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ABSTRACT

This study was prompted by a perceived need for a reliable method for determining olefin content in petroleum distillate fractions. Results from the standard Fluorescent Indicator Adsorption (FIA) method are highly dependent upon interpretation by the analyst, and the method is not applicable to boiling ranges higher than naphtha.

An accurate analytical method for the determination of olefin content in naphtha and higher boiling distillate fractions is described. The procedure comprises quantitative addition of diborane that specifically converts the olefins in the petroleum sample to alcohols. The reaction mixture is chromatographed on alumina, and alcohols are eluted with dichloromethane.

The procedure was applied to two hydrocarbon mixtures of 20 saturated, olefinic and aromatic hydrocarbons in the investigated boiling range. Naphtha (ibp-200°C) and light gas oil (200-350°C) fractions from the Lloydminster oil were also analyzed. Results are compared with the standard FIA method, and a method utilizing both the FIA and proton magnetic resonance spectrometry.

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INTRODUCTION

Several methods have been used for the determination of olefin content in petroleum fractions [1-5]. Results of the Fluorescent Indicator Adsorption (FIA) method, [1] which uses silica gel chromatography, are highly dependent upon interpretation by the analyst, and the method is not applicable to petroleum fractions higher than the naphtha boiling range. Because of the subjective judgements that have to be made in this and other methods, e.g., bromine number method [2] and a method utilizing FIA and proton magnetic resonance [3] (PMR), it is very difficult to obtain accurate results. Hydroboration of olefins in hydrocarbon mixture distillates was first investigated by Jackson et al. [4,5] in shale oil. To determine olefin content they used a lengthy procedure which involves determining the saturates and aromatic content by different standard methods, then hydroborating the olefins and calculating their content by difference. The procedure is not applicable to hydrocarbon mixtures in boiling ranges lower than 200°C.

This paper describes an analytical method based on the specific and quantitative addition of diborane to olefins which are converted to alcohols after oxidation with a basic peroxide solution. The hydroboration reaction of the distillate leads to a mixture of saturates, aromatics and alcohols. The alcohols are separated from the hydrocarbon mixture by chromatography on alumina. The quantitative recovery of the alcohols gives a more precise estimate of the actual amount of olefins present in the distillate. The amount of olefins in the sample is determined directly from simple calculations of 3 weighings: weight of oil sample, weight of hydroboration product mixture and weight of alcohols recovered from the reaction mixture. This procedure is applicable to the whole boiling range of petroleum distillate. Detailed derivation of the equation leading to the determination of olefin content is described in the experimental section. The overall time required for an analysis is about 4 h. The method was first tested on two standard mixtures of saturated, olefinic and aromatic hydrocarbons in the range ibp-200°C and 200-350°C (Table 1). The total conversion of olefins to alcohols was monitored by PMR. The hydroboration procedure was carried out in ether because of the ease of removing this solvent from the volatile hydrocarbons in naphtha without any appreciable losses.[6] Only the lighter C_5 paraffins in the naphtha can present a source of negligible error in the results. The accuracy of the determinations was about ±7% for the investigated samples.

EXPERIMENTAL

Procedure

1. Removal of polar material.

   The polar material was removed from the 200-350°C distillate by chromatography on an alumina column 30 cm x 2 cm O.D., and elution with 125 mL benzene. Partial elution of polar material together with the alcohols in the final recovery step would interfere with the olefin content determination.

2. Hydroboration-oxidation

   About 2.2 g of accurately weighed petroleum distillate was introduced to a 250-mL three-neck round-bottom flask containing 25 mL of dry ether and equipped with a magnetic stirring bar, a condenser and a dropping funnel. The system was purged with nitrogen, and a large excess (1 mL) of borane-methyl sulphide complex (10M in BH_3) was added slowly to the flask at $0^{\circ}C$ with a syringe through a septum[6]. The solution was agitated (for naphtha) or heated under reflux (for the 200-350°C fraction) for 1.5 h. The reaction mixture was then cooled to $0^{\circ}C$ and 15 mL of 3N sodium hydroxide added very slowly, followed by 15 mL of 30% hydrogen peroxide. The solution was stirred for an additional 1 h at room temperature.

