Fluorescent Indicator Adsorption Method for Hydrocarbon Type Analysis

Application to Traces and to Heavier Distillates

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The saturated, olefinic, and aromatic component types in lighter petroleum distillates are commonly determined by the fluorescent indicator adsorption (FIA) method in which a small sample is passed through a long narrow chromatographic column, and the composition is computed from the lengths of the zones. This simple method has been extended to the determination of hydrocarbon types in smaller than normal concentrations, and to the analysis of cracked gas oils and lubricating oils. For the determination of small quantities —0.1 to about 3%—of one type in the others, the pertinent zone developed by the usual procedure is too short to measure. This was circumvented by using a larger charge of measured volume and calculating the concentration of the trace by means of a calibration factor. Analysis of heavier distillates was accomplished by alteration of column dimensions, addition of a special dye, and dilution of the heaviest oils to reduce their viscosity.

IN 1948 Conrad (*2*) rendered the aromatic portion of gasoline in a chromatographic column visible in ultraviolet light by addition of a small amount of a fluorescent dye, whereby the aromatic content could be obtained simply by linear measurement. In 1951 Criddle and Le Tourneau (*3*) improved and extended the fluorescent indicator (FIA) method by using dyes which also marked the olefinic portion. Thus an excellent analytical tool was made available to the petroleum industry. By this means the concentrations of total saturates, total olefins, and total aromatics can be determined in gasolines, jet fuels, and kerosines more reliably and more simply than by any other routine procedure. (The aromatics aggregate includes olefinic aromatics which are classified as aromatics, together with sulfur, nitrogen, and oxygen compounds.) The method has found widespread use, and has been tentatively adopted by the American Society for Testing Materials (*1*). In principle, it operates as follows:

A small glass adsorption column with long narrow extension is packed with fine activated silica gel, a minute portion of which has been dyed with a fluorescent dye mixture. Approximately 0.75 ml. of sample is introduced and eluted with alcohol under pressure. The hydrocarbons separate according to their adsorption affinities into saturates, olefins, and aromatics, in that order, followed by the alcohol. The fluorescent dyes are also selectively adsorbed and appear at the boundaries of the hydrocarbon zones where they are visible under ultraviolet light. The volume per cent of each hydrocarbon type is computed from the length of each zone in the long narrow extension of the column, and of the sum of the zones, representing the whole sample. Results obtained with gasolines, jet fuels, and kerosines are usually accurate to ±1 or 2%, and 12 to 15 analyses can be completed in 8 hours.

In the present paper extensions of the scope of the FIA method are presented. Thus, with certain limitations, it has been made applicable to the determination of "trace" quantities of one hydrocarbon type in the others as well as to the analysis of heavier distillates.

HYDROCARBON TYPE ANALYSIS FOR TRACES

No reliable routine method has been available for the determination of relatively small quantities, in the order of 0.1 to 3%, of one of the hydrocarbon types in the others. It was therefore desirable to try to extend the FIA method to the analysis of materials like odorless kerosine and petroleum-derived aromatics, which contain predominantly one hydrocarbon type with traces of others. Moreover, by applying such a "Trace-FIA" method to the hydrocarbon-type aggregates, isolated by large scale development chromatography, slight overlapping of one type into another can readily be detected and accounted for.

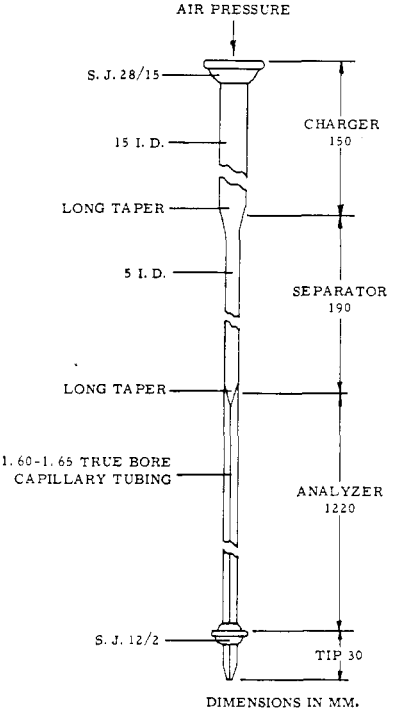

Figure 1. Fluorescent indicator adsorption column for lighter distillates

With the regular FIA method, as outlined above, the zone length of a hydrocarbon type present in very small concentration is too short for accurate measurement. The zone can be made longer by merely increasing the sample charge; but then the length of the zone in question cannot be related to the zone length of the total sample because the latter now more than fills the narrow extension of the column in which the measurements are made. However, this difficulty can be overcome by relating the volume of the liquid in the zone in question to the measured volume of the sample charge. The volume of the zone is obtained from its length by calibration of the packed column's long narrow extension made from true-bore capillary tubing.

