Identification of Heavy Residual Oils by GC and GC-MS

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ABSTRACT

Seven unweathered heavy residual oils, analyzed and compared for source identification purposes, demonstrate that the comparison of heavy residual oils must be performed with great care using a variety of analytical techniques and comparison methods. Furthermore, these methods are best applied to known common-source pairs and to known non-common-source pairs in addition to the unknown pairs. Physical and chemical tests showed that, for the most part, these properties for the seven oils were within the error range of the test. Visual comparison of the chromatograms also showed that they were very similar. Normalized normal paraffin and isoprenoid peak height profiles, when subjected to measurement-error and statistical comparisons, provided quantitative evaluations of the relative likelihood that the members of the various oil pairs were from a common source.

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INTRODUCTION

The source identification of oils has received considerable attention in recent years as evidenced by the wide selection of work reported in the literature. The primary interest has been in identifying the source of oils spilled on waterways. The Coast Guard[1] has used numerous analytical techniques to aid in matching weathered spills, usually crude oils, with the source. These include thin-layer chromatography, gas chromatography (GC), and fluorescent and infrared spectroscopy. Gas chromatography-mass spectrometry (GC-MS) has also been recommended.[2]

The overall methodology to identify a source of an oil is to compare properties of the oil in question to properties of known sources until a positive identification beyond a reasonable doubt is found or until the oils are demonstrated to be from different sources. Depending on the oils involved, the analytical requirements may range from only a GC analysis to an extensive assortment of tests. Bentz[3] reported that in the case of U.S. vs. Slade, Inc., the evidence on source identity was based on GC analysis only and was upheld in court.

In the case of the GC analysis, the normal paraffins and isoprenoids are compared in the approximate range from C-12 to about C-40 depending on the GC capabilities. Obviously, the difficulty in comparing oils depends on their degree of similarity in the range of comparison. The paraffin and isoprenoid concentrations may vary widely for crude oils. However, for heavy residual oils which have been extensively refined, the paraffin and isoprenoid concentrations are likely to be quite similar in many cases. As a result, extensive and careful comparisons of the GC results must be performed before a positive identification is made.

In the present work, several unweathered heavy residual oils were analyzed by GC and GC-MS and compared for source identification purposes. These unweathered oils provide a "best-case" situation with respect to weathering from the viewpoint of source identification or commonality. As such, they provide a limiting case from which to obtain a feel for the difficulty of matching and identifying weathered oils. The use of refined oils demonstrates the complications which arise when a component distribution bias is introduced by processing. The identification methodology based on GC and GC-MS analytical results is reviewed and then applied to the heavy residual oils. Additionally, a variety of physical and chemical properties are compared.

IDENTIFICATION METHODOLOGY BASED ON GC AND GC-MS RESULTS

Most of the early work before 1970 resorted to qualitative, visual observations of the actual chromatographic fingerprints. This has the well-known problem that identical size samples cannot be injected reproducibly into the chromatograph. Consequently, even repeat fingerprints of the exact same sample can be difficult to compare. More recently, quantitative comparisons based upon chromatographic peak heights or peak areas have been used in place of the complete fingerprint. In this way the major peaks of the chromatogram can be characterized for comparison in an objective manner, bypassing the subjectivity involved in comparing fingerprints directly.

A variety of normalization methods have been used over the years to determine concentration or relative concentration profiles of components in the oil sample. Normal paraffin profiles (plots of peak size versus normal paraffin carbon number) have been calculated by normalizing by one of the normal paraffins (e.g. C-13) or by the sum of all the normal paraffins. The latter method has two primary advantages. First, the numbers calculated for each normal paraffin have some physical significance in that they represent a relative distribution in terms of a fraction of the total. Second, and even more important for comparisons between oils, the numbers obtained are not distorted by excessive errors in the peak which may be used for the normalization. Clark and Jurs[4] and Illich, et al.[5] have normalized peak heights by the sum of the peak heights and Clark and Jurs[6] have normalized peak areas by the sum of the peak areas. Using peak heights is preferable since these are more objective measurements not affected by a sometimes questionable decision on the start and end points of a peak. A similar distribution can be calculated for the isoprenoid compounds and Illich, et al.[5] have normalized the isoprenoid peak heights by the sum of the isoprenoid peak heights. The isoprenoid compound peaks appear between normal paraffin peaks and are, in the words of Illich et al., "members of the homologous series characterized by multiples of the isoprene unit (2-methylbutane)."

