CXXXI.—*The Determination of Unsaturated and Aromatic Hydrocarbons in Light Oils and Motor Spirits.*

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In the course of a systematic examination of the various products of carbonisation of coal at different temperatures and in different types of retort, the problem arose of determining the composition of the light oils obtained. The study of these light oils, which have a boiling range of *ca.* 30—170°, throws considerable light on the processes occurring during carbonisation, and is of importance also as affecting the utilisation of the refined oils as motor spirits. In analysing light hydrocarbon oils of this character, it is sufficient for most purposes to determine the relative proportions of unsaturated, aromatic, naphthene, and paraffin hydrocarbons. It is evident that, if a method for such a determination is once established, a more complete knowledge of the composition of the oil is readily attained by applying the method to suitably chosen fractions of the original oil.

Details of typical methods which have been used for the analysis of light oils will be found in papers by, *e.g.*, Egloff and Morrell (*J. Ind. Eng. Chem.*, 1926, **18**, 354), Kattwinkel (*Brennstoff-Chem.*, 1927, **8**, 353), and Brame (*J. Inst. Pet. Tech.*, 1926, **12**, 48; Brame and Hunter, *ibid.*, 1927, **13**, 794). Such methods usually depend on observing the successive losses in volume when the oil is shaken (*a*) with a reagent which absorbs the unsaturated but not the aromatic hydrocarbons, and (*b*) with a second reagent which absorbs the aromatic but not the saturated hydrocarbons. To avoid the difficulty of completely separating the reagent and the oil, it has been proposed to calculate the percentage of aromatic hydrocarbons in oils from which the unsaturated hydrocarbons have been removed, from the change in some physical property of the oil, *e.g.*, its specific gravity (Thole, *J. Soc. Chem. Ind.*, 1919, **38**, 39T) or its "aniline point" (Tizard and Marshall, *ibid.*, 1921, **40**, 20T), before and after treatment with the reagent. As reagents for the first absorption, sulphuric acids of various concentrations from 80 to 87% have been proposed, but it has been shown (Brame, *loc. cit.*) that the 80% acid will not completely remove the unsaturated hydrocarbons, and the 87% acid attacks the aromatic hydrocarbons. A further difficulty arises from the polymerising action of the acid on the unsaturated hydrocarbons, with the formation of products which are insoluble in the acid. Sulphuric acids of concentrations from 97 to 100%, and also various concentrations of fuming acid, have been proposed as reagents for the removal of aromatic hydrocarbons, but again the difficulty arises of obtaining a sharp separation of the two classes of hydrocarbons. Appreciable errors can arise also from the solubility of the saturated hydrocarbons in the acid solution of the sulphonated aromatic compounds.

Methods of determining the unsaturated hydrocarbons from the bromine or iodine values of an oil can only be regarded as approximate, being liable to relatively large errors (Brame, *loc. cit.*).

Little progress has been made in the problem of determining the relative proportion of cyclic (naphthene) and straight-chain (paraffin) hydrocarbons in the oil from which the unsaturated and aromatic hydrocarbons have been removed. The use of the " aniline point " for this purpose is hardly legitimate in view of our scanty knowledge of the aniline points of the possible saturated hydrocarbons present in the light oil. Indeed, our limited knowledge of the properties of the individual hydrocarbons which might be present in the light oils under discussion, and the very small number of such hydrocarbons readily available in the pure state for making test mixtures of known composition, constitute fundamental difficulties in any investigation of methods of analysis of complex hydrocarbon oil mixtures.

In the search for a method which would avoid some, at least, of the difficulties discussed above, and which, moreover, could be used when only small quantities of the light oil were available, a line of investigation was followed which was suggested by the methods of gas analysis. A small quantity of the oil, vaporised in a current of air, was passed through a suitable reagent, the increase in weight of which was determined. A convenient and readily available form of apparatus consists of a stoppered U-tube and two potash bulbs in series. The light oil is weighed into the U-tube and the bulbs are charged with the absorbing liquid. A gentle current of dry carbon dioxide-free air (or nitrogen) is passed through the train until the oil has completely vaporised and the absorbing bulbs have attained constant weight. The reagent used is such that the constituent to be absorbed is taken up completely in the first set of bulbs. The function of the second set is discussed later.

With these experimental conditions the complete evaporation of an average sample of light oil (0·2—0·5 g.) requires 2—8 hours, but this could doubtless be expedited by improving the design of the U-tube. To avoid difficulties due to non-volatile residues it is sometimes advisable to redistil the oil immediately before the analysis.