The simplest form of trace analysis is represented by the cases where the type to be determined is more strongly adsorbed than

the rest of the sample—for instance, traces of aromatics and of olefins in saturates. A sample, larger than employed in the regular FIA analysis, is charged to the column, and the pertinent zone is measured and converted to volume as mentioned above. When the type to be determined is less strongly adsorbed than the rest of the sample, on the other hand, it is necessary first to pass the sample through a larger auxiliary column in which the weakly adsorbed trace material is allowed to develop and form a concentrate at the liquid front. The collected concentrate is then analyzed in the FIA column.

METHOD FOR TRACES

Apparatus and Materials. FIA Column for Lighter Distillates, consisting of a charger section, a separator section, and an analyzer section (long narrow extension), as shown in Figure 1. The analyzer section is made of true-bore capillary tubing of 1.60- to 1.65-mm. inner diameter. (Precision requirement for true-bore: 0.3-mm. maximum variation in the length of an approximately 100-mm. thread of mercury at several locations.) This column is also used for general hydrocarbon-type analyses of lighter distillates. It deviates from the original column in design (*3*) by elimination of the short capillary section between the charger and the separator sections, as superfluous; replacement of standard tubing in the analyzer section by true-bore tubing (permanently sealed on) to improve accuracy; and addition of a removable tip at the end of the column for convenience in inserting and removing the cotton plug which retains the adsorbent in the column.

Concentration Column as shown in Figure 2.

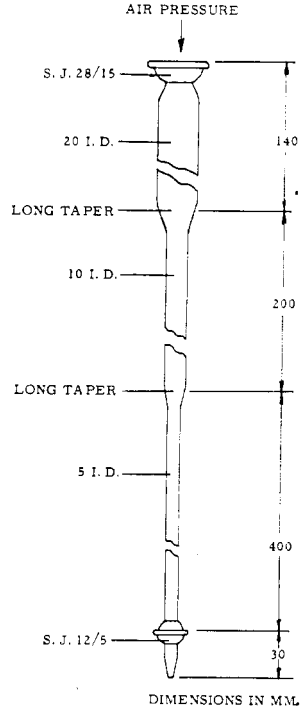

Figure 2. Concentration column

The columns should be mounted in a darkroom. A pipe manifold with a series of inner spherical joints for the columns and a series of meter rules placed adjacent to the analyzer sections makes a convenient arrangement. To facilitate the readings, every centimeter division on the rule may be marked with luminous paint, or the rule may be equipped with movable metal clips with similarly painted tips.

Concentrate Receiver, graduated at 0.5 and 0.6 ml., as shown in Figure 3.

Vibrator for packing of the silica gel. A small rubber-padded massage machine is satisfactory.

Ultraviolet Light Source. Radiation predominantly at 3660 A. A convenient arrangement consists of one or two 36-inch "black light" units mounted vertically along the apparatus.

Hypodermic Tubing for column cleaning; 19 stubs gage, about 90 cm. long, connected to tap water.

Silica Gel, grade 923 (100 to 200-mesh) from Davison Chemical Corp., Baltimore 3, Md.

Dyed Silica Gel. The "dye mixture for the FIA method of hydrocarbon type analysis," supplied by Patent Chemicals, Inc., Paterson, N. J., consists of a yellow-green-fluorescent olefin marker, a blue-fluorescent aromatic marker, both of petroleum origin, and a nonfluorescent red dye, Sudan III, as alcohol marker. It has been found advantageous, however, to amplify the latter by including Ethyl Red.

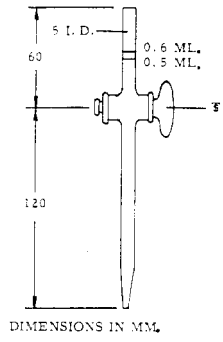

Figure 3. Concentrate receiver

While this dye mixture may be added to the sample, it is more convenient to affix it to a very small portion of the adsorbent, and insert the latter in the column. A supply of dyed silica gel is prepared by stirring 0.4 ml. of Patent Chemical's FIA dye mixture plus 7 mg. of Ethyl Red into 80 ml. of silica gel slurried in acetone, and evaporating the latter. A little acetone remaining does not interfere with the analysis. This quantity will suffice for about 1000 determinations. The dyed gel should be stored in the dark, as the aromatic marker will deteriorate in the light.