Other quantitative comparisons, in addition to the normal paraffin and isoprenoid profiles, are based on ratios of pairs of peaks (one peak is normalized by another). The most common ratios considered are the normal C-17/pristane (the C-19 isoprenoid) ratio and the C-18/phytane (the C-20 isoprenoid). The ratios of other normal paraffins to their nearest isoprenoid also may be considered and in fact this is suggested by the IP method for fingerprint analysis. The advantage of these ratios is that compounds that are close to each other on the chromatogram will undergo similar weathering and hence these ratios may be preserved in spite of weathering. Jackson, et al.[7] calculated the ratios of each of the normal paraffins C-14 though C-18, to it's nearest isoprenoid and used these ratios, along with the Ni/V ratio to compare an oil spill sample and a suspect bunker fuel oil that were considered to be the same. Additionally, the pristane to phytane ratio has been used to characterize oil samples.

Recent work has focused on statistical pattern recognition for evaluating the similarity of oils using the above measures.[8] Refined oils present a much more complicated pattern recognition problem than do crude oils in that the component distribution pattern is very strongly biased by the refining process. This paper demonstrates this bias and consequent complication.

ANALYTICAL METHODS

The physical and chemical property analyses used in the present work were performed by Southern Petroleum Laboratories, Inc., Houston, Texas, Caleb Brett U. S. A., Inc., Houston, Texas, and a private company laboratory. The tests were performed according to ASTM procedures where possible.

The GC and GC-MS analyses were performed by Southern Petroleum Laboratories using a Finnigan model 9610

GC with the option of a flame ionization detector or a Finnigan model 4023 mass spectrometer detector. The GC column was a DB-5, 30m, 0.25 capillary. The initial column temperature was 40^{o}C with a hold time of four minutes. The temperature program was 5^{o}C per minute with a final temperature of 300^{o}C. The same GC conditions were used for both the FID and the mass spectrometer detector analyses.

DISCUSSION AND ANALYSIS OF RESULTS

Seven residual oils were analyzed by various tests for physical and chemical properties, GC, and GC-MS and used for comparisons in the present work. These were identified as oils A through G. The identification methodology included the comparison of the physical and chemical properties, the visual comparison of the chromatograms, and the quantitative comparison of peak height ratios of the normal paraffins and isoprenoid compounds from the GC and GC-MS results.

Comparison of Physical and Chemical Properties

Tables 1 & 2. Physical and chemical analyses of heavy residual oils.

Lab:	Oil A			Oil B			Oil C	Oil D		Oil E		Oil F		Oil G	
Property	**CBL**	**SPL**	**PCL**	**CBL**	**SPL**	**PCL**	**SPL**	**SPL**	**PCL**	**CBL**	**SPL**	**CBL**	**SPL**	**CBL**	**SPL**
API Gravity @ 60^{o}F	24.5	-	24.4	24.5	-	-	-	-	24.4	24.7	-	23.8	-	23.8	-
Color ASTM (diluted)	3	-	-	3	-	-	-	-	-	>8	-	>8	-	>8	-
Flash Pt. PMCC	230+	-	-	230	-	-	-	-	-	210	-	210	-	230	-
Pour Pt. (^{o}F)	+70	75	80	+70	70	70	75	75	85	85	80	85	80	85	75
Viscosity (SUS)	55.8	59.02	-	54.7	57.15	57.15	54.18	63.15	-	59.7	57.23	53.0	57.29	55.1	56.23
Sulfur (Wt.%)	-	0.306	0.32	-	0.203	0.203	0.184	0.262	0.29	-	0.225	-	0.396	-	0.285
RI @ 67^{o}C	-	-	1.4860	-	-	-	-	-	1.4867	-	-	-	-	-	-
IBP (^{o}F)	-	-	602	-	-	-	-	-	420	-	-	-	-	-	-
10% cutpoint (^{o}F)	-	619	658	-	628	628	628	-	622	-	-	-	575	-	-
700^{o}F cutpoint (%)	-	23	19	-	23	28	23	-	25	-	-	-	26	-	-
BS&W (%)	-	-	0.05	-	-	-	-	-	-	-	-	-	-	-	-
Carbon Res. (%)	-	-	0.33	-	-	0.35	-	-	0.78	-	-	-	-	-	-
Analine Pt. (^{o}F)	-	-	186	-	-	184	-	-	194	-	-	-	-	-	-
Vanadium, ppm	-	-	0.63	-	-	0.6	-	-	3.7	-	-	-	-	-	-
Nickel, ppm	-	-	0.38	-	-	2.8	-	-	1.3	-	-	-	-	-	-
Iron, ppm	-	-	2.66	-	-	0.6	-	-	3.2	-	-	-	-	-	-

