DETERMINATION OF COMPOUND TYPES IN COMPLEX MIXTURES USING SUBTRACTION AND GAS CHROMATOGRAPHIC READOUT

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ABSTRACT

The need for improved compound-type analyses of shale-oil fractions resulting from the lack of specificity of chromatographic adsorbents or from the poor precision of the methods of quantitation is discussed.

A subtractive analytical technique using a gas chromatographic (g.c.) readout step is illustrated for several compound types found in shale oils. This method consists of adding an appropriate internal standard to the sample, applying a specific subtractive technique, and determining the amount of a compound type from comparison of the before and after gas chromatograms. The method is applied to hydrocarbon types (alkane-alkene-aromatic) and polar materials including acids and bases. The presence of an internal standard throughout the material handling steps eliminates such precision-degrading operations as quantitative separation of phases and solvent removal so that a wide variety of chemical characterization methods become feasible. In many cases a test that is more definitive for a given purpose may be devised because of the flexibility added by gas chromatographic readout. Oil samples of 0.1 ml are readily handled with the method.

The precision and detection limits are set by the precision of the gas chromatographic readout at about ±1%, which is a great improvement over presently used routine methods. Although the subtractive technique with g.c. readout is not useful for trace analyses, the greater reliability of the data for compound types present in shale oil at the few percent level allows use of the method for more detailed characterization of polar materials by comparing results from use of a multiplicity of polar-subtractive agents as well as correlation with independent methods such as nonaqueous potentiometric titration.

INTRODUCTION

Routine compound-type determinations have long been used in the characterization of crude oils and their distillates, and the methods for these determinations have been reduced to sequences of manipulations and measurements. Acids; bases; and aromatic, olefinic, naphthenic, and paraffinic hydrocarbons are examples of compound types for which methods are available. The sample size required ranges from 10 ml to 300 ml, and neat samples are necessary. In addition, the methods of handling subject the sample to loss and are often ambiguous in the readout or data-producing step. In many cases the specificity of the compound-type separation is poor.

Typical examples of materials on which it would be useful to carry out compound-type determinations are fractions and distillates from extracts of raw oil shale, of partially retorted oil shale, and of tar sands. These samples are frequently available in our research and development in amounts smaller than 1 ml and are sometimes in dilute solutions. To accomplish these determinations, miniaturized methods were essential. If additional precision, convenience, and versatility could be achieved, the older methods might be replaced. This paper reports on development of such methods.

Gas chromatography (g.c.) is inherently well adapted to small samples as well as to automation, and many g.c. methods have been developed for determining low-boiling compound types[1-3]. Present methods for high-boiling materials, however, give only semiquantitative information[4]. The requirements for shale-oil research are for quantitative characterization of distillates boiling to 1,000° F. This paper reports the adaptation of the g.c. technique of simulated distillation (s.d.)[5-8] to be used as the readout step in compound-type determinations. It also compares the results of the g.c. technique with the results of other methods of compound-type determinations.

EXPERIMENTAL

Apparatus, Materials, and Conditions

A Beckman GC-4 gas chromatograph*with a hydrogen-flame ionization detector was used as previously described[9]. The

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*Reference to specific brand names is made for identification purposes only and does not imply endorsement by the U.S. Bureau of Mines to the exclusion of others that may be suitable.

"Superior numbers refer to similarly-numbered references at the end of this paper."