Isopropyl Alcohol refined 99%, hydrocarbon-free.

Pressuring Gas. Air (or nitrogen), delivered to the top of the column at a regulated pressure up to 15 pounds per square inch.

The column for lighter distillates, vibrator, ultraviolet light source, hypodermic tubing, and silica gel, dyed silica gel, isopropyl alcohol, and pressuring gas apply also to the regular method of analysis for hydrocarbon types in lighter distillates (gasolines, jet fuels, and kerosines).

Procedure. Column Calibration. Put a piece of cotton in the tip of the FIA column (Figure 1) and pack it with silica gel, applying the vibrator as needed, until the separator section is about half full. Add a 3- to 5-mm. layer of dyed gel and continue vibrating and adding gel until it extends about 40 mm. into the charger section.

By means of a pipet introduce 0.50 ± 0.02 ml. of a hydrocarbon, such as iso-octane, and apply a pressure of 2 to 5 pounds per square inch until the sample is just absorbed. Cover with an approximately 15-mm. layer of additional gel (to prevent intermixing), and fill the charger section with isopropyl alcohol. Apply a pressure of 5 to 10 pounds per square inch, and when the red alcohol front has advanced about 300 mm. into the analyzer section, measure the hydrocarbon zone ahead of the alcohol in ordinary light. (For zone reading see below.)

Release the pressure, disconnect the column, and remove the used gel by inverting the column above a sink and rinsing with water from the inserted hypodermic tubing. Rinse with acetone or alcohol and dry.

Calculate the calibration factor, F, as follows:

$$F = \frac{50}{\text{zone, mm.}}$$

(With the prescribed column and silica gel F = ca. 0.11.)

The procedure for analysis is divided into three parts according to the nature of the hydrocarbon type to be determined in traces.

1. Aromatics and/or Olefins in Saturates (one-column operation). Pack the FIA column (Figure 1) as described above.

Add by means of a pipet 5 ± 0.10 ml. of sample if the content of hydrocarbons to be determined is 1% or less, or 2 ± 0.05 ml. if it is greater than 1%, and apply a pressure of 2 to 3 pounds per square inch until the sample is absorbed. Cover with an approximately 15-mm. layer of additional gel, and fill the charger with isopropyl alcohol. Apply a pressure of 10 to 15 pounds per square inch; if olefins are present, their front will be sharper if the pressure is reduced to 3 pounds per square inch when the red alcohol front enters the analyzer section. When this front has advanced about 300 mm. further, take readings as directed below. (Collect the bulk of the saturates in a convenient receptacle, and discard.)

2. Saturates and/or Olefins in Aromatics (two-column operation). Pack the concentration column (Figure 2) with silica gel to about 25 mm. in the widest (top) section, omitting the dyed gel.

Add by means of a pipet 5 ± 0.10 ml. of sample if the content of hydrocarbons to be determined is 1% or less, or 2 ± 0.05 ml. if it is greater than 1%, and apply a pressure of 1 pound per square inch until the sample is absorbed. Cover with an approximately 15-mm. layer of additional gel, fill with isopropyl alcohol, and resume the pressure. Collect in the concentrate receiver (Figure 3) between 0.5 and 0.6 ml. of the first effluent, which represents a concentrate of the saturates and/or the olefins.

Transfer the concentrate to the packed FIA column, washing it in with a little alcohol, and proceed with the adsorption as above, but under a pressure of 3 to 5 pounds per square inch only. Read the saturates and/or olefins zone as directed below.

3. Olefins in Saturates Plus Aromatics (two-column operation). Pack the concentration column (Figure 2) as for saturates and/or olefins in aromatics, but insert an approximately 1-mm. layer of dyed gel in the middle section.

Proceed as above, but discard the saturates, and, in ultraviolet light, collect in the concentrate receiver 0.5 to 0.6 ml. of effluent. This will include the olefins, beginning just before the yellow-green zone appears and ending beyond the beginning of the blue zone. Transfer the concentrate to the packed FIA column and continue as for aromatics and/or olefins in saturates, but under a pressure of 3 to 5 pounds per square inch only.