CBL - Caleb Brett Laboratory SPL - Southern Petroleum Laboratory PCL - Private Company Laboratory

As shown in Tables 1 and 2, various physical and chemical property tests were performed on the oils by three different laboratories. Given the scatter of the data between the laboratories and the accuracies stated in the methods for the various tests, all of the oils appear to be very similar. The most notable differences are in the initial boiling points (IBP), suggesting that oils A, B and D are different. However, by another comparison, the 10% cut point for oils A, B and D are very close and are within the interlaboratory scatter. The 10% cut point for oil F is about 50^{o}F lower than oils A, B and D. This difference should be well outside the range of experimental error.

Visual Comparison of Chromatograms

The chromatograms from the GC and GC-MS analyses were visually compared for presence or absence of any compounds, for different peak height ratios and for any other distinguishing characteristics. The comparison of the chromatograms was greatly facilitated by making overhead transparencies and overlaying these transparencies. The chromatograms for all of the oils were quite similar except for oil F which was distinctly different. An example of the degree of apparent similarity is illustrated by the segment of the GC-MS results shown in Figure 1 for oils A and C. These two oils are known to be from different sources yet their chromatograms are quite similar in a qualitative sense. Thus, for residual fuel oils, further comparisons using techniques which are as quantitative as possible are absolutely necessary.

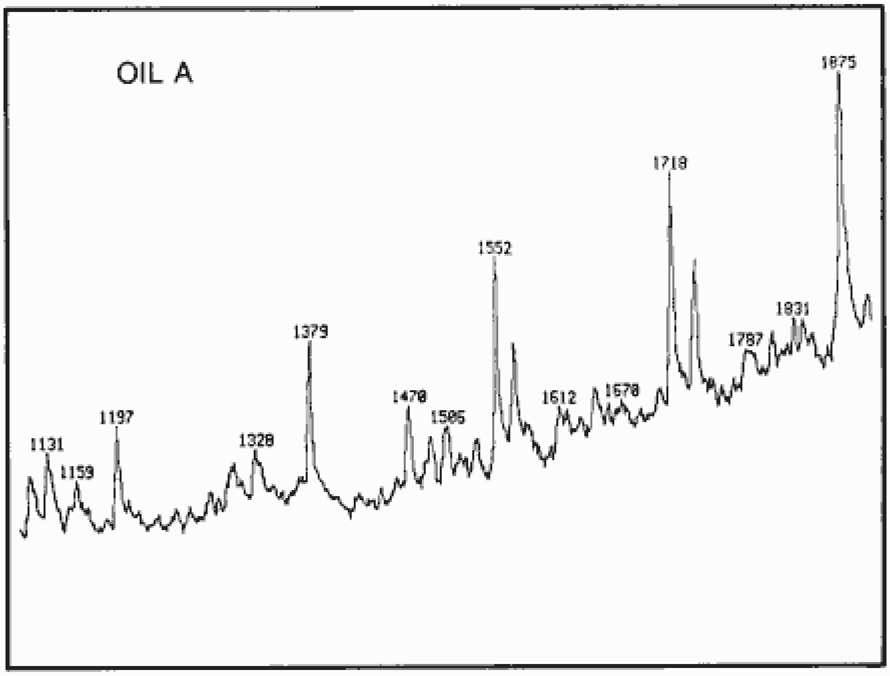

Figure 1a. GC-MS chromatogram for oil A.

