

General Disclaimer

One or more of the Following Statements may affect this Document

- This document has been reproduced from the best copy furnished by the organizational source. It is being released in the interest of making available as much information as possible.
- This document may contain data, which exceeds the sheet parameters. It was furnished in this condition by the organizational source and is the best copy available.
- This document may contain tone-on-tone or color graphs, charts and/or pictures, which have been reproduced in black and white.
- This document is paginated as submitted by the original source.
- Portions of this document are not fully legible due to the historical nature of some of the material. However, it is the best reproduction available from the original submission.

**NASA TECHNICAL
MEMORANDUM**

NASA TM -73829

NASA TM -73829

(NASA-TM-73829) HYDROCARBON GROUP TYPE
DETERMINATION IN JET FUELS BY HIGH
PERFORMANCE LIQUID CHROMATOGRAPHY (NASA)
13 p HC A02/MF A01 CSCL 21D

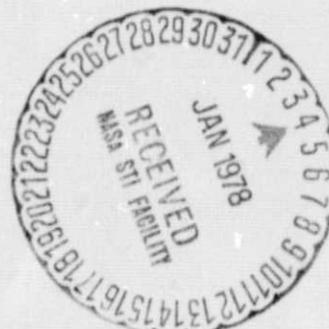
N78-13233

Unclas
55241
G3/28

**HYDROCARBON GROUP TYPE DETERMINATION IN JET
FUELS BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY**

by Albert C. Antoine
Lewis Research Center
Cleveland, Ohio 44135

TECHNICAL PAPER presented at the
Fourth Annual Meeting of the Federation of
Analytical Chemistry and Spectroscopy Societies (FACSS IV)
Detroit, Michigan, November 7-11, 1977



HYDROCARBON GROUP TYPE DETERMINATION IN JET FUELS

BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY

by Albert C. Antoine

National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135

ABSTRACT

Results are given for the analysis of some jet and diesel fuel samples which were prepared from oil shale and coal syncrudes. Thirty-two (32) samples of varying chemical composition and physical properties were obtained. Hydrocarbon types in these samples were determined by fluorescent indicator adsorption (FIA) analysis, and the results from three (3) laboratories are presented and compared. Recently, rapid high performance liquid chromatography (HPLC) methods have been proposed for hydrocarbon group type analysis, with some suggestion for their use as a replacement of the FIA technique. Two of these methods were used to analyze some of the samples, and these results are also presented and compared. Two samples of petroleum-based Jet A fuel are similarly analyzed.

INTRODUCTION

The usual way that aromatics content of fuels is determined is by the ASTM D1319 FIA (Fluorescent Indicator Adsorption) analysis (ref. 1). This method covers the determination of saturates, nonaromatic olefins, and aromatics in petroleum fractions that distill below 589 K (600^o F). It is routinely used in analyzing jet fuels to determine if specifications are being met. Recently, there has been concern expressed about the applicability of the method to fuels other than gasolines, for which the

method was developed. There is also concern that the dyes being used as indicators today are not completely comparable to those used many years ago when the method was developed, and further, may vary from lot to lot. These concerns need added consideration as we plan the use of broad-specification jet fuels and jet fuels prepared from alternate sources. Broad specification fuels may include fuels with higher final boiling points than now used, and fuels with both higher final boiling points and lower initial boiling points. Fuels from alternate sources may include varying concentrations of constituents that may affect the dyes differently. With the development of HPLC (High Performance Liquid Chromatography), suggestions are being made that this technique can be used effectively to separate hydrocarbon group types in fuels. Several separation schemes have been proposed and are under development. A recent publication (ref. 2) presents an analytical liquid chromatographic method for analyzing gasoline-range materials 333 to 544 K (140° to 520° F) for their group types: saturates, olefins and aromatics. This rapid HPLC method is proposed as an alternative for the FIA method. And, although a typical jet fuel has a higher boiling range than the usual gasoline, the method is still applicable. Another publication (ref. 3) shows a quantitative hydrocarbon type analysis of middle distillate petroleum products, with special emphasis on straight-run (olefin-free) diesel fuels. The purpose of this effort was to have a number of jet fuel samples prepared from oil shale and coal syncrude oils (ref. 4), analyzed by these two HPLC methods and compared to the results of the conventional FIA method. The fuel samples had been prepared to meet certain yield and specification requirements. The sample properties which were varied on a controlled basis were boiling range and percent hydrogen and nitrogen. Aromatics content and percent sulfur also varied as a result. The amount of jet fuel produced from a given amount of syncrude was also varied. Thus, some samples contained material which had been obtained by hydrocracking of the heavier syncrude fractions.