4. Zone Reading and Calculation. The following directives for reading of the zones apply to the FIA method in general; in the case of trace FIA, the predominant hydrocarbon types are disregarded.

Measuring in ultraviolet light, the saturates extend from the colorless liquid front to the lowest point of maximum yellow-green fluorescence, the olefins extend from there to the lowest point of strong blue fluorescence, and the aromatics from there to the highest point of strong red or reddish brown color, the latter being best observed in ordinary light. Quickly mark the boundaries with a glass-writing pencil, or by means of movable metal clips on the meter rule, mounted close to the analyzer section. Take additional readings at 50- to 100-mm. intervals until repeatable measurements are attained. If a zone is only 1 or 2 mm. long, consider the pertinent hydrocarbon type as absent.

Calculate the trace hydrocarbon content for each type as follows:

$$\text{Trace hydrocarbon type, vol. \%} = F \frac{\text{zone, mm.}}{\text{sample, ml.}}$$

where F is the column calibration factor.

APPLICATIONS AND RESULTS

The method is applicable to lighter petroleum distillates when the hydrocarbon type present in traces is more strongly adsorbed than the predominant type. The analysis is carried out in one column and requires 2 to 5 hours of elapsed time, depending on the size of the sample, or about 0.5 hour of operating time.

When the hydrocarbon type present in traces is less strongly adsorbed than the predominant type, on the other hand, the method is applicable to simple mixtures only. Concentration of the trace material is required, and this analysis is therefore carried out with two columns and takes 4 to 5 hours of elapsed time or about 1 hour of operating time.

Examples of analyses of the first category are given in Table I. The samples represent known blends of saturates, olefins, and aromatics aggregates, isolated from a gasoline and a kerosine by large scale elution development chromatography. As may be seen from this table, the accuracy obtained is within ±0.05% for values below 0.5% and within ±0.10% for higher concentrations.

Table I. Determination of Traces of Hydrocarbon Types

(Petroleum distillates)

Main Constituents	Traces, Volume %: Known[a] Aromatics	Known[a] Olefins	Found Aromatics	Found Olefins	Error, Volume %: Aromatics	Error, Volume %: Olefins
Gasoline saturates	1.00	1.00	0.97	0.92	−0.03	−0.08
	1.00	1.00	0.99	1.01	−0.01	+0.01
	0.40	0.40	0.36	0.40	−0.04	0.00
	0.10	0.10	0.13	0.13	+0.03	+0.03
	0.50	..	0.46	..	−0.04	..
	..	0.40	..	0.40	..	0.00
Gasoline olefins	0.40	..	0.36	..	−0.04	..
Kerosine saturates	1.94	..	2.00	..	+0.06	..
	1.94	..	1.94	..	−0.04	..
	0.49	..	0.45	..	+0.01	..
	0.49	..	0.49	..	0.00	..

[a] Blends made from type aggregates isolated by large scale development chromatography.

Examples of analyses of the second category are given in Tables II and III; the reliability is about the same as above. Attempts to determine traces of saturates in olefins were not successful, but whether this is due to incomplete type separation or to inadequate marking of the olefin front by the dye is not known.

Table II. Determination of Traces of Saturates and Olefins in Aromatics

(Simple mixtures)

Sample	Traces, Volume %: Known Saturates	Known Olefins	Found Saturates	Found Olefins	Error, Volume %: Saturates	Error, Volume %: Olefins
Reference toluene	..	..	0.00	0.00	0.00	0.00
Iso-octane in ref. toluene	0.27	..	0.27	..	0.00	..
Methylcyclohexane in ref. toluene	0.33	..	0.27	..	−0.06	..
Diisobutylene in benzene, C.P.	..	0.40	0.28[a]	0.35	..	−0.05

[a] Apparently the benzene contained some saturates as impurity.