3. Extraction

   The reaction mixture was transferred to a 250-mL separatory funnel, diluted with 100 mL of ether and washed with saturated NaCl solution (4 portions of 100 mL each) and 100 mL of water. The resulting ether solution was dried overy anhydrous sodium carbonate and filtered into a preweighed round-bottom flask.

4. The solvent was removed by distillation at a temperature not exceeding 45°C (for naphtha) or on a rotary evaporator with a slight vacuum (for the 200-350°C fraction) till the weight became constant.

5. The mixture of saturates, aromatics and alcohols was weighed accurately.

6. The saturated and aromatic hydrocarbons were separated from the alcohols by chromatography on alumina in a glass column (30 cm x 2 cm O.D.) and eluted with 60 mL of 1% benzene in pentane for naphtha, or 75 mL of 2% benzene in pentane for the 200-350°C fraction.

7. The alcohols were quantitatively recovered from the column in a 250-mL pre-weighed flask by elution with 125 mL of dichloromethane.

8. The dichloromethane was removed on a rotary evaporator under slight vacuum and the alcohols weighed. A schematic of the procedure is shown in Figure 1.

9. Calculation

   The weight of the oil sample after removal of the polar material can be expressed as:

$$W_{oil} = W_{SA} + W_{OL} + W_{AR} \quad (1),$$

where W_{oil} = weight of total oil sample,
W_{SA} = weight of saturates,
W_{OL} = weight of olefins, and
W_{AR} = weight of aromatics,

Saturates and aromatics in the oil sample are not affected by hydroboration. Therefore, the weight of the hydroboration product mixture can be expressed as

$$W_{HB} = W_{SA} + W_{AR} + W_{AL} \quad (2),$$

where W_{HB} = weight of hydroboration reaction products and
W_{AL} = weight of alcohols in the mixture.

From equation 1, $W_{SA} + W_{AR} = W_{oil} - W_{OL}$ (3)

By substituting in equation 2,

$$W_{HB} = W_{oil} - W_{OL} + W_{AL} \quad (4),$$

where $W_{OL} = W_{oil} + W_{AL} - W_{HB}$ (5)

and wt % olefins $= \frac{W_{OL}}{W_{oil}} \times 100$

The relation $W_{HB} \geqslant W_{oil}$ should always hold; otherwise the analysis has to be repeated.

RESULTS AND DISCUSSION

This analytical procedure was first tested with two synthetic mixtures of aliphatic and aromatic hydrocarbons containing known amounts of olefins (Table 1). The results show considerably narrower deviation from the actual percentages, in comparison with results obtained by the FIA method[1] or the proton magnetic resonance spectroscopy method[3] (Table 2).

It should be pointed out that compounds which contain an olefinic double bond, e.g., 1, 1-diphenylethylene, regardless whether it is attached to an aliphatic or aromatic alkyl moiety, will react as olefins in hydroboration. The API method for separation of hydrocarbon-types[8] does not differentiate olefins from other hydrocarbon classes. Examination of the PMR spectra of the alcohol mixture resulting from hydroboration indicated the presence of aromatic protons in the 200-350°C fraction, which suggests the presence of aromatic olefins in this fraction. No aromatic protons were traced in the naphtha fraction.

Polar materials found in the higher boiling fractions must be removed before the hydroboration step because they contribute to the alcohol fraction recovered by dichloromethane elution. This is easily accomplished by chromatography on alumina. Table 3 shows the analysis result of a light gas oil fraction containing 6.7% by weight of polar material. Removal of the polar material reduces the determined olefin content by over 4%.

Results obtained by the FIA method suffer from the incomplete separation of the hydrocarbon groups. Subjective judgments have to be made by the analyst to determine the boundary lines between the various hydrocarbon zones on the chromatographic column. Also the FIA method is not applicable to petroleum fractions boiling higher than the naphtha range[1]. The higher results reported for olefins determined by FIA[3] have also been observed in this investigation (Table 4).

