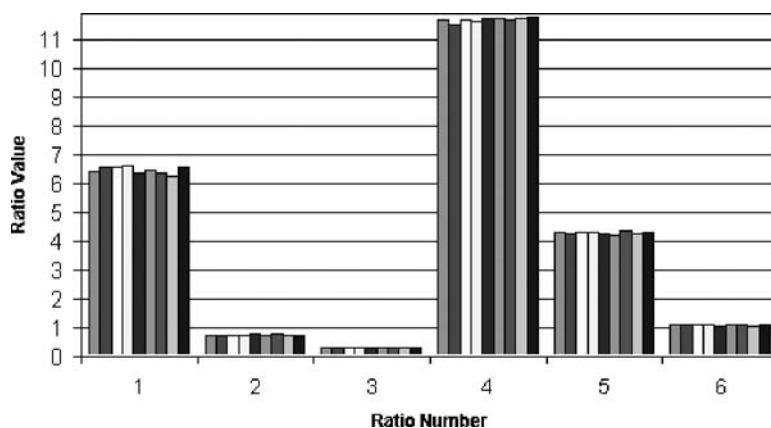


FIG. 2—Graphs illustrating reproducibility within a sample. Nine runs of unevaporated gasoline #5 using headspace sampling at room temperature (Part I).

50% evaporated, and 75% evaporated gasoline samples. The target response information for the compounds of interest was copied into a spreadsheet template, which included formulas to calculate sequential ratios and to determine averages and standard deviations for these ratios. Similarity among ratio values was based upon a standard deviation of 5%.

In selecting valuable ratios for comparison, the ratio must remain similar when gasoline is compared with gasoline from the same source but at a different stage of evaporation. Ratios obtained from the 50% evaporated gasoline samples were compared with those obtained from the unevaporated source gasoline. This was done for 16 different gasoline sets. The same method of data analysis was applied to the 75% evaporated gasoline and its unevaporated source gasoline using ten different gasoline samples.

The first step for determining useful ratios involved insuring that the ratios selected would be reproducible within a given sample. The datasets for the individual injections from a sample were compared and found to be within 5% standard deviation of one another. This demonstrated that the ratios selected are reproducible within each sample. Figure 2 illustrates reproducibility within a sample by showing the values obtained from nine runs of the same sample (Part I). The next step involved comparing ratios from an evaporated gasoline to its unevaporated source gasoline. For each gasoline sample there were two sets of values to be compared with one another: the average of each ratios value for the evaporated gasoline and the average of each corresponding ratios value for the unevaporated gasoline. The two values for each corresponding ratio were compared with one another by calculating their percent standard deviation. Ratios that fell within 5% standard deviation of each other were selected for further comparisons. This process showed that the selected ratios did not change significantly during the evaporation process and therefore could potentially be used as points of comparison.

Each ratio that was determined to be potentially useful was then examined to determine if it exhibited sample-to-sample variability. For each evaporated gasoline, the values for the ratios that were found to be potentially useful were compared with the corresponding values for all unevaporated gasolines used in the study. Only ratios that were useful in discriminating different sources of gasoline were selected. This step showed that an evaporated gasoline sample could be associated with its source and discriminated from other sources of gasoline through the comparison of the selected ratios.

TABLE 1—Compound names and retention times used to generate ratios.

Compound No.	Compound Name	Retention Time (min)
Part I—50% Comparisons		
1	a dimethylcyclopentane	15.19
2	a methylcyclohexane	15.26
3	a dimethylhexane	15.50
4	a dimethylhexane	15.62
5	a trimethylcyclopentane	15.98
6	a trimethylpentane	16.37
7	a trimethylcyclopentane	17.38
8	a dimethylcyclohexane	17.53
9	a dimethylcyclohexane	18.32
10	a dimethylcyclohexane	18.53
Part II—75% Comparisons		
1	a dimethylhexane	15.50
2	a dimethylhexane	15.62
3	a trimethylcyclopentane	15.98
4	a tetramethylbenzene	25.92
5	a methylindane	26.30
6	a methylnaphthalene	28.68
7	a methylnaphthalene	28.93

Results

Part I—50% Comparisons

The six ratios used in the comparisons are illustrated in Fig. 3. The compounds used to generate the ratios are listed in Table 1. Figure 4 illustrates graphs of the six ratios used to compare the 16 gasoline samples. The 50% evaporated gasoline samples recovered from charred pine were found to be similar to the corresponding values of their source gasolines. The 16 gasolines used in this part of the study were readily distinguished from one another using these six ratios. It should be noted that different gasolines may have some similar ratio values. For example, in Fig. 4a the values for ratio 1 of gasolines #1 and #8 had values close to four. However, when all six ratios are taken into account, each of the tested gasolines was discriminated from one another. In Fig. 4b–f the values for ratios 2–6 differ when gasoline #1 and #8 are compared.