The samples, thirty-two (32) in number, approximated either a JP -4,

JP-5, Diesel No. 2 fuel, or a wide boiling range fuel incorporating the volatility of a JP-4 and the end point of a Diesel No. 2. They were each analyzed by the FIA technique by three (3) laboratories, ARCO, NASA-Lewis, and the Gulf Research and Development Co. They were also analyzed by the Gulf Co. using its HPLC method (ref. 2). The U.S. Army Fuels and Lubricants Research Laboratory (AFLRL) used its HPLC method to analyze sixteen (16) of the samples, those approximating the JP-5 and Diesel No. 2 type fuels. The samples were submitted to the two laboratories for HPLC analyses by their routine techniques, without any special attention being asked or given. Two commercially available petroleum-based Jet A samples were similarly analyzed.

ANALYTICAL METHODS AND PROCEDURES

FIA (Fluorescent Indicator Adsorption) Method ASTM D 1319

This method has been the standard in the petroleum industry for several years for determining saturates, nonaromatic olefins, and aromatics. Its limitations are recognized. Aromatic olefins, some diolefins, and compounds containing sulfur, nitrogen, or oxygen are determined as aromatics. High saturate values and low aromatic and olefin values may result if samples containing significant amounts of C_5 and lighter hydrocarbons are not depentanized. Further, dark materials sometimes require distillation to remove interfering colored compounds. The procedure is as follows:

"Approximately 0.75 ml of sample is introduced into a special glass adsorption column packed with activated silica gel. A small layer of the silica gel contains a mixture of fluorescent dyes. When all the sample has been adsorbed on the gel, alcohol is added to desorb the sample and force it down the column. The hydrocarbons are separated according to their adsorption affinities into aromatics, olefins, and saturates. The fluorescent dyes are also separated selectively, with the hydrocarbon types, and make the boundaries of the zones visible under ultraviolet

light. The volume percentage of each hydrocarbon type is calculated from the length of each zone in the column." The time for a typical analysis is at least one hour.

Gulf Research and Development Company HPLC Method

The sample is injected directly into the chromatograph by means of a three-microliter shaft injection valve. The column is a 4 mm × 30 cm stainless steel tube packed with 10 μ m silica gel. A mobile phase of low solvent strength and low refractive index (n-hexane) is used at a flow rate of 3.5 ml min⁻¹. After the saturates and olefins elute, the aromatics are then eluted as a single peak by backflushing the column at a predetermined time. The result of backflushing is to make the analysis time shorter and quantitation more accurate. Further, the system is calibrated with a blend of aromatics approximating that found in a typical gasoline. A blend of monoaromatics is used since their refractive indices are relatively constant (over the range of C₆-C₁₂ benzenes). Only cyclodiolefins will be eluted with the aromatics, with olefins and diolefins separated sharply from both the aromatics and the saturates. This separation is an advantage when samples of varying olefin type and amount are being analyzed, since the olefin boundaries are difficult to determine in the FIA method. For jet fuels, the olefin content is usually small, and the lower limit of detectability by this method was determined to be 0.5 percent. An exception to the statement above about the sharp separation of olefins must be noted. Low boiling olefins, pentene -1 and lower, will elute with the saturates. But, since the concentration of these compounds is very low, little error is encountered. Also, it should be noted that samples containing C₅ and lighter hydrocarbons need not be depentanized before analysis in this method. The total time for an analysis is about ten minutes.

U. S. Army Fuels and Lubricants Research Laboratory HPLC Method

This method was developed to give quantitative hydrocarbon type analysis of middle distillate petroleum products, with emphasis on straight run (olefin-free) diesel fuels. The detection limit for olefins under the experimental conditions is about one percent. It was shown with model compounds that saturate, olefinic, and aromatic hydrocarbons could be separated over 37-75 μm or over 10 μm particle size silica gel adsorbents with no cross-contamination of fractions. In the absence of olefins, the method was developed to give two fractions, saturates, and aromatics plus polar compounds. The intent then was to find a representative sample for the saturate portions of these fuels and use it as a reference standard for comparison with the total fuels' saturate fraction. This proved to be unsatisfactory, and thus an attempt was made to obtain a response factor that could be used for all fuels within the same boiling range by averaging the results from several preparatively cut saturate fuel fractions. This also was unsatisfactory, and it was concluded that, "(the) best data were obtained when the saturate fraction of each fuel was cut by preparative scale HPLC and response from this fraction was compared to that of the neat fuel." This procedure thus was followed in the analysis of the fuels in this report. Each of the samples was separated into a saturated paraffinic and an aromatic/polar fraction by preparative scale HPLC over 35-75 μm particle size silica gel. The saturated compounds were eluted by hexane, while the second fraction was recovered by methylene chloride backflush. The response factor was determined on each of the separated paraffinic fractions and compared to the response of the respective complete fuel using 10 μm particle size silica gel.