Table III. Determination of Trace of an Olefin in a Saturate-Aromatic Mixture

Sample	Trace, Volume %: Known	Trace, Volume %: Found	Error, Volume %
Diisobutylene in iso-octane and benzene	1.00	1.07	+0.07

Table IV. Applicability of Trace FIA Method

Trace Type	Predominant Type	Material	Procedure No.	No. of Columns
Aromatics	Saturates	Lighter distillates	1	1
	Olefins	Lighter distillates	1	1
	Saturates plus olefins	Lighter distillates	1	1
Olefins	Saturates	Lighter distillates	1	1
	Aromatics	Simple mixtures	2	2
	Saturates plus aromatics	Simple mixtures	3	2
Saturates	Olefins		None	
	Aromatics	Simple mixtures	2	2
	Olefins plus aromatics		None	

The scope of the trace FIA method is summarized in Table IV. So far it has not been extended beyond the kerosine boiling range, but it probably could be, if required.

HYDROCARBON TYPE ANALYSIS OF HEAVIER DISTILLATES

There is an increasing need of a reliable routine method, such as FIA, for the determination of the three principal hydrocarbon

types in cracked gas oils. This need prevails also with straight-run materials, including lubricating oils, because the sulfuric acid extraction method for determination of the saturates/aromatics split is not applicable to the heavier distillates.

A prerequisite to research along this line is the procurement of a collection of higher boiling distillates of reasonably well known composition with which to experiment. Such reference samples can now be realized as a result of work carried out here and elsewhere (*6*, *8*) on the composition of gas oils and lubricating oils. Techniques have been established involving large scale elution development chromatography followed by spectrometric and chemical analyses of numerous cuts recovered; from these laborious analyses it was possible to arrive at figures for type composition which in most cases were accurate to ±1 to 2%.

Attempts to apply the FIA method to heavier distillates met with several difficulties. As would be expected, the high viscosity caused channeling in the column, at times to the extent of allowing the eluent to bypass a considerable portion of the sample. When the oil was not too viscous (light gas oils), these difficulties could be overcome simply by making the separator section narrower and longer (see Figure 4). With more viscous materials (lubricating oils) it was necessary also to dilute the sample with known quantities of solvents representing the three principal hydrocarbon types, such as iso-octane, diisobutylene, and benzene, and to make appropriate corrections in the calculation. (Reduction of the viscosity by increasing the temperature should be avoided because it affects the behavior of the dyes.)

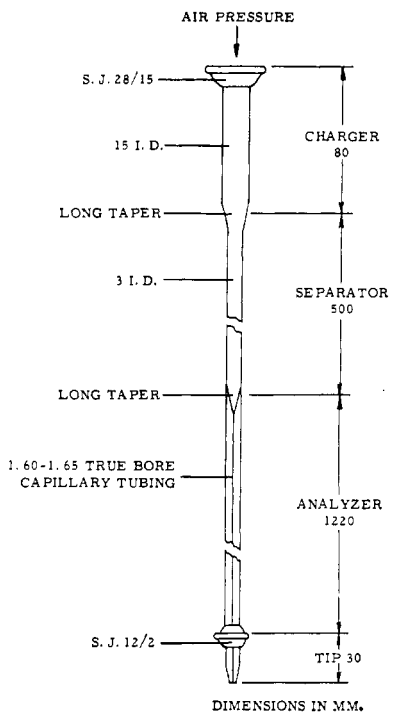

Figure 4. Column for heavier distillates

The aromatics marking component of the FIA dye is more strongly adsorbed than the highly alkylated monoaromatics, and therefore fails to mark the front of the aromatics zone. This behavior is, of course, due to the fact that the monoaromatics become more paraffinic with increasing molecular weight and, consequently, less strongly adsorbed. The difficulty was circumvented by supplementing the regular dye mixture with a less strongly adsorbed aromatics indicator, recovered from Patent Chemicals' Oil Color No. 50, the material from which this firm prepares the olefin marker.

Oxidation products, formed in some of the reference oils during storage, occasionally interfered with the separation. These dark products, even though present in very low concentration, migrated down the column and obscured the indicators. This situation could be corrected by replacing the upper portion (60 to 70 mm.) of the regular Davison's silica gel grade 923 (pore diameter 32 A. and surface area 800 square meters per gram) by Davison's silica gel grade 70 (pore diameter 100 A. and surface area 330 square meters per gram), which adsorbs the oxidation products more strongly than the regular gel. The latter is retained in the critical lower part of the column to provide better surface area. The oxidized molecules are relatively large, and the much improved retention on grade 70 gel may be due to the large pore size of this gel. It is also possible that the general reluctance of the oxidation products to separate can be explained by the formation of an asorbotropic mixture, one that will pass through the column unaltered (in analogy with azeotropic distillation). These hypotheses the authors have presented in connection with the chromatographic determination of gum (*7*).