In addition, the data from each evaporated gasoline was compared with the data from all of the unevaporated gasolines. By using the six ratios, each evaporated sample was successfully associated with its known source gasoline. All of the other unevaporated samples were eliminated as being a potential source. The sources of five samples

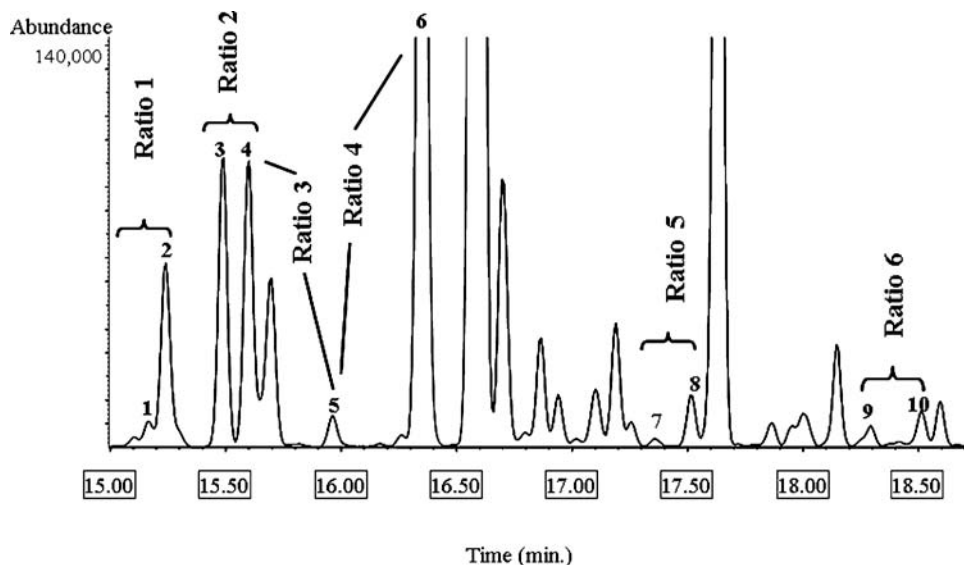


FIG. 3—Ratios used in the 50% comparisons (Part I). The ratios were determined by dividing base peak abundance of the later eluting compound by base peak abundance of the earlier eluting compound.

selected from the 16 gasoline samples were correctly identified in a blind study.

Part II—75% Comparisons

Four ratios were used to compare the ten gasoline samples. The four ratios are outlined in Fig. 5. The compounds used to generate the ratios are shown in Table 1. Ratios one and two correspond to ratios two and three of the 50% comparisons, indicating it may be possible to use those two ratios for cases involving gasoline up to 75% evaporated.

When simple substrates were spiked with 75% evaporated gasoline, values obtained for the four ratios were found to be similar to those obtained from the corresponding source gasolines. Comparing data obtained from each 75% evaporated gasoline to all ten unevaporated gasolines, only the gasoline from the same source shows similar values for all four ratios (Fig. 6). As noted for the tests using 50% evaporated gasoline, these comparisons also require the use of all specified ratios for an adequate comparison. This is due to the fact that different gasolines may have some similar ratio values; however, when all four specified ratios are used all of the tested gasolines were discriminated from one another. In addition, the sources of three samples selected from the ten gasoline samples were correctly identified in a blind study.

Discussion and Further Research

The results of the comparisons in this study demonstrate that for cases involving gasoline as an accelerant that has been evaporated up to 50% and extracted from charred pine, it is possible to conduct comparisons of gasoline in debris to a possible gasoline source. This type of comparison is particularly useful for eliminating gasolines originating from different sources, but also can be used to indicate the possibility of a common source. The results of the 75% comparisons suggest that it may be possible to apply the same type of comparison methodology to cases involving 75% evaporated gasoline. It is important to mention that this study, while able to differentiate each source of gasoline from one another and correctly associate an evaporated gasoline sample to its source, was

conducted on a relatively small sample. It is understood that there may potentially be gasolines that have different sources that are not distinguishable by this method. For this reason, when a comparison is conducted, and the gasolines cannot be distinguished from one another, it is important that the analyst's statement of conclusions reflect that a common origin is not a certainty.