RESULTS AND DISCUSSION

The results for the aromatics determination are given in Table 1, a-i. In columns 2, 3, and 4, are the FIA values reported by three laboratories, ARCO, NASA-Lewis, and Gulf. Column 5 gives the

maximum difference found in the three values. The reproducibility expected in the ASTM D1319 test method is shown in column 6. This value is the maximum difference allowed before the results from two laboratories should be considered suspect. In columns 8 and 11, respectively, are the HPLC results obtained by the Gulf and AFLRL methods, with columns 9 and 12 giving the difference between these values and the average FIA value. Columns 10 and 13 give the percent difference from the average FIA value. In Table I(a), the results for the fuel samples prepared from shale oil, with a nominal boiling range of 394 to 561 K (250⁰ to 550⁰ F) are given. The level of aromatics in these samples, determined by FIA, ranged from about 22 percent down to about 13 percent. In all instances, the maximum difference in values from the three laboratories using the FIA method was less than the reproducibility value given by the ASTM, so that the values should not be considered suspect. The values for aromatics obtained by the HPLC methods were in all instances greater than the values found by FIA. It can be seen that some values differed from the FIA average by less than the reproducibility value, but most did not. On a percentage basis, the Gulf values ranged from about 10 percent to about 36 percent above the average FIA value, while the AFLRL values ranged from about 20 percent to about 36 percent higher. In 3 of the 4 cases, the AFLRL value was higher than the Gulf value. A comparison of the values is shown in figure 1(a), with the HPLC values plotted against the FIA averages. Included in the plot are the results from the petroleum samples (described in Table 1(e)). It can be seen that, in contrast to the petroleum samples, and as noted above, the HPLC values were consistently higher than the FIA average. In Table 1(b), the values for shale oil derived fuel samples with a nominal boiling range of 394 to 616 K (250⁰ to 650⁰ F) are given. In this set, there were 2 values obtained by FIA analysis that were discounted since they seemed obviously to be in error. These are shown in parenthesis. With those values discounted, the maximum difference of all the others were within the allowed reproducibility. In this set, the Gulf HPLC values were closer to the FIA average values, ranging from

about 10 percent below to four percent above. The AFLRL values were again substantially higher, ranging from about 10 percent to 30 percent above the FIA average value. The comparison for these values are shown in figure 1(b).

The results from the fuel samples derived from a coal syncrude and having a nominal boiling range of 394 to 561 K (250⁰ to 550⁰ F) are given in Table 1(c). In this set, the levels of aromatics content are quite different, with two values below 10 percent and two around 30 percent. One FIA value was discounted. The remaining values fell within the allowable ASTM reproducibility. In regard to the HPLC results, the Gulf values were all higher than the FIA values, ranging from about 10 to about 20 percent above the FIA average. The AFLRL values for higher aromatics content are rather close though lower than the FIA average, while the lower content values were about 30 percent higher than the FIA average. The results are also shown in figure 1(c), with the values for the petroleum samples added. As noted, the coal samples differ considerably in their aromatics content, but the scatter in the data is no greater than previously noted.

The fuel samples with the boiling range from 394 to 616 K (250⁰ to 650⁰ F) (table 1(d)) had aromatic levels comparable to the set (1(c)) above, with two samples about 10 percent and two about 30 percent. In one instance, the difference in values for the FIA analysis fell outside of the allowed reproducibility value. The HPLC values from the Gulf method were relatively close to the FIA averages, ranging from about 10 percent below to a like number above; also, three of the difference values were less than the reproducibility value. The AFLRL results also ranged above and below the FIA average, but not for the same samples. The high aromatics content values were about 15 percent below the FIA average, while the low content values ranged up to 30 percent above the average. A comparison of the FIA average and the HPLC values is shown in figure 1(d). The results are about comparable to those shown in figure 1(c).