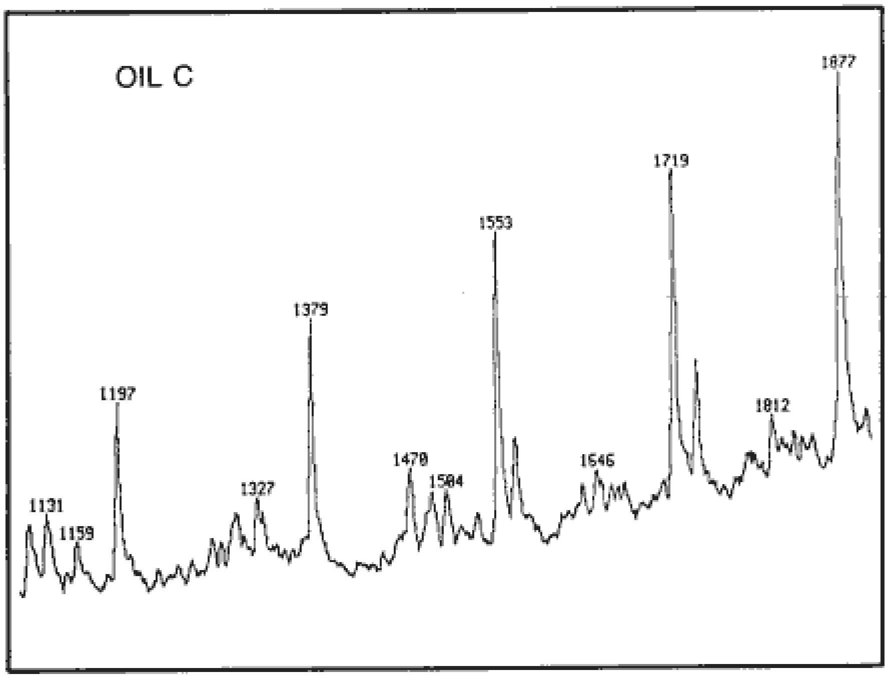

Figure 1b. CG-MS chromatogram for oil C.

Quantitative Comparison of Chromatograms

Normalized normal paraffin profiles were prepared using the method proposed by Clark and Jurs[4] and Illich et al.[5] This consisted of dividing the peak height for each normal paraffin between C-15 and C-31 by the sum of all of the peak heights between C-15 and C-31. This sum of peak heights serves as a self internal standard which allows oils to be compared on a common basis. The profile is shown in Figure 2 for the GC results. Visual comparison of these profiles indicates that all of the oils are quite similar in general profile except for oil F. This similarity is promoted by the refining process. Similarly determined normal paraffin profiles for the GC-MS data are shown in Figure 3. These profiles show much greater differences between several of the oils than do the GC results and provide an excellent complement for evaluating source commonality. Again, oil F is noticeably different from the rest and, in addition, A, B, and C are more separated from the others at low carbon number.

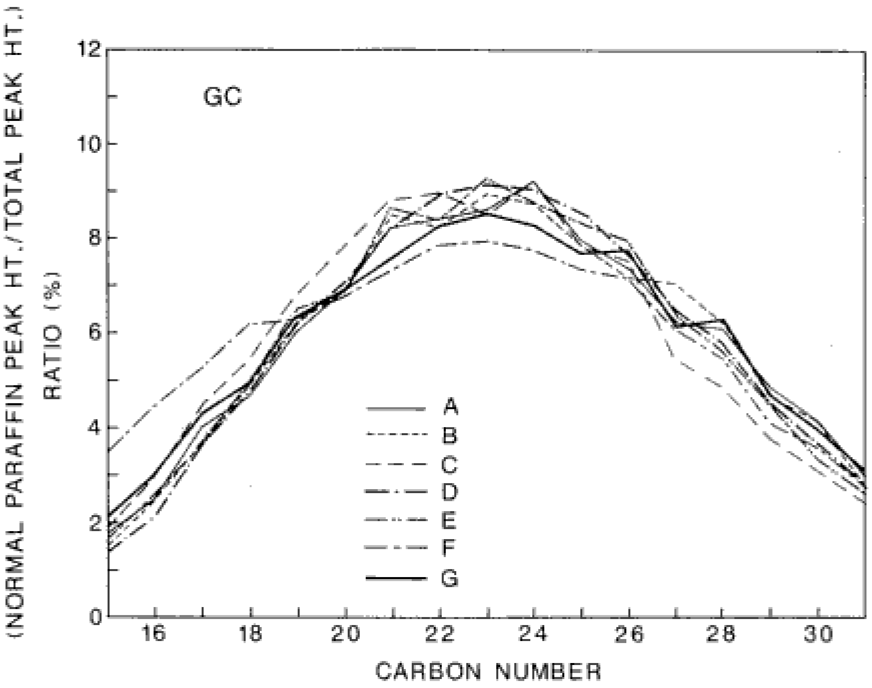

Figure 2. GC normal paraffin profiles for heavy residual oils.