Examination of the data from Part I demonstrates the presence of the wood substrate does not adversely affect the comparison process. The reproducibility for the ratios obtained in Part II was very good. This may be due to the use of an autosampler as well as to the lack of a complex substrate. In Part II, an autosampler was used as opposed to manual injections, which were used in Part I. The use of an autosampler improves reproducibility due to the elimination of the human factor in the injection process. In addition, the presence of a complex substrate could potentially adversely affect the reproducibility; however, in this part of the study, a simple substrate was used.

This study was an initial attempt at determining the feasibility of comparisons of 75% evaporated gasolines; therefore further research will be needed to determine the effects of a complex substrate on comparisons involving gasolines evaporated to this extent. As with the method used in Part I, this comparison method looks promising for cases involving softwoods such as pine because terpenes will not interfere with the compounds used in this comparison process. Also, because two of the four ratios used in Part II involve compounds eluting in the late region of the chromatogram, attempts to do this type of comparison on even more highly evaporated gasolines may prove feasible.

This study involved comparisons of gasolines from a relatively small distribution area that possibly could have received gasoline from the same refinery and/or production batch, or terminal. Numerous factors such as new shipments of gasoline, the storage conditions of the gasoline, and the amount of residual gasoline in a tank all contribute to the compositional differences of gasolines that are the basis for this method of comparison. Because these samples from a relatively small area were distinguished from one another, comparisons involving gasoline from a broader distribution area are expected to result in an even greater degree of discrimination.