Bromine number determination is another existing method for determination of olefin content in naphtha[2]. This method is not applicable to higher boiling range fractions. There is a large deviation between experimental and theoretical bromine number values because of the presence of dienes, S- and some N-containing compounds in petroleum samples.

The PMR procedure developed by Ozubko et al.[3] determines the percentage olefinic carbon. The technique is incapable of independently determining an olefin concentration. Results of FIA and bromine number analyses, with their inherent limitations, have to be correlated to the PMR results to give some estimate of the olefin content. The presence of tetrasubstituted olefins in the sample will lead to erroneous results.

Comparison of the olefin content determinations by hydroboration, FIA and PMR analyses for the two investigated petroleum distillate fractions is shown in Table 4.

CONCLUSION

Hydroboration analysis offers several advantages over other methods of estimating olefin content in fossil hydrocarbon mixtures, the most compelling of which is the ability to analyze any boiling range of distillate with relatively higher accuracy. The results obtained by this procedure show better agreement with the expected values. This procedure accomplishes the material separation of olefins from the saturated and aromatic hydrocarbon mixtures. The presence of olefins with the aliphatic compounds, particularly cycloalkanes, poses problems for further characterization by mass spectrometry.

REFERENCES

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Table 1

SATURATED, OLEFINIC AND AROMATIC HYDROCARBONS USED IN SYNTHETIC MIXTURES

Mixture I (ibp-200°C	B.P.(°C)	Mixture II(200-350°C)	B.P.(°C)
4-methyl-1-pentene	53	n-dodecane	216
2-methyl-1-pentene	62	n-tridecane	235
1-hexene	64	1-tetradecene	251
2-ethyl-1-butene	64	n-tetradecane	253
n-hexane	68	biphenyl	255
1-heptene	94	n-pentadecane	270
n-heptane	98	1,1-diphenylethylene	270
isooctane	99	1-hexadecene	274
toluene	110	n-hexadecane	286
B-pinene	165	2-nonadecene	328

Table 2

DETERMINATION OF THE OLEFIN CONTENT (wt%) IN SYNTHETIC MIXTURES BY DIFFERENT METHODS

	HYDROBORATION			FIA			PMR		
Sample	Actual	% * Found	Deviation	Actual	*% Found	Deviation	Actual	% Found	Deviation
Mixture I	25.0	26.5	6.0	20.0	23.0	15.0	24.9	32.9	32.1
				25.0	28.2	12.8			
Mixture II	14.3	13.3	7.0	15.0	–	–	14.3	9.6	32.8

* Average of three determinations

Table 3

DETERMINATION OF THE OLEFIN CONTENT (wt%) IN PETROLEUM DISTILLATES BY HYDROBORATION

	Determination			
Sample	1st	2nd	3rd	Average
Naphtha (ibp-200°C)	27.3	26.1	27.0	26.8
200-350°C*	16.0	14.8	15.2	15.3
200-350°C**	20.3	18.7	19.0	19.3

* Polar material removed from the sample prior to hydroboration.