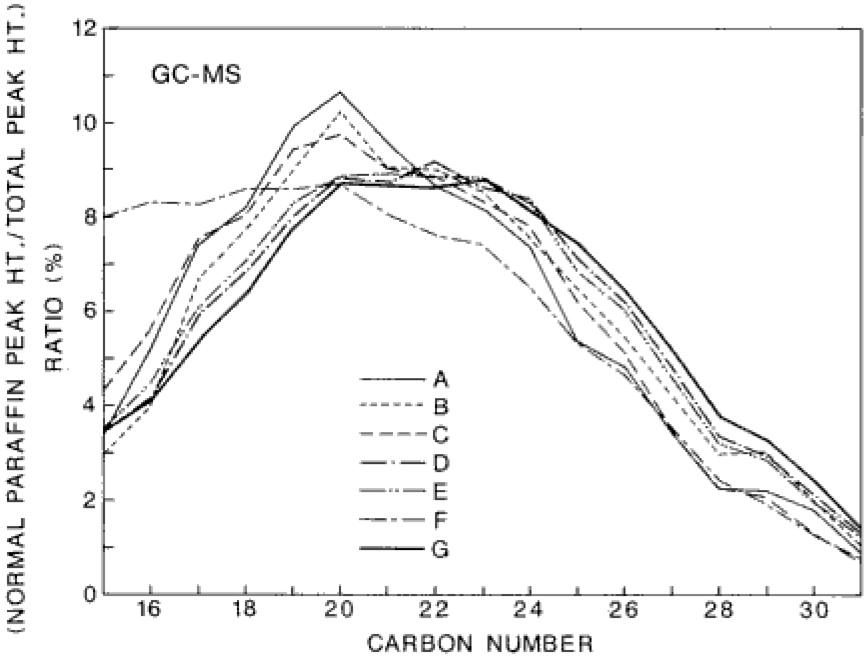

Figure 3. GC-MS normal paraffin profiles for heavy residual oils.

Distinct isoprenoid peaks were obtained near normal paraffin carbon numbers 16-18, 30 and 31 for the GC results and 16-18 and 29-31 for the GC-MS results. Isoprenoid profiles also were calculated by dividing the isoprenoid peak heights by the sum of the n-paraffins. This normalization procedure avoids individual peak errors which would distort the results within each oil if a different peak were used for normalizing each isoprenoid compound. It also tends to provide a more consistent basis for comparison between oils as random differences will tend to cancel in the sum. The isoprenoid ratio plots are shown in Figures 4 and 5 for the GC and GC-MS results, respectively. Interestingly, the isoprenoid ratio profiles from the GC results show much greater differentiation between the oils than the normal paraffin profiles.

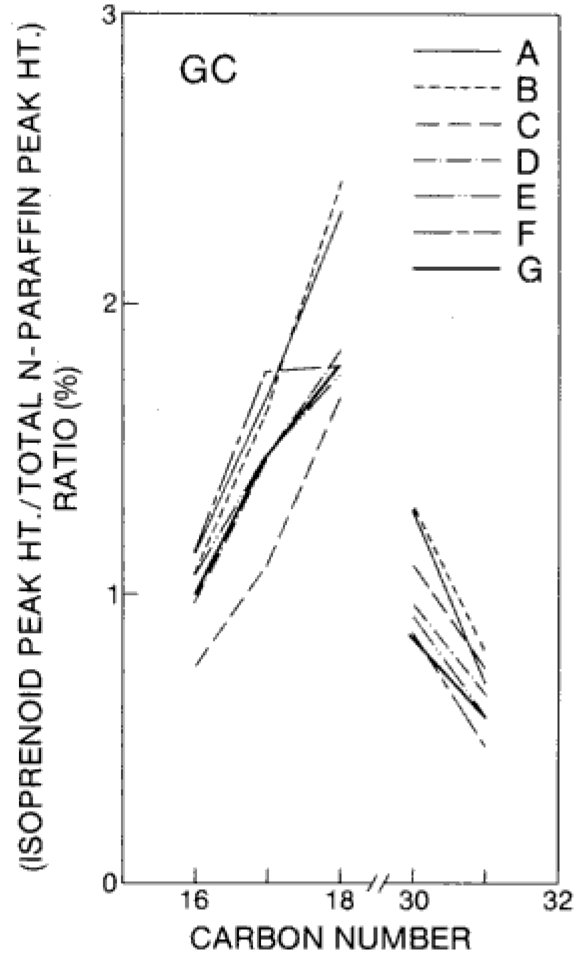

Figure 4. GC isoprenoid profiles for heavy residual oils.