on-column inlet heater in the gas chromatograph was modified to eliminate cold spots[10]. To decrease heat capacity, however, each inlet was shrouded individually with a heating block to allow quick cooling and heating of the inlet area of the column. The inlet was a 12.7-cm (5-in) section of 0.637-cm (0.25-in) o.d. tubing packed with 100-120 mesh silanized borosilicate glass beads with a small plug of glass wool to keep the beads in place. Syringe sample injections were made with the inlet at 170° C to minimize fractionation; then the inlet was very quickly (ca 10 min) heated to 375° C to minimize peak distortions in the resulting chromatogram. The chromatographic column used was 45.7 cm (18 in) x 0.637 cm (0.25 in) o.d. Initial loading of liquid phase before conditioning was 5% Dexsil on 70-80 mesh acid-washed HMDS-treated Chromosorb W. Column helium carrier gas flow was 90 ml/min. Linear temperature programming between 50° C and 350° over 30 minutes was used. The hydrogen flame ionization detector was operated at a total flow of 120 ml/min helium. Hydrogen flow was adjusted for maximum response at this helium flow. Air flow was 400 ml/min. A Vidar Model 6300 electronic digital integrator was used in a simulated distillation mode.

Titrations were made with a Beckman Model 1063-1065 automatic recording titrimeter. Bases were titrated in acetonitrile-benzene solution with perchloric acid in dioxane as the titrant[11] and acids in pyridine-benzene solution with tetrabutyl ammonium hydroxide in benzene-methanol as the titrant[12].

Internal standards and solvents were from a variety of sources. Freedom from impurities eluting in interfering regions or chemically active impurities with respect to the reagents involved was checked before use in compound-type analyses. Reagents used in tests based on ASTM methods met the specifications for those methods. Ion-exchange resins used were Rohm and Haas Amberlyst 15 cation-exchange resin and Amberlyst A-29 anion-exchange resin. The resins were activated by leaching with hydrochloric acid or sodium hydroxide, thoroughly washed with water and then with methanol and benzene, and vacuum dried before using.

Simulated Distillation Methodology Using an Internal Standard

The quantitative aspects of using g.c. as the readout step in the determination of compound types in complex mixtures can best be understood by considering the quantification of simulated distillation. The technique of s.d. by g.c. is illustrated in Figure 1. The chromatograms in this figure were obtained by using linear temperature programming so that the abscissa, which is recorded as time, can be calibrated to be the boiling point of the emerging components. This calibration is accomplished using normal alkanes in the range C_2 (-127° F) through C_{42} (1,000° F). The emergence times of two of the normal alkanes, C_{25} and C_{37}, are shown in the figure.

The bottom g.c. trace is for a whole, wet crude shale oil. The middle trace is for the topped crude oil with quantita-tively added internal standard. The topping step is necessary to remove water and to make a window in the chromatogram in which the internal standard will appear without interference from the shale oil. As shown in the middle trace, the internal standard appears in a window that is completely separate from the topped crude. This makes it possible to calculate the area (integral) that is obtained per unit weight of internal standard for each separate injection. In the s.d. technique, equal response factors are assumed for sample and standards--i.e., the area per unit weight of sample is considered to be the same as for the internal standard.

By knowing the weight ratio of the topped crude to internal standard and the area due to internal standard, the area that would result from the topped crude shale oil if it were completely eluted from the column can be calculated. The fraction of the topped crude remaining on the column (residue) is determined as the difference in the observed total area from that calculated area. The concentration of the residue in the original crude oil can then be calculated by comparing an equivalent region in the bottom and middle traces. The ratio of the areas in these regions will be the same as the ratio of the areas of the residues missing from each trace. In the middle and bottom traces, shown in Figure 1, the region between C_{25} and C_{37} is used for this calculation.

The upper trace is a chromatogram of the light ends from an inefficient, yet adequate topping step and is shown here only to verify that compounds from the reference region, C_{25} to C_{37}, do not appear in the light ends. The chromatogram of the light ends is not run routinely in s.d. determinations. Simulated distillation of distillates is usually simpler because distillates are dry, have a chromatographic window for the internal standard, and therefore do not need topping.

To make a compound-type determination based on the methods of simulated distillation, an appropriate internal standard is added to the sample, a specific subtractive technique is applied, and s.d. is used in the readout step to determine that fraction of the sample removed in the subtractive step (missing in the chromatogram). The fraction of sample removed in the subtractive step can be calculated from the chromatograms of sample plus internal standard before and after the subtractive step. The selection of a particular subtractive technique, the requirements for an appropriate internal standard, the calculation of a compound type from the gas chromatographic readout, and some advantages of the use of the new technique will be illustrated in the next section.