** Oil sample containing 6.7% by weight of polar material determined by the modified API-procedure [7].

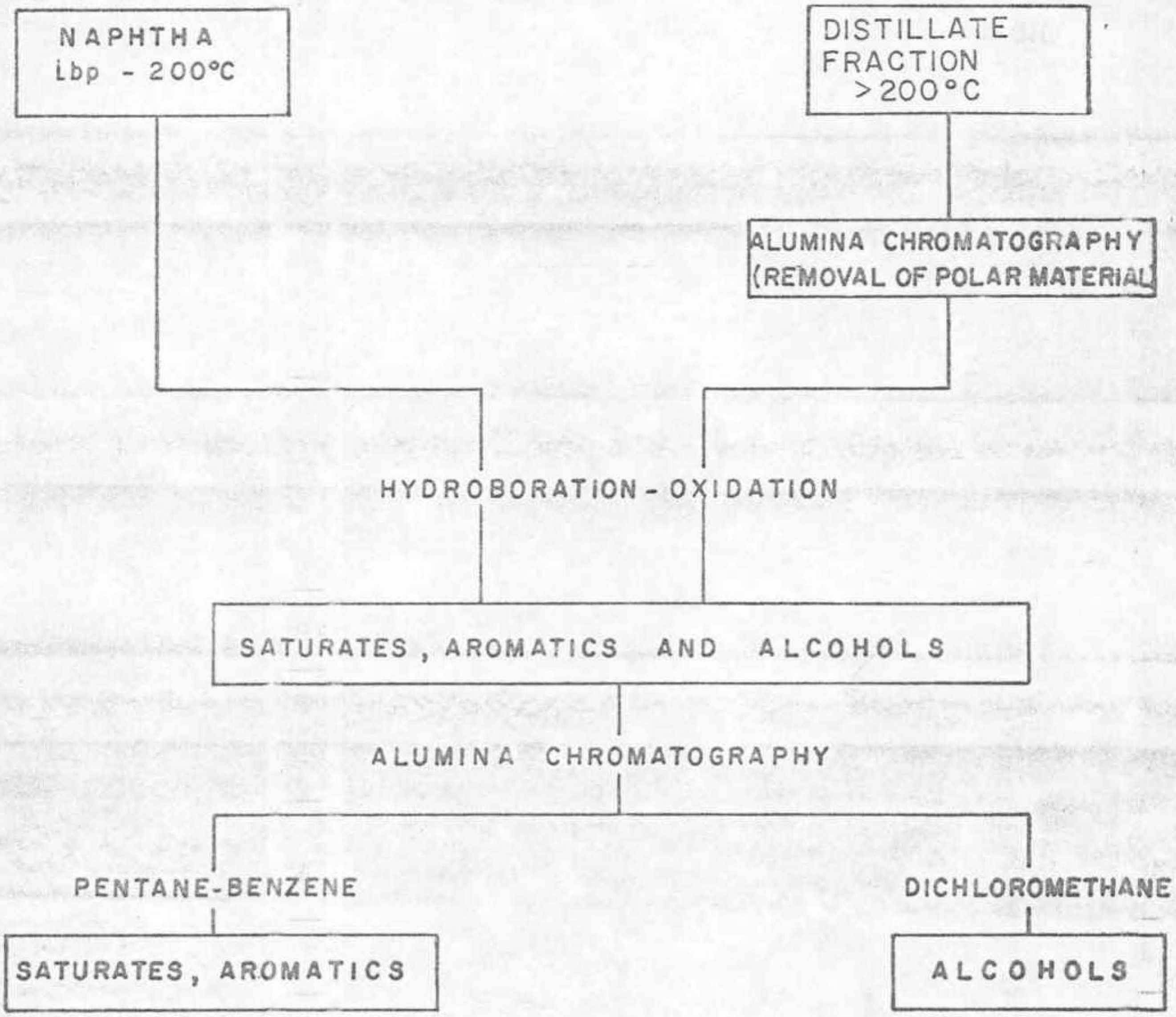
Table 4

DETERMINATION OF THE OLEFIN CONTENT (wt%) IN PETROLEUM DISTILLATES BY DIFFERENT METHODS

Sample	Hydroboration	FIA	PMR
Naphtha (ibp-200°C)	26.8	39.0	49.3
Light gas oil (200-350°C)	15.3	-	7.1

CAPTIONS

Figure 1	Procedure for the determination of olefin content in petroleum distillates


NAPHTHA
ibp - 200°C
DISTILLATE FRACTION >200°C
ALUMINA CHROMATOGRAPHY (REMOVAL OF POLAR MATERIAL)
HYDROBORATION - OXIDATION
SATURATES, AROMATICS AND ALCOHOLS
ALUMINA CHROMATOGRAPHY
PENTANE-BENZENE
DICHLOROMETHANE
SATURATES, AROMATICS
ALCOHOLS