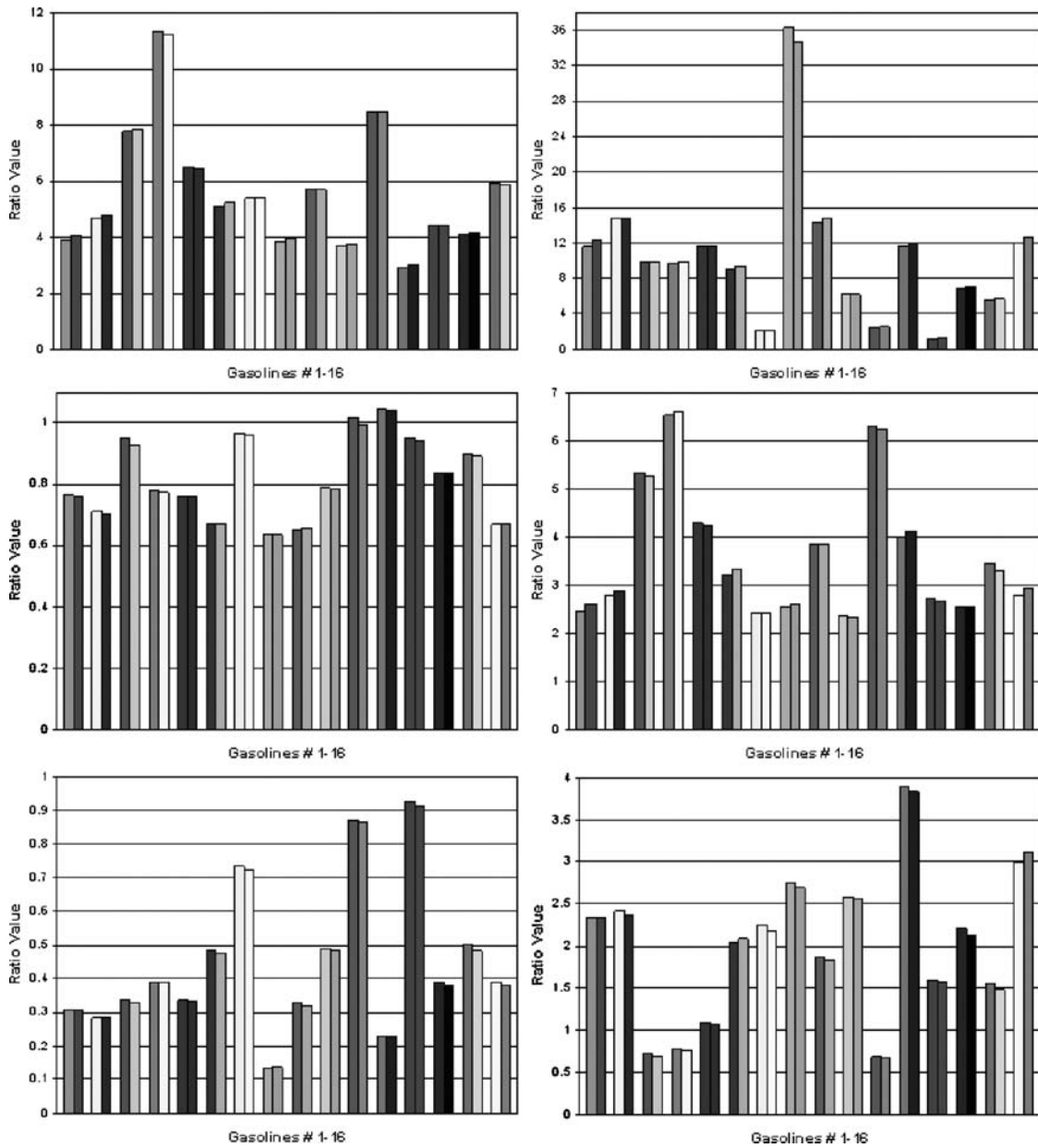


FIG. 4—Graphs of ratios used to compare the sixteen gasolines (Part I). Each color pair represents one gasoline: unevaporated (left bar) and 50% evaporated debris extract (right bar): (a) Upper left—Ratio 1; (b) Middle left—Ratio 2; (c) Bottom left—Ratio 3; (d) Upper right—Ratio 4; (e) Middle right—Ratio 5; and (f) Bottom right—Ratio 6.

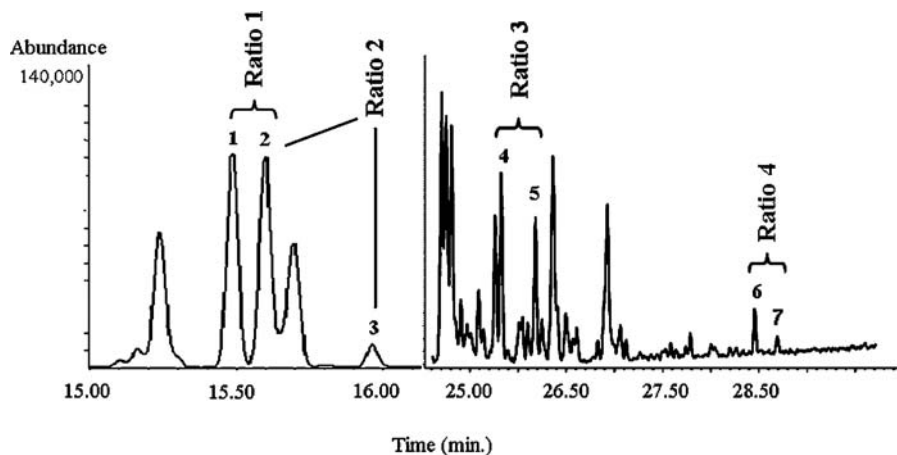


FIG. 5—Ratios used in the 75% comparisons (Part II). The ratios were determined by dividing base peak abundance of the later eluting compound by base peak abundance of the earlier eluting compound.

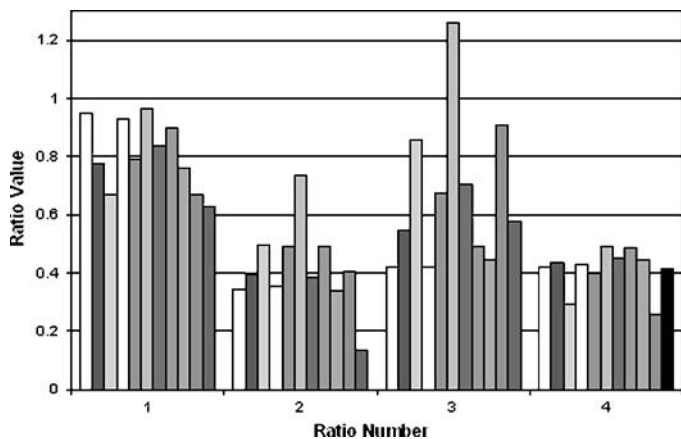


FIG. 6—Comparison of 75% evaporated gasoline #3 versus unevaporated gasolines #1–10 (Part II). The first white bar in each graph indicates the 75% evaporated gasoline extract #3. The rest of the bars indicate gasolines #1–10 unevaporated. The second white bar indicates the same source gasoline (#3) unevaporated.

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