Selection of a Subtractive Technique

The selection of a subtractive technique will often be dictated by the desire to give data comparable to that from established methods. For instance, if one wanted to determine the concentration of tar bases in a light distillate, then the choice would likely be that of 10% H_2SO_4 extraction. If one desired to determine the olefinic plus aromatic hydrocarbons in a neutral distillate, then a test similar to ASTM D 1019[13] employing a $P_2O_5 + H_2SO_4$ sulfonation mixture would likely be the choice.

Requirements for an Internal Standard

The requirements for an internal standard are twofold: (1) It must be unaffected by the subtractive step and (2) in the g.c. step, it must appear in the trace separate from the raffinate. Thus if one were going to determine the tar bases in a 400° F E.P. naphtha by 10% H_2SO_4 treatment, then a mixture of neutral hydrocarbon boiling between 450° and 600° F could be used. However, the requirements for an internal standard in the determination of the olefinic–plus–aromatic hydrocarbons in a 400° F E.P. neutral naphtha by sulfonation are much stricter. In this case the mixture of neutral hydrocarbons would have to be free of olefins and aromatics.

Gas Chromatographic Readout of Compound-Type Data

Figure 2 shows the before and after chromatograms for the 10% H_2SO_4 extraction of bases from a 0.1-ml sample of a 400° F E.P. shale-oil naphtha. In order to have enough material to physically handle in this extraction, the 0.1-ml sample of the naphtha was dissolved in 1 ml of decylcyclohexane before the extraction. The internal standard was a mixture of hydrocarbons boiling between 550 and 700° F. The amount of the naphtha that is removed as tar bases is $(1-a/b) \times 100\%$ where a is the ratio of the sample area to internal standard area after the treatment, and b is this ratio before. For this sample of naphtha, the amount of tar base removed was 6.1%.

The precision of this method of g.c. is limited to about ±0.5%, and an absolute accuracy of the order of ±1.0% is the limit where a single analytical result requires two chromatograms. Therefore, the subtractive method is not generally useful for trace analysis.

Advantages of Gas Chromatographic Readout

The above example serves to demonstrate that small samples (0.1 ml) in solution (10%) can be successfully analyzed by this s.d. technique. Further advantages can be illustrated using Figure 3 which shows the before and after chromatograms of the nonaqueous cation-exchange extraction of a 600° F–1,000° F heavy gas oil. The solvent in this case was cyclohexane, and the internal standard was a mixture of hydrocarbons boiling between 300° and 500° F. This example serves to demonstrate two additional advantages of the technique. First, it is possible to make determinations on materials that are not analyzable by other techniques. Determination of the tar bases in this shale-oil heavy gas oil using 10% H_2SO_4 and observing the decrease in volume of the oil is not possible because of the formation of a stable emulsion. This emulsifying tendency is not a problem when a solution of the heavy gas oil is extracted with aqueous reagents or cation-exchange resins because a complete separation of the raffinate from solvent is not required. All that is required is a small (approximately 50-μl) aliquot of the raffinate–plus–internal–standard solution. Second, it is possible to make compound determinations on boiling ranges narrower than the true boiling range of a sample. The gas oil used for the determination shown in Figure 3 has material

boiling above 1,000° F. This is evidenced by the fact that the trace has not returned to baseline at 1,000° F. This does not interfere with our making the determination on only that material boiling between 600° and 1,000° F. This gas oil was shown to contain 24.3% tar bases.