In one instance of rather severe oxidation the dark materials were not sufficiently retarded even by grade 70 silica gel. However, such extreme materials can still be analyzed if isopropyl alcohol is replaced by isopropyl chloride. This eluent displaces the hydrocarbons but not the oxidation products. But isopropyl chloride does not displace the red eluent marking dye, and as no other dye has been found, the aromatics zone cannot be measured. In this case, therefore, a column with calibrated analyzer section (see trace FIA method) is used so that the volumes of the saturates and the olefins can be computed from their zone lengths and related to the known volume of the sample, and the aromatics, including the oxidation products, obtained by difference.

Wax may interfere by precipitation in the column if the quantity is too large to remain dissolved in the diluent. The tolerance has not been studied; therefore, if the oil contains much wax, it may be necessary to remove at least some of it prior to analysis.

In the course of this work it was also found that a fairly good value for the content of polyaromatics (including diaromatics and resins) in lubricating oils can be obtained. This is done in a separate test with the FIA column packed with alumina (Alcoa F-20) which is an excellent adsorbent for polyaromatics. No dyes are used because the polyaromatics are inherently strongly fluorescent in ultraviolet light and therefore self-indicating. As viscosity reducer, a solvent mixture containing only iso-octane and benzene is employed, diisobutylene being omitted because it interferes with the separation. This method is not applicable to gas oils because they contain very little fluorescent material and no suitable indicator dye is known.

METHOD FOR HEAVIER DISTILLATES

Apparatus and Materials. These items are the same as required for the FIA method for lighter distillates and for the trace FIA method, except for the following:

FIA column for heavier distillates, as shown in Figure 4. (The concentration column and receiver are not used.)

Syringe, 1-ml. capacity, graduated to 0.01 ml.

Two diluents. Iso-octane (technical) plus diisobutylene (technical) plus benzene (reagent grade), equal volumes, and isooctane plus benzene, equal volumes; the latter for the polyaromatics procedure.

Dyed silica gel for heavier aromatics, prepared as follows. Pack an adsorption column of approximate dimensions 20 × 200 mm. about three quarters full with Davison's Grade 923 silica gel, and charge it with a solution of 0.2 ml. of Patent Chemical's Oil Color No. 50 in 10 to 20 ml. of iso-octane. Add 25 ml. of diisobutylene, rinsing in the last of the iso-octane solution with the first small portions. Then follow with 25 ml. of benzene, in the same manner, and finally with isopropyl alcohol. In ordinary light, collect the approximately 2 ml. of rose-colored benzene effluent in a vessel containing 3 ml. of silica gel, and evaporate the benzene in a stream of air until the dyed gel is free-flowing. This quantity will suffice for about 40 determinations. Store the dyed gel in the dark.

Activated alumina, Alcoa, Grade F-20 (80 to 200-mesh) from the Aluminum Co. of America, Pittsburgh, Pa.; for the polyaromatics procedure.

Procedure. The procedure is divided into three parts according to the type of oil to be analyzed and hydrocarbons to be determined.

1. Saturates, Olefins, and Aromatics in Light Gas Oils. Put a piece of cotton in the tip of the FIA column (Figure 4) and pack it with silica gel, applying the vibrator as needed, until the separator section is about half full. Add a 10-mm. layer each of the regular dyed gel and the dyed silica gel for heavier aromatics. Continue to vibrate and add gel until it fills all but 20 to 30 mm. of the separator section.

Add by means of a pipet 0.50 ± 0.05 ml. of sample and apply a pressure of 3 pounds per square inch until the oil is absorbed. Then carefully rinse the walls with a few drops of isopropyl alcohol. Cover with an approximately 10-mm. layer of gel, and fill the charger section with alcohol. Again apply the pressure of 3 pounds per square inch, and when the liquid front is half-way through the analyzer section, take readings as directed under the preceding trace FIA method.

Calculate the percentages of the hydrocarbon types as follows:

$$\text{Hydrocarbon type, volume \%} = 100 \frac{\text{zone, mm.}}{\text{sum of zones, mm.}}$$

2. Saturates, Olefins, and Aromatics in Heavy Gas Oils and Lubricating Oils. Pack the FIA column (Figure 4) as described above in the procedure for light gas oils.