The results for the two petroleum samples are shown in table 1(e). The boiling ranges, as determined by ASTM D86 test, are given. Only two FIA determinations were made, and the values agreed rather well. The HPLC results were varied, but consistent. The Gulf values were both low, about 20 percent below the FIA average, while the AFLRL values were within a few percent of the average, above and below.

Table 1(f) gives the results for the fuels prepared from shale which approximated a JP-4 type fuel. The level of aromatics in these samples ranged from about 18 percent down to about 11 percent. In all instances, the maximum difference in FIA values from the three laboratories was less than the reproducibility value. The HPLC values were all higher than the FIA average, and only one difference less than the reproducibility value. The comparison is shown in figure 1(f). In Table I(g), the wide boiling range fuel results are given. In this group, two FIA values are questioned. For the last sample, the difference in maximum and minimum value is larger than the allowable reproducibility. With these exceptions noted, the remaining values are, for the most part, rather close to the HPLC values. This is reflected in the comparison plot shown in figure 1(g). Tables I(h) and (i) give the results for the similar fuels prepared from coal syncrudes. It should be noted again that each group has a pair of relatively low aromatics content fuels and one pair with considerably higher aromatics content. In Table I(h) two values for the maximum difference are larger than the reproducibility, while in Table I(i), one value is larger. It can be seen that the HPLC values are all larger than the FIA averages, though for all of the low aromatics content fuels, the differences are rather small. The HPLC values for the higher aromatics content fuels in Table I(h) were about 20 percent greater than the FIA average, while those in Table I(i) were about 15 percent higher. A comparison of the FIA average and the HPLC values is shown in figures 1(h) and (i).

Each of the HPLC methods detected no olefins, so that we assume that they are present at less than one percent concentration. The saturates concentration, then, in the fuels is the difference from 100 of

the aromatics value given in the table. It should be noted again, though, that in the AFLRL method it is the saturates fraction that is measured and the aromatics obtained by difference.

CONCLUDING REMARKS

The purpose of this report is to compare the results of the conventional FIA analysis with those from some recent HPLC methods. In so doing it was recognized that the FIA method was being used with some samples whose final boiling point exceeded the limit given in the test method. This appeared not to cause a problem, though it was noted that the maximum-minimum differences in the aromatics determination for the higher boiling sets were somewhat greater than those for the lower boiling sets. However, again excluding those values that appeared to be completely in error, the values with few exceptions were within the reproducibility value given. Thus, using the average FIA value and also using the allowable reproducibility value as a measure, we can compare these results with the results from the HPLC methods. We observe that for JP-5 and diesel No. 2 fuels prepared from shale that the HPLC values are all higher, though with about one-half of them, the difference is less than the reproducibility value. For the JP-5 and diesel fuels prepared from the coal syncrudes, again about one-half of the HPLC values differ by less than the reproducibility value, but the seeming 'trend' toward higher values is no longer evident, with several values being lower than the FIA value. For the JP-4 type fuels prepared from shale and from coal, all of the HPLC values were higher with less than one-half of them differing by less than the reproducibility value. This 'trend' toward consistently higher values is again not evident with the wide boiling range fuels, with more than one-half differing by less than the reproducibility value and not all being higher than the FIA average value. With no constant differences showing between the FIA and HPLC methods, no firm conclusions can be reached. Detailed analyses of fuel composition, and measurements of known mixtures will help determine the accuracy of

these methods and indicate when they differ, which of them is correct. The results indicate, though, that a rapid (10 min) determination of the aromatics content could be made with HPLC and a value obtained which would differ no more than 35 percent from the FIA value.

REFERENCES

1. Hydrocarbon Types in Liquid Petroleum Products by Fluorescent Indicator Adsorption. Am. Soc. Test. Mater. Stand. D1319-70 (Reapproved 1975), 1975.
2. Suatoni, J. C.; Garber, H. R.; and Davis, B. E.: Hydrocarbon Group Types in Gasoline-Range Materials by High Performance Liquid Chromatography. J. Chromatogr. Sci., vol. 13, no. 8, Aug. 1975, pp. 367-371.
3. Fodor, George E.; and Newman, Frank M.: The Application of High-Performance Liquid Chromatography to the Analysis of Petroleum Materials. Part 2. Quantitative Hydrocarbon-Type Analysis. Final Report, Southwest Research Inst., 1975. (AFLRL-63, AD-A014995.)
4. Gallagher, J. P.; et al.: Synthesis and Analysis of Jet Fuel from Shale Oil and Coal Syncrudes. (M1. 76-1, Atlantic Richfield Co.; NASA Contract NAS3-19747.) NASA CR-135112, 1976.