SUBTRACTIVE TECHNIQUES WITH GAS CHROMATOGRAPHIC READOUT APPLIED TO SHALE-OIL DISTILLATES

The utility of this technique of compound-type determination will be demonstrated by comparing its results with the results of the methods currently being used by the Bureau of Mines. For this comparison, the compound types to be discussed are tar acids; tar bases; and aromatic, olefin, and saturate hydrocarbons. Distillates from three different crude shale oils will be used. For the comparisons to be meaningful for this paper, a short description of each of the other methods will be necessary.

Determination of Tar Acids and Tar Bases

The present (called classical for this paper) method of determining tar acids in naphtha and light distillate fractions of shale oil consists of extracting from 10 to 50 ml of the fraction with 10% NaOH and observing the volume shrinkage. Tar bases are determined on the raffinate from the tar acid extraction in the same manner by extraction with 10% H_2SO_4. The readout step in these two methods is the visual observation of the volumetric location of the interface between the oil and the aqueous layers. With low-boiling shale-oil fractions, which are dark and which often form quite stable emulsions, the task of observing this interface is difficult. With fractions boiling above 600° F, the task is impossible because of the stability of the emulsions.

We have already seen illustrated the application of g.c. readout in observing the amount of tar bases removed in subtractive, tar base determinations. Tables 1 and 2 compare, for two light distillates, the results of the classical method of determining tar acids and tar bases with the results from aqueous extraction using g.c. readout and with ion-exchange resin extraction with g.c. readout. Also included for comparison are the results from determining the tar acids and tar bases by nonaqueous titrimetry. In Table 1, for the in situ oil, the acid and base values obtained using ion-exchange extraction agree closely with the titration values. In Table 2 is a similar comparison of results for a simulated "in situ" light distillate from the Bureau of Mines 150-ton retort. The differences in values from the various methods are larger. These differences are probably real. The various techniques used are not entirely equivalent where molecular shape factors are involved.

The oil from the Bureau of Mines 150-ton retort (Table 2) appears more complex from the standpoint of our titration values which show the presence of both weak acids (pKa = +3 to +10) and very weak acids (pKa = +10 to +12), as well as weak bases (pKa = +2 to +8) and very weak bases (pKa = -2 to +2). In these data only the total value of titratable acids and bases have been reported. The in situ oil (Table 1) just discussed showed only weak bases and acids, with no
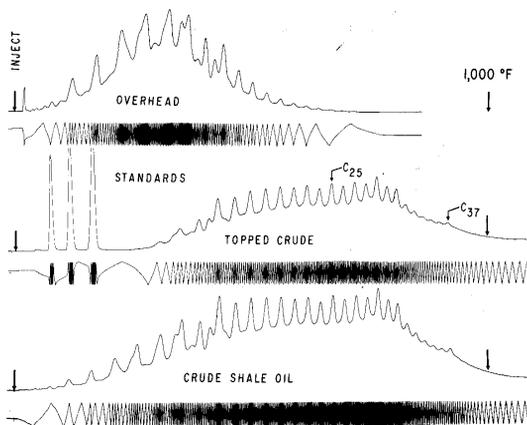
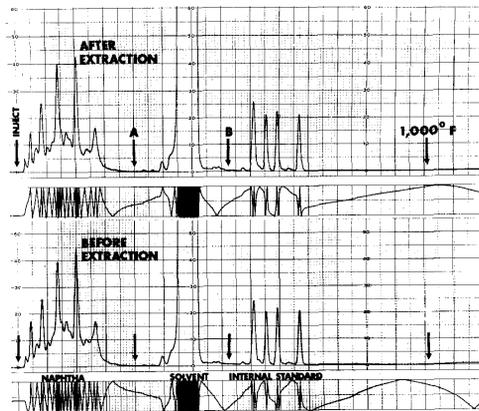FIGURE 1. - Gas chromatograms from simulated distillation of a shale-oil crude oil.

