

COMPARISON OF MASS SPECTROMETRIC AND NUCLEAR MAGNETIC RESONANCE
TECHNIQUES FOR HYDROCARBON TYPE DETERMINATION

by

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ABSTRACT

The hydrocarbon type content of petroleum fractions has traditionally been determined using different techniques, but often with poor agreement among the various results for a given sample. In this study, three different fractions were analyzed using mass spectrometric (MS), nuclear magnetic resonance (NMR), and fluorescent indicator analysis (FIA) techniques. The ^{13}C and ^1H NMR results were first converted from an atomic to a molecular basis. The MS, NMR, FIA and bromine number results are compared, with special attention given to the olefinic contents. The assumptions involved in, and limitations of, each technique are identified. The analysis of light fractions free of dienes, olefins and heteroatom-containing species is best performed by MS methods. The atomic hydrogen and carbon distribution from the NMR method is found to be applicable to all samples examined. While this atomic data can be correlated with the fractions' properties, the NMR results on a molecular basis are uncertain because of the number of assumptions involved.

Performance characteristics and other properties of petroleum products depend on their chemical compositions. Among the determining factors is the content of aromatic, olefinic and saturated hydrocarbons. For example, the amounts of aromatic and saturated hydrocarbon affect the combustion properties of fuels, while olefins have a marked effect on a fuel's stability.

To meet final product specifications, petroleum fractions must be subjected to various refining treatments. Such treatments always lead to a change in the constituent hydrocarbons. A rapid method of determining the proportions of the hydrocarbons would be a valuable tool for controlling technological parameters during production.

With the introduction of mass spectrometric (MS) techniques a number of analytical methods for hydrocarbon types have been developed and standardized(1). These can be applied with good precision to samples which fall within the limitations of the methods. Two important limitations are that there be very low amounts of olefins and of heteroatom (i.e. S-, N-, O-) containing compounds. Both these classes of compounds are a source of interference in the calculations based on the spectral information. It appears, therefore, that MS methods are suitable only for analyzing refined products from which these interferences are usually absent.

As olefinic and heteroatom-containing species do not interfere in nuclear magnetic resonance spectrometry (NMR), this technique has been proposed for the analysis of such materials (2). An additional advantage of NMR over MS is NMR's ability to analyze non-volatile samples, including sem-solids and solids.

The gas chromatographic-mass spectrometric (GC/MS) technique acts at a molecular level; that is, there is a molecular separation followed by detection and analysis of molecules. The NMR method, on the other hand, observes the carbon or hydrogen on an atom-by-atom basis and is therefore classified as an "atomic" analysis. In a ^{13}C spectrum, one observes and distinguishes carbons primarily on the basis of carbon type (i.e. sp^3 , sp^2 , or sp) and secondarily on the environment in which the carbon is found. In a ^1H spectrum, NMR separates hydrogen by the type of carbon to which it is bonded and also by the environment in which it is located. To compare these results with those from MS techniques, the contents of aromatic, olefinic and saturate carbon and hydrogen atoms from the NMR analyses must be converted to a molecular basis.

Interpretation of NMR data on a molecular basis and the subsequent comparison of these results with those derived from MS and fluorescent indicator analysis (FIA) are the subjects of this report. Three samples with widely different compositions were chosen for this study, and to minimize the interferences, light fractions boiling under 200°C were selected. This report gives the results for these samples and points out the complications and assumptions inherent in each technique when used for the quantitative determination of hydrocarbon types.

EXPERIMENTAL

The three samples used in this work were petroleum fractions boiling below 200⁰C and were selected to show variability in chemical composition.

The ASTM D1319 method was used for the FIA analysis. Bromine numbers (BR No) were determined in accordance with ASTM D1159. The values were then used to calculate olefin contents in accordance with ASTM D875.

Average molecular weights were determined from the freezing point depression using Cryette A automatic cryoscope.

Elemental analysis was performed on a Perkin Elmer 240 Analyzer.

Mass Spectrometric Procedure

A Finnigan GC/MS with an INCOS data system was used. The samples were injected onto a 1.83-m.(6 ft.) column packed with 3% dexil 300 on acid washed Chromosorb W and temperature programmed from 40⁰C to 250⁰C at 10⁰C/min. This procedure accomplished two purposes; it removed any involatile impurities and it achieved some separation of the sample components to simplify individual mass spectra. The mass spectrometer was operated in chemical ionization (CI) mode with methane as the reagent gas. Successive three second scans were acquired as long as material eluted from the GC column.

The calculations were based on the summation of a series of peaks characteristic of a given class of compounds; the sums, then, being treated as individual components. The sums used were:

$$\begin{aligned}\Sigma 71 &= H71 + H85 + \dots + H169 && \text{for saturated hydrocarbons} \\ \Sigma 69 &= H69 + H83 + \dots + H167 && \text{for monocyclic saturated hydrocarbons} \\ \Sigma 67 &= H67 + H81 + \dots + H165 && \text{for dicyclic saturated hydrocarbons} \\ \Sigma 79 &= H79 + H93 + \dots + H177 && \text{for monoaromatics} \\ \Sigma 129 &= H129 + H143 + \dots + H185 && \text{for naphthalenes}\end{aligned}$$

Empirical corrections, based on the spectra of pure olefins were then applied for the contribution of olefins to monocyclic, dicyclic and saturate summations. A synthetic mixture containing 10% olefins, 19% aromatics, 12% monocyclics and 59% paraffins was used to obtain sensitivity factors for the various classes of compounds and to monitor day-to-day performance of the instruments.