ORIGINAL PAGE IS
OF POOR QUALITY

TABLE I. - AROMATICS DETERMINATION BY FIA AND HPLC METHODS

	Aromatics, volume percent											
	FIA						HPLC					
	ARCO	Lewis	Gulf	Maximum difference	Reproducibility, ASTM D1319	Average	Gulf			AFLRL		
							Gulf	Gulf-FIA average	$\frac{\text{Gulf-FIA}_{av}}{\text{FIA}_{av}} \times 100$	AFLRL	AFLRL-FIA average	$\frac{\text{AFLRL-FIA}_{av}}{\text{FIA}_{av}} \times 100$
a. Shale 394-561 K (250 ^o -550 ^o F)	22.2 17.1 17.9 13.2	21.4 14.6 17.3 12.8	21.5 15.5 17.5 13.5	0.8 2.5 .6 .7	3.2 3.2 3.2 2.4	21.7 15.7 17.6 13.2	25.0 21.3 19.3 15.3	3.3 5.6 1.7 2.1	15.2 35.7 9.7 15.9	29.4 20.8 22.4 15.8	7.7 5.1 4.8 2.6	35.5 32.5 27.3 19.7
b. 394-616 K (250 ^o -650 ^o F)	25.9 17.4 20.3 15.4	23.8 18.1 18.5 14.6	(39.0) 16.0 (38.0) 14.5	2.1 2.1 1.8 .9	3.7 3.2 3.2 3.2	24.9 17.2 19.4 14.8	23.9 17.9 20.1 13.2	-1.0 .7 .7 -1.6	-4.0 4.0 3.6 -10.8	27.6 21.3 25.2 18.0	2.7 4.1 5.8 3.2	10.8 23.8 29.9 21.6
c. Coal 394-561 K (250 ^o -550 ^o F)	30.9 5.8 7.2 25.2	31.4 6.6 6.4 27.6	30.5 5.5 7.5 (11.5)	0.9 1.1 1.1 2.4	3.7 1.7 1.7 3.7	30.9 6.0 7.0 26.4	35.9 7.1 7.8 30.3	5.0 1.1 .8 3.9	19.1 18.3 11.4 14.8	26.0 8.1 9.2 26.1	-1.9 2.1 2.2 -.3	-6.1 35.0 31.4 -1.1
d. 394-616 K (250 ^o -650 ^o F)	33.8 6.7 11.6 28.5	36.3 7.4 9.2 27.4	33.5 6.0 17.5 31.0	2.8 1.4 4.3 3.6	3.7 2.4 2.4 3.7	34.5 6.7 11.4 21.0	38.6 7.3 10.4 30.2	4.1 .6 -1.0 1.2	11.9 9.0 -8.8 4.1	29.3 8.7 11.5 25.2	-5.2 2.0 1 -3.8	-15.1 29.8 .9 -13.1
e. Petroleum Jet A Boiling range 380-535 K (225 ^o -504 ^o F) 411-531 K (280 ^o -496 ^o F)		21.4 17.2	21.0 17.5	0.4 .3	3.2 3.2	21.2 17.4	17.6 13.4	-3.6 -4.0	-17.0 -23.0	21.3 16.4	0.1 -1.0	0.5 -5.7
f. Shale IBP-561 K (IBP-550 ^o F)	19.0 13.5 13.7 11.4	18.8 14.1 13.9 11.6	17.5 12.5 13.0 9.5	1.5 1.6 .9 2.1	3.2 2.4 2.4 2.4	18.4 13.4 13.5 10.8	22.9 17.4 16.7 13.1	4.2 4.0 3.2 2.3	22.8 29.9 23.7 21.3			
g. IBP-616 K (IBP-650 ^o F)	21.9 13.7 15.7 12.1	21.2 13.6 18.1 14.3	(30.5) 13.5 (27.5) 10.5	0.7 .2 2.4 3.8	3.2 2.4 3.2 2.4	21.6 13.5 17.9 12.3	21.6 16.3 16.0 13.4	0 2.7 -.9 1.1	0 19.9 -5.3 8.9			
h. Coal IBP-561 K (IBP-550 ^o F)	26.3 5.5 5.4 20.1	27.5 6.5 5.9 23.1	26.5 4.5 5.0 19.5	1.2 2.0 2 3.6	3.7 1.7 1.7 3.2	26.8 5.5 5.4 20.9	33.0 5.9 6.3 24.7	6.2 4 9 3.8	23.1 7.2 16.7 18.2			
i. IBP-616 K (IBP-650 ^o F)	29.7 5.9 9.3 22.4	26.3 7.6 8.5 23.8	28.5 5.0 7.5 21.5	1.3 2.6 1.8 2.3	3.7 1.7 2.4 3.2	29.3 6.2 8.4 22.9	33.8 6.3 8.8 26.3	4.5 3 4 3.7	15.4 4.8 4.8 16.4			

() Discounted from average and difference.