Measuring with the syringe, dilute 0.70 ml. of oil with an equal volume (±0.01 ml.) of the iso-octane plus diisobutylene plus benzene diluent, and add 0.50 ± 0.05 ml. of the diluted sample to the column. Follow the procedure for light gas oil (above), but apply a pressure of only 1 pound per square inch, and, when the liquid front enters the analyzer section release the pressure.

Calculate the percentages of the hydrocarbon types as follows:

$$\text{Hydrocarbon type, volume \%} = 200 \frac{\text{zone, mm.}}{\text{sum of zones, mm.}} - 33.3$$

If the yellow-green-fluorescent olefins marking dye is closely followed by the blue-fluorescent aromatics marking dye, the olefins cannot be distinguished from the aromatics, and therefore only their sum can be determined.

3. Polyaromatics in Lubricating Oils. Pack the FIA column (Figure 4) with activated alumina, F-20, applying the vibrator as needed, until the level is 20 to 30 mm. below the top of the separator section.

Measuring with the syringe, dilute 0.70 ml. of oil with an equal volume (±0.01 ml.) of the iso-octane plus benzene diluent and add 0.50 ± 0.05 ml. of the diluted sample to the column. Proceed as for heavy gas oils and lubricating oils (above).

In ultraviolet light, measure the length of the fluorescent polyaromatics zone, extending from the lowest point of strong blue fluorescence to the top of the reddish brown zone; also measure the length of the total sample zone.

Calculate the percentage of polyaromatics (including diaromatics and resins) as follows:

$$\text{Polyaromatics, volume \%} = 200 \frac{\text{polyaromatics zone, mm.}}{\text{sum of zones, mm.}}$$

RESULTS AND DISCUSSION

Table V shows examples of results that can be obtained with catalytically and thermally cracked light gas oils. The highest boiling fraction, 300° to 400° C., borders on a heavy distillate; it required dilution prior to analysis. As might be expected, the reliability is better for the lighter fractions than for the heavier ones. The deviations from the "true" compositions were 1 to 4% with an average of 2%, but for the 300° to 400° C. fraction, 2 to 6%; however, the true composition values for the latter are relatively uncertain.

It was discovered that these oils could be analyzed just about as well when the special dye for indication of heavier aromatics was omitted, using only the regular dye as employed in the analysis for lighter distillates (gasolines, jet fuels, and kerosines); the difference in results was not statistically significant. As mentioned earlier, the ability of the aromatics to displace the regular dye depends on their molecular weight. For lubricating oils the special dye is indispensable, and it may therefore be advisable to include it in the borderline cases discussed here.

Examples of the analyses of dewaxed lubricating oil base stocks are shown in Table VI. These oils are straight-run distillates; all but one are olefin-free, which greatly simplifies the analysis. In spite of the relatively high molecular weight of the oils, therefore, the results are rather good, the errors being 0 to 4%, or 2% on the average. The exceptional oil (the first in the series in Table VI) is derived from a Pennsylvania crude oil, and contains a substantial amount of olefins. The presence of olefins in a virgin crude oil is extraordinary, but has definitely been established here and in other laboratories in oils of similar origin (*4*, *5*).

The fact that this unsaturated heavy oil could be analyzed satisfactorily by means of the FIA method indicates that cracked heavy gas oils can be so analyzed, although, with the exception of the 300° to 400° C. fraction (Table V), no tests with the latter were carried out. However, the olefins-aromatics split could not be observed in oils of higher average molecular weight than about 400, corresponding to a mid-boiling point of ca. 450° C. (as referred to atmospheric pressure), because strong blue fluorescence then appeared just above the olefin marking dye. This is attributed to displacement of certain highly alkylated and therefore weakly adsorbed polyaromatics by diisobutylene. This displacement of fluorescent components of heavy oils by diisobutylene was observed even in a column of alumina which is considered superior for segregation of polyaromatics. Hence the olefin was eliminated from the diluent mixture in the analysis for polyaromatics.

The errors in the values for polyaromatics were likewise 0 to 4%, with an average of 2%.

This analysis requires about 0.5 hour of operator time, but the elapsed time may be as much as 10 to 15 hours, depending on the viscosity of the oil.