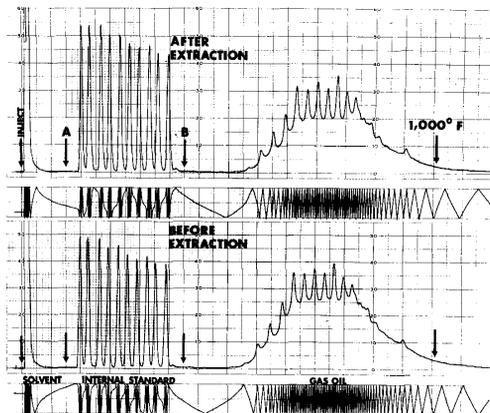FIGURE 2. - Gas chromatograms from aqueous acid subtraction of bases from a shale-oil naphtha.

FIGURE 3. - Gas chromatograms from nonaqueous cation-exchange subtraction of bases from a shale-oil heavy gas oil.
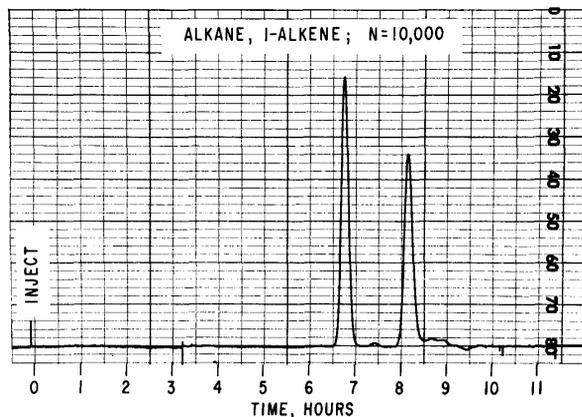

FIGURE 4. - Liquid elution chromatogram of an n-hexadecane--n-hexadecene-1 mixture.

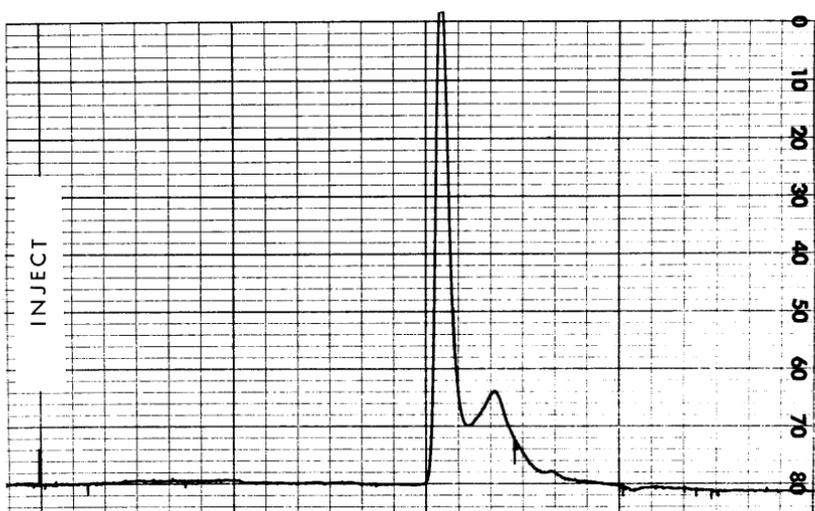FIGURE 5. – Liquid elution chromatogram of a saturate-olefin concentrate from a shale-oil light distillate (400° F–600° F).

FIGURE 6. – Liquid elution chromatogram of a saturate-olefin concentrate from a shale-oil heavy gas oil (800° F–1,000° F).

very weak acids or bases appearing to be titrated. These results, when more thoroughly interpreted, should give a clearer picture of the nature of these ill-described polar materials.

Determination of Hydrocarbon Types

Hydrocarbon types in light distillates are presently determined using displacement chromatography on silica gel[14] (also called classical in this paper). This determination is accomplished on the neutral raffinate from the tar acid and tar base determinations. A 10-ml sample of the neutral raffinate is put on a silica-gel column, and an alcohol is used to displace the entire hydrocarbon portion. Refractive index measurements are taken on constant-volume fractions through the course of the displacement, and the saturate-olefin, olefin-aromatic, and aromatic-alcohol boundaries are determined from points of maximum rate of change of refractive index. Relative portions of the various hydrocarbon types are determined from the number of fractions recovered from the silica gel for each type, and the concentration of each type in the original distillate is determined by adjusting this relative portion for the amount of the distillate removed as tar acids and tar bases.