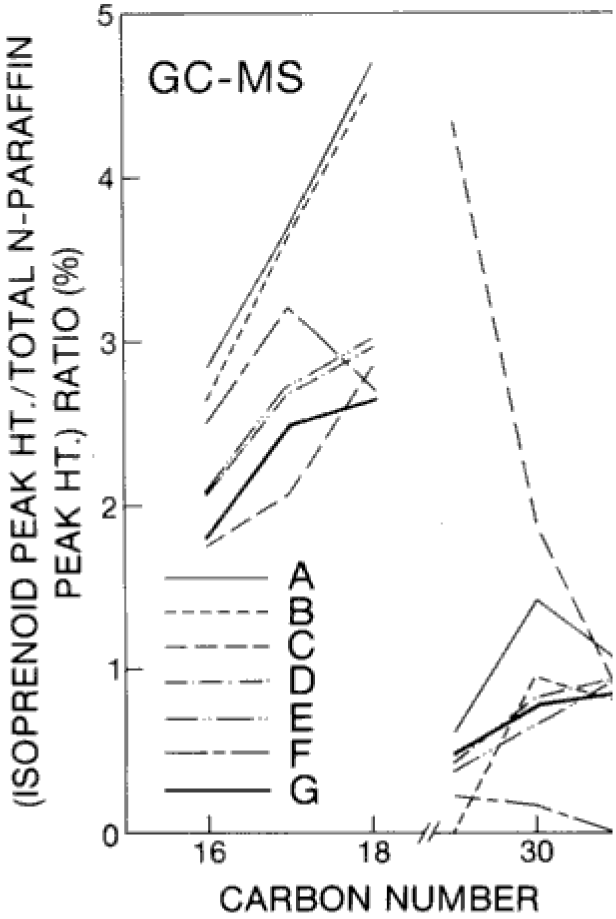

Figure 5. GC-MS isoprenoid profiles for heavy residual oils

Further differentiation between the oils based on the GC and GC-MS results must rely on a more quantitative approach. ASTM D-3415-79 and D-3328-78 have stated that, "many similarities (within uncertainties of sampling and analysis) will be needed to establish identity beyond reasonable doubt."[9,10] Although there have been no detailed analyses of the errors reported in the literature, it has been suggested that, if two oils are within 10% of each other, a match is concluded for that carbon number.[11]

How many chromatogram peaks should compare to within 10% to satisfy the "many similarities" concept is unstated, however. The number of peak comparisons, relative to the total, which are within 10% for each oil pair of this study are shown in Table 3 for the n-paraffin profiles and Table 4 for the isoprenoids. In these tables, the data in the upper right triangle correspond to the GC-MS comparisons and those in the lower left correspond to the GC calculations. The oil pairs being compared are indicated by the letter coordinates (row-column) of the table.

Table 3. Oil pair similarities for the n-paraffin profiles.

Table 4. Oil pair similarities for the isoprenoid profiles.