Determination of Aromatic Hydrocarbons in Mixtures containing no Unsaturated Hydrocarbons.—Preliminary experiments on mixtures of this type showed that 98% or even 100% sulphuric acid failed to absorb benzene and toluene completely. The 98% acid, for example, took up only about 70% of the benzene present. Complete absorption took place with fuming sulphuric acid (5% SO_3), but this reagent also attacked the saturated hydrocarbons. It was found, however, that the addition of 2—3% of silver sulphate to the 98% acid greatly accelerated the sulphonation of benzene and its homologues, and did not affect the action of the acid on the saturated hydrocarbons. This reagent proved entirely satisfactory for the analysis of these oils. Under the experimental conditions described, there is always a slight absorption of the saturated hydrocarbons, varying from 0·1 to 1·0%, but the use of a second set of absorbing bulbs through which only the saturated hydrocarbons pass, permits a correction to be made for this absorption. For instance, in one experiment with a synthetic mixture of benzene and saturated hydrocarbons containing 16·3% of the former, the absorptions in the two sets of bulbs were 17·15 and 0·80% respectively, giving a corrected figure of 16·35% for the aromatic hydrocarbons. The method has been found satisfactory for the determination of aromatic hydrocarbons in motor spirits which do not contain cracked distillates, and for the determination of paraffins in technical benzol, toluol, and xylol. The application of the method is illustrated by the following results :

(I) Synthetic mixture containing 4·4% of benzene and 95·6% of saturated hydrocarbons. Found : 4·45%.

(II) Synthetic mixture containing 48·5% of aromatic hydrocarbons (benzene, toluene, and xylene in approximately equal amounts). Found : 48·4%.

(III) An aviation spirit. Found : 18·4% of aromatic hydrocarbons. Calculated from the weight of aromatic nitro-compounds formed (see below) : 18·5%.

(IV) A technical toluol. Found : 94·3% of aromatic hydrocarbons, *i.e.*, 5·7% of paraffins.

Determination of both Unsaturated and Aromatic Hydrocarbons in Hydrocarbon Mixtures.—Sulphuric acid of various concentrations from 80 to 90% was found incapable of removing unsaturated hydrocarbons completely without attacking aromatic hydrocarbons ; moreover some of the unsaturated hydrocarbons polymerised to form volatile compounds which were not retained by the acid. The procedure finally adopted was to absorb unsaturated and aromatic hydrocarbons together in a suitable nitrating mixture (10% concentrated nitric acid, or preferably about 16% of potassium nitrate, in concentrated sulphuric acid), a second absorber being used as before. The correction found is usually somewhat higher (0·5—2·0%) than with the silver sulphate–acid reagent, but the absorption of both unsaturated and aromatic hydrocarbons by the nitrating mixture is complete and difficulties due to polymerisation do not arise. The corrected increase in weight of the absorbing bulbs, therefore, gives the total aromatic and unsaturated hydrocarbon content of the oil. To determine the aromatic hydrocarbons separately they are then isolated in the form of their nitro-derivatives. The solution in the acid mixture, preferably with the addition of a little more nitric acid, is heated in the water-bath for 2—3 hours in order to complete the nitration of the aromatic hydrocarbons and the oxidation of the unsaturated hydrocarbons. After cooling, the acid solution is poured into excess of water and the nitro-compounds are extracted with three 50 c.c. portions of benzene. The benzene solution is then extracted with a 10% solution of sodium hydroxide, washed with water, evaporated nearly to dryness in a tared flask, dried in a current of air at room temperature, and finally in a vacuum desiccator. The weight of nitro-compounds multiplied by the factor 0·452 gives the weight of the corresponding aromatic hydrocarbons present in the light oil. The value of this factor is based on experiments with the pure hydrocarbons, benzene, toluene, and *m*-xylene, which are converted, respectively, into dinitrobenzene and trinitro-toluene and -*m*-xylene in 96% yield in each case, and the conversion factors calculated on this basis are 0·485, 0·422, and 0·456 respectively; mean 0·452. The other aromatic hydrocarbons which might be present in light oils yield in general trinitro-derivatives, and only in very exceptional oils would they occur in such amount as appreciably to affect this factor. Under the experimental conditions used, the unsaturated hydrocarbons are oxidised almost completely to carbon dioxide, water, and products (presumably acidic) soluble in water or in aqueous sodium hydroxide.