Before we look at the determination of these three hydrocarbon types by using the g.c. readout method, let us examine some shortcomings of the classical methods. Aromatics are easily separated from olefins because of favorable equilibria. Separation of olefins from paraffins, however, is much less favorable. In Figure 4 we see a high-resolution (10,000 theoretical plates) liquid elution chromatographic separation of n-hexadecane from n-hexadecene-1. These compounds are well separated. The small bands near the baseline eluting before n-hexadecene-1 are sterically hindered olefins, trans and cis internal olefins, and those eluting after the main olefin peak are diolefin types. In a complex material, such as shale oil, this separation would be poor. Figure 5 shows that this is certainly the case for a saturate-olefin concentrate from a shale-oil light distillate. Any of the obvious cut points would give an erroneous result. If the first appearance of olefins is used as a cut point, the olefin fraction is grossly contaminated with saturates. If the valley between bands in the chromatogram with refractive index detection is used, obviously the saturate fraction is grossly contaminated with olefins. Figure 6 shows a chromatogram for a saturate-olefin concentrate from a shale-oil heavy gas oil. The separation appears even poorer because of the multiplicity of hindered olefin types present. The use of silica gel modified with silver nitrate can give some improvement in light distillate analyses, but is not expected to give complete olefin-saturate separation for more complex fractions.

In the hydrocarbon-type method using g.c. readout, aromatics and polars are subtracted from the whole oil in a liquid elution chromatography step with a nonpolar eluent. The polar compounds are mostly the acids and bases whose determination was covered previously. However, the polar compounds may contain neutral compounds that would be displaced after the aromatics in the classical analysis and thus be lost from the analysis. Gas chromatographic readout from the liquid elution step gives a value for aromatics plus polars which were chromatographically removed. The oil solution eluted from the silica gel is treated for subtraction of olefins with sulfuric acid and phosphorus pentoxide[13]. The sulfonated olefins are extracted into the acid layer and discarded. Gas chromatographic readout of a sample from the organic layer gives a value for olefins removed and saturates remaining. No liquid-liquid interfaces need to be read. The only requirement for g.c. is a sample from the homogeneous phase away from the interface.

Hydrocarbon-type data for the two light distillates previously discussed concerning acids and bases, each analyzed by the described classical method and by the g.c. method, are shown in Tables 3 and 4. Table 3 shows the comparison of results for an in situ retorted oil. The second column is for the classical method of displacement chromatography. As noted before, the amounts of the tar acids and tar bases by the classical method are extremely variable in practice because of the problem in reading a dark interface. Any change in these values would be reflected directly in different values for aromatics, olefins, and saturates. Also the total material balance is in error by the amount of materials that are not extracted by base and acid but are left on the silica gel. In the method with g.c. readout after subtraction, we have used three techniques to determine polar materials—i.e., titration, ion-exchange subtraction, and aqueous-acid and aqueous-base subtraction. The values from the different methods were seen to vary appreciably, probably because of the nonequivalence of the three methods. In the g.c. readout method, however, only the aromatic value depends on what we choose to call polars. We get an absolute value for aromatics plus polars (all left on silica gel) and absolute values for olefins (extracted by sulfuric acid - P_2O_5), and that which finally remains is only saturated hydrocarbons. By contrast in the classical method, which includes a very poor polar determination and requires complete displacement of hydrocarbons from silica gel, each hydrocarbon value depends on the polar determination and, in addition, on a rather difficult cut point determination between the hydrocarbon types. It is fortuitous that the old method in Table 3 gives a saturated-hydrocarbon-type value in good agreement with the new method. For the in situ oil in Table 4, the olefin and saturate values by the classical method differ from 10% to 35% from the values by the new method.