A	B	C	D	E	F	G	OIL	A	B	C	D	E	F	G
No.<10% t-test: x^2:	8/17 0.00 0.00	13/17 0.04 0.00	4/17 0.00 0.00	5/17 0.00 0.00	6/17 0.01 0.00	4/17 0.00 0.00	**A**		3/6 0.26 0.00	0/6 0.05 0.00	0/6 0.00 0.00	0/6 0.01 0.00	0/6 0.05 0.00	0/6 0.00 0.00
15/17 0.69 0.63		9/17 0.01 0.00	7/17 0.00 0.00	13/17 0.00 0.00	1/17 0.00 0.00	6/17 0.00 0.00	**B**	4/5 0.91 0.74		0/6 0.07 0.00	0/6 0.17 0.00	0/6 0.13 0.00	1/6 0.05 0.00	1/6 0.13 0.00
7/17 0.01 0.00	7/17 0.00 0.00		4/17 0.00 0.00	6/17 0.00 0.00	8/17 0.01 0.00	4/17 0.00 0.00	**C**	1/5 0.04 0.00	0/5 0.02 0.00		2/6 0.16 0.00	2/6 0.14 0.00	1/6 0.04 0.00	3/6 0.19 0.00
14/17 0.42 0.15	15/17 0.91 0.30	7/17 0.01 0.00		17/17 1 0.99	3/17 0.00 0.00	14/17 0.09 0.45	**D**	1/5 0.04 0.01	0/5 0.03 0.00	1/5 0.04 0.03		4/6 1 0.84	1/6 0.09 0.00	4/6 0.36 0.36
15/17 0.45 0.05	13/17 0.85 0.091	10/17 0.02 0.00	15/17 1 0.57		2/17 0.00 0.00	10/17 0.01 0.01	**E**	1/5 0.05 0.00	2/5 0.10 0.00	1/5 0.04 0.00	4/5 1 0.86		1/6 0.10 0.00	1/6 0.09 0.17
8/17 0.02 0.00	6/17 0.03 0.00	5/17 0.01 0.00	8/17 0.04 0.00	8/17 0.03 0.00		2/17 0.00 0.00	**F**	2/5 0.13 0.00	2/5 0.10 0.00	1/5 0.03 0.00	2/5 0.14 0.13	3/5 0.49 0.48		1/6 0.07 0.00
14/17 0.73 0.18	12/17 0.31 0.00	8/17 0.02 0.00	12/17 0.10 0.00	10/17 0.12 0.00	10/17 0.05 0.00		**G**	0/5 0.03 0.00	1/5 0.05 0.00	1/5 0.01 0.01	3/5 0.86 0.88	5/5 0.24 0.98	2/5 0.45 0.36	

Looking at the GC and GC-MS normal paraffin and isoprenoid comparisons, some conclusions are evident. We can see that some pairs stand out as being obviously similar whereas others stand out as being definitely dissimilar. Still others fall in-between with a fairly good number of similarities but possibly not enough to indicate common source. Also, it is evident that the GC-MS analysis is more discriminating in all of these comparisons than is the GC; the number of close matches is clearly less for the GC-MS analysis than for the GC. Concerning specific pairs, the close similarity of the D-E pair is seen in each comparison. Additionally, considerable similarity appears to exist for the D-G pair and some similarities exist for the A-C pair, at least in the normal paraffin profiles.

Because the pristane/phytane ratio is commonly used for comparisons in the literature, the application to residual oils using this 10% criterion is also of interest. The results from both the GC and GC-MS analyses are shown in Table 5 and suggest cases of high similarity (A-B, D-E, D-G, E-G), partial similarity (B-C), and low similarity (F with all the oils).

Table 5. Pristane/Phytane ratios for residual oils.

Oil	Pristane/Phytane ratio by GC	Pristane/Phytane ratio by GC-MS
A	0.73	0.79
B	0.67	0.79
C	0.65	0.70
D	0.80	0.89
E	0.85	0.90
F	0.99	1.17
G	0.82	0.94

While this kind of comparison gives some good clues as to the similarity of the oil pairs, it is somewhat less than satisfying in that it does not say anything about just how far out of bounds the outliers are or about relative probabilities that oil pair members are from a common source.

In addition to visual comparisons of the chromatograms and considerations of experimental error to account for differences between chromatograms, statistical tests can be made of the similarity of two patterns. For this work we have chosen two tests, the unequal variance t-test and the chi-square test.[12]

The unequal variance t-test can be used to determine the probability that two normally and distributed samples with different variances have the same mean. For the comparisons of this paper, if two oils are the same, except for random sampling and analysis errors, then we might expect the differences between corresponding normalized peak height measurements, expressed as a fraction of the average of the two peak heights and calculated for each n-paraffin, to be distributed essentially randomly about zero. Alternatively, the absolute values of these differences would be distributed from zero to some maximum percent error (say 10%). This distribution can be characterized by a mean and a standard error. For each comparison pair, then, we can calculate this mean and standard error which should give an indication of the extent to which these analyses agree, i.e., the extent to which the oils of this pair are from a common source. Based upon the visual comparison and error discussions above, it is reasonable to assume that oils D and E are the same oils and therefore that these differences, calculated for this pair, can be used to calculate a mean and standard error which is representative of what is to be expected for two that are the same. Then, we can use the differences calculated for this pair to provide a mean error to which the differences for other oil pairs can be compared. The appropriate test for such a comparison is the unequal variance t-test which allows for the possibility of different variances in the data sets. The calculations provide assessments of the relative probability that the members of each oil pair are the same.