The value for the percentage of aromatic hydrocarbons obtained from the weight of nitro-compounds is, however, always slightly high, owing to contamination with products from the unsaturated hydrocarbons. The error is variable but may be given as roughly one unit on the percentage for every 20% of unsaturated hydrocarbons present. It is serious when the oil contains a high proportion of unsaturated and only small quantities of aromatic hydrocarbons. It can, however, be diminished by removing some of the unsaturated hydrocarbons before passing the vapour into the nitrating mixture. This may be done by interposing in the absorbing train a vessel charged with 70% sulphuric acid, which has no effect on the aromatic hydrocarbons but removes some of the more troublesome of the unsaturated hydrocarbons. It is preferable, therefore, to run two experiments in parallel, one for the determination of the unsaturated and aromatic hydrocarbons together, using the apparatus described, and a second for the separate determination of the aromatics only. A convenient form of train for the latter consists of a U-tube, a set of potash bulbs charged with 70% sulphuric acid, and two stoppered gas-washing bottles of 30—40 c.c. capacity, charged with the nitrating mixture. In this determination it is necessary to weigh only the U-tube. Moreover, the subsequent treatment of the nitrating mixture is facilitated by the use of the gas-washing bottles instead of potash bulbs.

A more accurate value for the percentage of aromatic hydrocarbons and some knowledge of the relative proportions of the different members of the series present are obtained by fractionating the oil through an efficient column, fractions being taken at 95° and 124°. The aromatic hydrocarbons in the three fractions are then determined separately, 0·485, 0·422, and 0·456, respectively, being used as factors for the conversion of the weights of the nitro-compounds into those of the corresponding hydrocarbons. Instead of being weighed, the nitro-compounds may be determined by titration with titanous chloride, but there is no advantage in using this reagent when the total aromatic hydrocarbons are being determined in an oil in which the relative proportions of benzene, toluene, etc., are unknown. The method should always be used, however, for oils high in unsaturated but low in aromatic hydrocarbons, the oil being first fractionated in order to separate the latter. The following results illustrate the use of the method.

	% Calc.	% Found.
I. Synthetic mixture.		
Benzene	39·6	40·2
Amylene	22·1	21·7
Saturated hydrocarbons	38·3	38·1
II. Synthetic mixture.		
Aromatic hydrocarbons (benzene, toluene, and xylene)	7·8	7·8*
Unsaturated hydrocarbons (amylene and hexylene)	12·8	12·3
*cyclo*Hexane	79·4	79·9
Other saturated hydrocarbons		
III. Crude light oil from carbonisation of coal at 625°.	Found.	
Benzene	8·2%	24·7%
Toluene	10·7	
Xylene and higher aromatic hydrocarbons	5·8	
Unsaturated hydrocarbons	42·0	
Saturated hydrocarbons	33·3	
IV. The same light oil after refining.		
Aromatic hydrocarbons	32·5	
Unsaturated hydrocarbons	28·5	
Saturated hydrocarbons	39·0	
V. A power petrol.		
Aromatic hydrocarbons	8·9	
Unsaturated hydrocarbons	16·8	
Saturated hydrocarbons	74·3	
VI. A light oil obtained from the hydrogenation (" berginisation ") of coal.		
Benzene	3·4%	27·6%
Toluene	6·2	
Xylene and higher aromatic hydrocarbons	18·0	
Unsaturated hydrocarbons	10·4	
Saturated hydrocarbons	62·0	

* By titration; but 8·5% from the weight of nitro-compounds.

A few points of interest which have arisen during the present investigation may be mentioned.

When amylene is vaporised in a current of air and passed into 97% sulphuric acid, it is at first apparently absorbed, but soon begins to separate again on the surface of the acid as an insoluble mixture of polymerides, which are slowly volatilised with continued passage of air until almost the whole of the amylene is again removed from the acid. This result confirms the observation of Ormandy and Craven (*J. Soc. Chem. Ind.*, 1928, **47**, 317T) on the polymerisation of olefins by sulphuric acid. No such polymerisation occurs when amylene is passed into the nitrating mixture or into sulphuric acid containing 10% of chlorosulphonic acid.

Under the experimental conditions above described, aromatic hydrocarbons are attacked to a greater or less extent by sulphuric acid of 80% or higher concentration, but not by 70% acid.

When benzene is passed into the nitrating mixture the product of the reaction even in the cold is dinitrobenzene; no mononitrobenzene is formed. The dinitrobenzene remains unchanged during the subsequent heating. Toluene is converted directly into the dinitro-derivative in the cold, but on heating to 100° this is further nitrated to trinitrotoluene.

An attempt is being made to extend the method in order to obtain some information as to the composition of the saturated hydrocarbons.

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