Depending on the way in which the polars are described— titration using total or only weak acids and bases, ion exchange, or aqueous extraction—the derived aromatic value for either oil changes. However, the total material held up on silica gel is determined concretely by the new g.c. method, as are the olefins and saturates. This illustrates the power of the new method in that saturate, olefin, and aromatic plus polar values can be obtained that do not depend on a knowledge of the polar materials.

Characterization of Polar Material

As we have previously discussed, the definition chosen for the polar materials in the oils affects the aromatic hydrocarbon value in the new method. For this reason we have

studied a number of oils in various distillate ranges to try to improve our knowledge of polar materials. The new g.c. method has been very helpful in allowing comparisons of these materials measured by the ion-exchange and aqueous subtraction with nonaqueous titration values. To illustrate this, we need not fully interpret the data, but rather intend to show how useful the new method has been in raising interesting questions about the acids and bases because of the reliability of the g.c.-derived values.

In Table 5 are shown acid and base determinations for three distillates of an in situ crude shale oil. We have previously discussed the hydrocarbon-type determination for the light distillate. As already mentioned, the light distillate from this oil shows no very weak acids or bases by titration. For the two lighter distillates, all methods give similar results, with the ion-exchange method agreeing very closely with the titration values and the aqueous extraction agreeing less well. For the heavy distillate, the aqueous extraction gives a low value for the bases when compared with titration. For the acids, all methods give small values. The failure of the aqueous extraction method for the heavy distillates is probably a matter of the low solubility of the inorganic salts of the bases and acids in water when the acids and bases are in the gas-oil range (average molecular weight here is 320).

The data for the simulated "in situ" oil in Table 6 shows that both very weak bases and very weak acids appear in titrations of this oil. Yet, in the naphtha both weak and very weak bases and acids are removed to a large degree by either ion-exchange or aqueous means. In the light distillate only the weak bases appear to be extracted, whereas in the acid removal an appreciable part of the very weak acids is extracted. The gas oil bases are extracted by the cation-exchange resin but only poorly by aqueous means, as was noted for the gas oil from the previous in situ oil. The very weak acids in the gas oil are largely unextracted by either means.

Explanation of the behavior of bases and acids which titrate as very weak yet extract under conditions which one would expect to remove only strong and weak bases or acids probably lies in the steric factors of the molecules concerned. With the new method, which gives back almost instant data on this behavior, these effects can be studied readily.

In Table 7 data for similar determinations on a gas-combustion-retorted shale oil are presented. The naphtha fraction was not available for study. In the light distillate only the weak bases, weak acids, and part of the very weak acids extract as in the previous light distillate. The weight average molecular weights of the two gas oils are 280 and 397. The data for the light gas oil show the ion-exchange method of subtraction even in this molecular weight range to be more effective than aqueous extraction of bases when compared to the titration values. Furthermore, the ion-exchange extraction of bases works well for this heavy gas oil. The extraction of acids by either agent is comparable, as was the case for the light distillate.

SUMMARY

A method for giving rapid, reliable, compound-type analyses on distillates from crude oils has been discussed and compared with a classical method for tar acids, tar bases, aromatics, olefins, and paraffins. The new method, using gas chromatographic readout before and after the subtraction of a compound type from a distillate with an internal standard, can be performed on very small samples or dilute solutions. In addition, the new method gives absolute values for saturates, olefins, and aromatics plus polars if polars are defined as those materials staying on silica gel with the aromatics when a nonpolar eluent is used. The determination of tar acids and tar bases has no effect on the saturate and olefin values, only on the aromatic value.

Because the extractive determinations using gas chromatographic readout produce results having greater reliability and precision than older methods, the g.c. readout method is useful for compound-type characterization work on polar materials. By comparison of results obtained using a variety of polar-subtractive reagents with those results available from nonaqueous titrimetry or other independent methods, new information on the chemical nature of polar materials can be obtained.