A second statistical test for comparing two oils’ profiles is the chi-square test. The form which we have used in this paper is the two bins test which evaluates whether two samplings of data in a number of different categories (bins, in this case peak heights at each carbon number) fit the same distribution pattern (peak profile). In this test a value of chi-square is calculated from which a probability that the two patterns agree is estimated. The probabilities, however, must be interpreted only as relative indications of the likelihood that any pair of oils are the same rather than absolute probabilities. Different from the t-test, this chi-square test does not use the D-E pair to provide a reference degree of similarity. Instead, each pair is evaluated solely on its own merits and used to estimate commonality.

The unequal variance t-test and chi-square probabilities of source commonality also are shown in Table 3 for both the GC-MS and GC n-paraffin profiles. Because the profile differences for the D-E pair were used as a basis of comparison for the other pairs for the t-test, the value calculated for this pair for this test (comparing the D-E pair to itself) is identically unity. The other values in the table are relative statistical probabilities that those pairs are from a common source. Table 4 contains similar results for both the t-test and the chi-square test for the isoprenoid compounds.

A number of conclusions concerning the normal paraffin profiles and oil pair similarities are evident based on these statistical tests. First, the t-test and chi-square test generally are in agreement about the similarity of two oils. If one is high, so is the other and vice-versa. The notable exceptions to this are for the GC chromatograms of the n-paraffin profiles for the A-E and the B-E comparisons. Second, for the GC-MS analyses, we see that the only strongly positive comparison is with the D-E pair. One other comparison shows some degree of similarity, the D-G pair. All other pairs show quite low probabilities in one or both of these statistical tests. Finally, looking at the GC normal paraffin data, it becomes apparent that this analysis is considerably less discriminating than the GC-MS for these refined, unweathered oils in that quite a few of the comparisons produce fairly high probabilities. The D-E pair again shows high similarity, but so also do the A-B, A-D, B-D, A-G, B-E, and perhaps some others. Oil C, whose chromatogram segment is compared to Oil A in Figures 1a and 1b, shows low similarity probabilities with each of the other oils, including A, and in fact, this oil is known to be of a different source than all of the others.

Table 4 shows some similar conclusions for the isoprenoid compounds. Again, for the GC-MS comparisons, the D-E pair shows a high probability of common source, and the D-G pair shows some significant similarities. Also, as for the n-paraffin profiles, the GC calculations show some favorable comparisons where the GC-MS do not. Again, the A-B pair stands out with quite high probabilities. Unlike the n-paraffin profiles, however, the D-G pair and the E-G pair show some significant similarities for the isoprenoid profiles. The A-B pair for the GC-MS isoprenoid results show some degree of similarity by the t-test, but a very low similarity by the chi-square test.

These results show that in order for the members of an oil pair to be considered from a common source, they should appear common by a number of measures such as both the normal paraffin and isoprenoid profiles of GC and GC-MS analyses. If any one of these measures is out-of-bounds or indicates a low probability of commonality, then, in fact, commonality is suspect. This is especially true for refined oils where there is a strong bias towards similar profiles introduced by the processing.

SUMMARY AND CONCLUSIONS

Seven heavy residual oils were analyzed by gas chromatography (GC) and gas chromatography- mass spectrometry (GC-MS) and compared for source identification purposes. Visual comparison of the chromatograms showed general similarity between all of the oils. Because heavy residual oils have undergone processing to remove as much of the lighter, more valuable products as possible, this similarity was not unexpected and necessitated quantitative and statistical comparisons to establish source commonality.

Chromatogram peak height profiles, normalized by the sum of the n-paraffin peak heights, served as useful quantitative measures for comparison. Both n-paraffin and isoprenoid profiles were used. All oil pairs were tested for similarity using three approaches: (1) comparing differences with expected sampling and measurement error, (2) t-test and (3) chi-square test.

Based on these data, several conclusions can be made. First, these three tests, applied to both the GC and GC-MS analyses of n-paraffin and isoprenoid profiles, serve to provide a good feel for pair-comparisons which suggest a common source. Second, they indicate that the GC-MS analysis can be more discriminating than GC for source determination. Third, when comparing refined oils of the same or very similar distillation cut, it is very useful to include several such oils, with some of them of known different source, to help establish similarities which can be introduced by the refining process, and at least one pair of known common source to help evaluate sampling and analysis variability. Finally, the use of several such tests together helps to establish confidence in any conclusions of commonality.

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