On the whole, the reliability of the FIA method as applied to heavier distillates is within about ±2%, but errors as high as 5 or even 6% have occasionally been observed. Better accuracy is desirable and will no doubt be achieved, for it is now generally realized that in routine analyses usable values for hydrocarbon-type distribution can only be obtained by chromatography. An

Table V. Analyses of Cracked Distillates of Light Gas Oil Boiling Range

Sample	Boiling Range, ° C.	Composition, Volume % Known[a] Saturates	Olefins	Aromatics	Found Saturates	Olefins	Aromatics
Catalytically cracked gas oil fractions	230–337	55	4	41	53	5	42
	230–320	55	4	41	51	6	43
	286–314	59	3	38	58	6	36
	314–337	62	3	35	61	6	32
Thermally cracked gas oil fractions	170–310	48	16	36	47	15	38
	300–400[b]	36	9	55	34	5	61

[a] Accuracy of known values ±1 to 2%; 2 to 3% for 300°–400° C. fraction.
[b] This sample was more viscous and, like lubricating oils, required dilution.

Table VI. Analyses of Dewaxed Lubricating Oil Base Stocks

Average Molecular Weight	Composition, Volume %: Known[a] Saturates	Olefins	Monoaromatics	Polyaromatics[b]	Found Saturates	Olefins	Monoaromatics	Polyaromatics[b]
340	69	11	11	9	66	14	7	13
390	60	1	14	25	60	0	12	28
400[c]	48	0	15	37	46	0	13	41
420	61	0	19	20	60	0	23	17
440	61	0	17	22	60	0	18	22
450	58	0	14	28	55	0	18	27
460	46	0	14	40	46	0	13	41

[a] Accuracy of "known" values, ±1 to 2%.
[b] Including diaromatics and resins.
[c] Owing to presence of dark products of oxidation, isopropyl chloride was used as eluent in this case.

alternative that naturally comes to mind would be the determination of saturates by acid absorption, olefins by halogenation, and aromatics by difference. As might be expected, however, this approach fails because the olefin-aromatic ratio so obtained is entirely erroneous. This may be illustrated by the results of a cooperative testing carried out by several laboratories with the lightest of these oils, the thermally cracked gas oil of boiling range 170° to 310° C. (see Table V). Its true composition is considered accurate to within ±1%. This oil is still light enough for determination of saturates by acid absorption to within 1 or 2% of the known value of 48%. Bromine numbers by various methods ranged from 31 to 38 grams per 100 grams. In calculating the olefin content from these bromine numbers by aid of the determined molecular weight of the sample, 191, one obtains values of between 37 and 45% as compared with the known value of 16%; this leaves only 8 to 16% for the aromatics, the known content of which is 36%. With the FIA method the same laboratories obtained results which, on the average, deviated from the known values by only −1.9, −0.5, and +2.4% for saturates, olefins, and aromatics, respectively.

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Full Luminescence at Liquid-Air Temperature of Methyl-1,2-benzanthracenes and Methylbenzo[c]phenanthrenes

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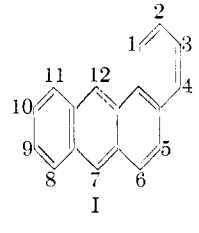
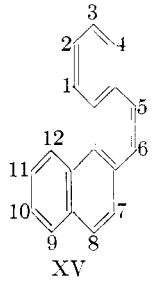
At liquid-air temperature, in a mixture of solvents which sets to a rigid clear glass, the full luminescence of the monomethyl derivatives of the methyl-1,2-benzanthracene and methylbenzo[c]phenanthrene series shows distinctive spectra in relation to that of the parent compound. The significant changes in the spectrum caused by the introduction of the methyl group in different positions can be used for the identification of any methyl derivative of 1,2-benzanthracene or benzo[c]phenanthrene. The afterglow of the most carcinogenic compounds of the benzanthracene series is specifically different from that of all the other members of these series.

IN ACCORDANCE with the reversible nature of absorption and emission of light it has been found that groups of compounds produce characteristic patterns of fluorescence spectra. On this basis biologically active polycyclic hydrocarbons have been identified by fluorescence spectrography in the past 20 years (*1, 2, 4, 10*). Because the accuracy of the fluorescence data depends on the sharpness and fine structure of the bands, better results may be obtained when the fluorescence is studied at low temperatures.

In the case of the methyl derivatives of 1,2-benzanthracene (I) and benzo[c]phenanthrene (XV) the methyl position has little influence on the fluorescence spectra of the parent hydrocarbons at room temperature.



I



XV

The benzanthracenes and the benzo[c]phenanthrenes are sensitive to ultraviolet irradiation; therefore, when their fluores-

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