COMPARISON OF AROMATICS CONTENT

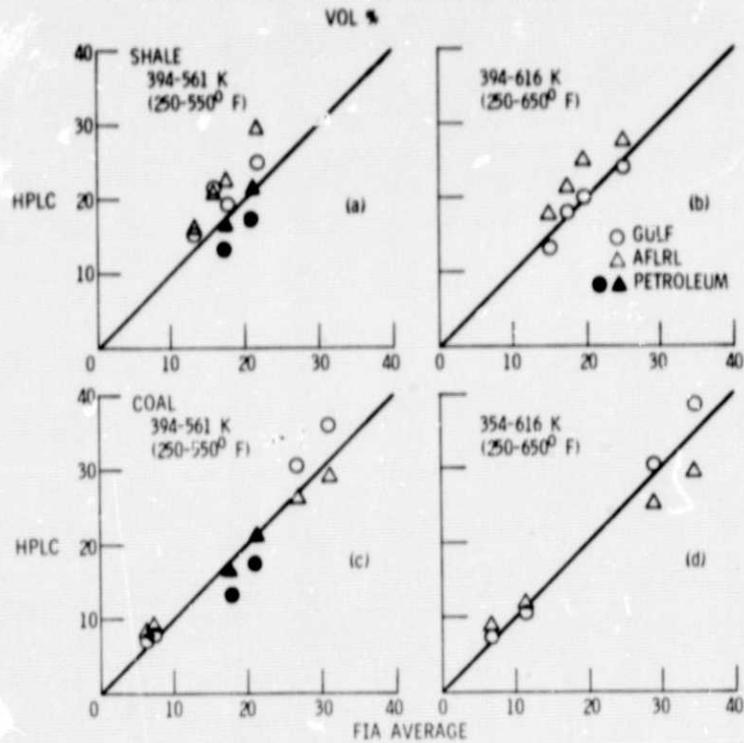


Figure 1.

COMPARISON OF AROMATICS CONTENT

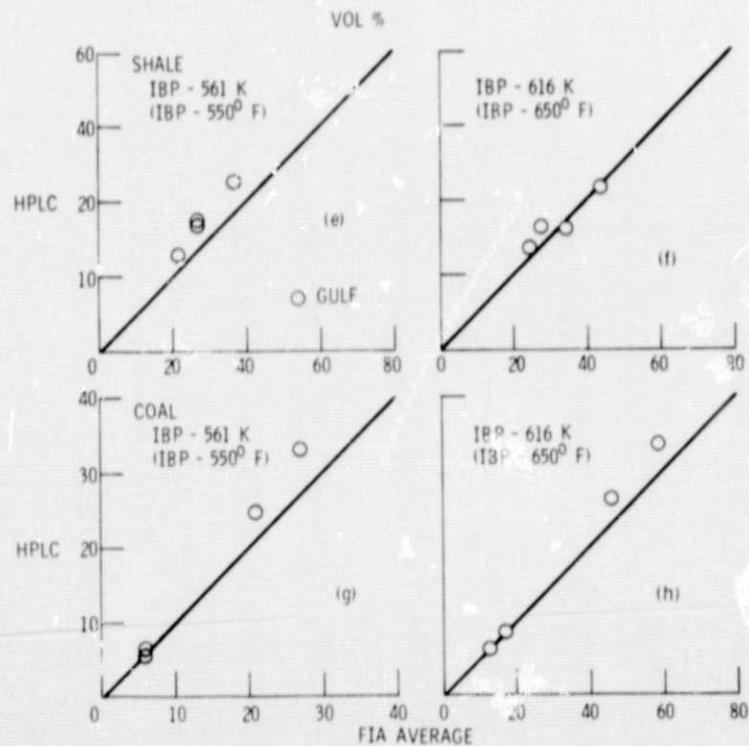


Figure 1. - Concluded.