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TABLE I

ACIDS AND BASES IN AN IN SITU LIGHT DISTILLATE
(400° F–600° F)

Type	Titration, Wt %	G.C. with Subtraction, Wt %		Classical, Vol %
		Ion Exchange	Aqueous Extraction	
Tar Acids	4.0	4.0	2.5	1.4
Tar Bases	12.1	12.1	11.2	10.7

TABLE 2

ACIDS AND BASES IN A 150-TON RETORT LIGHT
DISTILLATE (400° F–600° F)

Type	Titration, Wt %	G.C. with Subtraction, Wt %		Classical, Vol %
		Ion Exchange	Aqueous Extraction	
Tar Acids	6.4	3.3	3.7	1.0
Tar Bases	15.5	12.8	11.5	10.0

TABLE 3

COMPOUND TYPES IN AN IN SITU LIGHT DISTILLATE
(400° F–600° F)

Type	G.C. with Subtraction, Wt %	Classical, Vol %
Aromatics + Polars	25.3	30.8
Olefins	10.0	14.4
Saturates	54.7	54.8

TABLE 4

COMPOUND TYPES IN A 150-TON RETORT LIGHT
DISTILLATE (400° F–600° F)

Type	G.C. with Subtraction, Wt %	Classical, Vol %
Aromatics + Polars	42.8	33.3
Olefins	23.0	20.6
Saturates	34.2	46.1

TABLE 5

POLAR MATERIALS BY DIFFERENT METHODS FOR AN
IN SITU SHALE OIL

Method	Nominal Distillate Cut		
	Naphtha IBP to 400° F	Lt. Distillate 400° F to 600° F	Gas Oil 600° F to 1,000° F
Bases, Wt %			
Titration: Weak, Very Weak	6.7, 0.0	12.1, 0.0	22.9, 0.0
Ion Exchange	5.5	12.1	21.0
Aqueous Extraction	6.1	11.2	12.0
Acids, Wt %			
Titration: Weak, Very Weak	1.8, 0.0	4.0, 0.0	0.2, 0.0
Ion Exchange	1.0	4.0	0.7
Aqueous Extraction	0.0	2.5	0.0

	TABLE 6				TABLE 7		

TABLE 6

POLAR MATERIALS BY DIFFERENT METHODS FOR A 150-TON RETORT SHALE OIL

Method	Nominal Distillate Cut		
	Naphtha IBP to 400° F	Lt. Distillate 400° F to 600° F	Gas Oil 600° F to 1,000° F
	Bases, Wt %		
Titration:			
Weak, Very Weak	7.1, 3.6	13.1, 2.4	27.9, 0.0
Ion Exchange	10.2	12.8	24.3
Aqueous Extraction	11.2	11.5	12.0
	Acids, Wt %		
Titration:			
Weak, Very Weak	1.0, 3.9	0.8, 5.6	0.3, 8.0
Ion Exchange	4.2	3.3	1.1
Aqueous Extraction	5.0	3.7	1.2

TABLE 7

POLAR MATERIALS BY DIFFERENT METHODS FOR A GAS-COMBUSTION SHALE OIL

Method	Nominal Distillate Cut		
	Lt. Dist. 400° F to 600° F	Lt. Gas Oil 600° F to 800° F	Hvy. Gas Oil 800° F to 1,000° F
	Bases, Wt %		
Titration:			
Weak, Very Weak	10.6, 4.8	20.2, 0.0	30.4, 0.0
Ion Exchange	11.5	20.4	27.1
Aqueous Extraction	10.2	13.3	----
	Acids, Wt %		
Titration:			
Weak, Very Weak	2.0, 6.2	1.5, 7.7	0.3, 0.0
Ion Exchange	2.9	3.4	1.1
Aqueous Extraction	3.4	5.5	---

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