NMR Procedure

Individual samples were prepared for the ^1H and ^{13}C NMR analyses in 5 and 10 mm tubes respectively. The reference compound, hexamethyldisiloxane (Merck, Sharps and Dohme), and the material to be analyzed were weighed directly into the NMR tube. For the ^1H NMR analysis, deuteriochloroform (CDCl_3) was added as a solvent and internal lock; the tube was sealed with a rubber stopper and Parafilm, and the contents mixed thoroughly. In the ^{13}C NMR analysis, chromium (tris) acetylacetonate ($\text{Cr}(\text{ACAC})_3$), was added to the sample to give a concentration of 0.08-0.15 M in the final solution. This concentration decreased all the ^{13}C T_1 's to the point that a rapid pulse repetition rate could be used without severe line broadening or shifting(3). Finally, for ^{13}C analysis, CDCl_3 was weighed into the sample tube to serve as solvent, secondary reference compound and internal lock. The tube was corked tightly, sealed with Parafilm, and mixed thoroughly. In the ^{13}C spectra there was close agreement between the absolute carbon analysis derived from the two reference compounds. Also, good agreement of the carbon and hydrogen analyses by a combustion technique (Perkin Elmer 240 Analyzer) with that obtained from the ^{13}C and ^1H analyses was observed.

The ^1H and ^{13}C NMR spectra were obtained at 80 and 20 MHz, respectively, on a Varian CFT-20 pulse Fourier transform spectrometer. For the ^1H spectra the following parameters were used: transmitter positioned ca. 2.3 ppm upfield from TMS, sweep width of 1202 Hz, Butterworth filter bandwidth of 2 KHz, 8192 data points, 3.407 s. acquisition time, a 42° rf pulse of 12 μs duration, a 300 s. delay after each transient, and five transients for each spectrum. The ^{13}C spectra were obtained with:

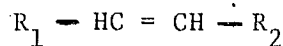
transmitter positioned ca. 14 ppm upfield from TMS, sweep width of 5000 Hz, Butterworth filter bandwidth of 8 KHz, 8192 data points, 0.819 s.

acquisition time, a 90° rf pulse of 17 μ s duration, 3.6 s. delay after each transient, ca. 15000 transients accumulated for each spectrum, and gated proton noise decoupling (to eliminate residual NOE differences) (3). Each free induction decay was transformed without sensitivity enhancement.

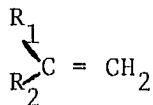
For the ^1H spectrum, three spectral regions were integrated: $\delta=0.2-3.5$ for all saturated hydrogen, $\delta=4.3-6.5$ for olefinic hydrogen, and $\delta=6.5-8.5$ for aromatic hydrogen. Typically, the olefinic hydrogen continuum returns to baseline by $\delta=6.1$, but one of the samples used in this work gave resonances in the region $\delta=6.0-6.5$. It was felt that these represented the hydrogen of conjugated dienes and thus the integral over this region was included with that of the olefinic hydrogen rather than with that of the aromatic hydrogen. Use of the reference compound data allowed for the calculation of moles aromatic hydrogen, olefinic hydrogen, and saturate hydrogen per gram of sample. This was then converted to the percentage of aromatic, olefinic and saturate hydrogen, H_A , H_O and H_S , respectively.

In the ^{13}C spectrum only two regions were integrated: $\delta=5-70$ for saturate (sp^3) carbons, and $\delta=100-170$ for aromatic plus olefinic carbons. Use of the reference compound allowed a simple calculation of the number of moles of saturate carbons per gram of sample and the number of moles of aromatic plus olefinic carbon per gram of sample. Since there is no ready way of separating the aromatic and olefinic carbons in the ^{13}C spectrum, it was necessary to estimate the amount of olefinic carbon per gram of sample from the ^1H results. This value was then subtracted from the ^{13}C aromatic plus olefinic carbon result to give the amount of aromatic carbon per gram of sample. Estimating the amount of olefinic carbon per gram of sample involved assuming that for every olefinic carbon there is one olefinic hydrogen. Thus the value obtained for moles olefinic hydrogen per gram in the ^1H analysis was the value used for moles olefinic carbon per gram of sample. This 1:1 assumption is quantitative for structures I and II, under-estimates in the case of structures III and IV, and over-estimates in the case of structure V. The validity of this assumption is difficult to assess and so it must be

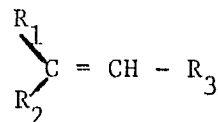
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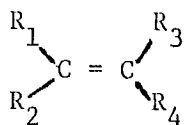
I



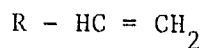
II



III



IV



V

approximation. Intuitively, it would seem to be a reasonable determination of a sample's olefinic carbon, as well as leading to a more accurate estimate of its aromatic carbon. It should be accurate enough to allow comparison of results between samples and development of trends in a series.

Once the moles of aromatic, olefinic and saturate carbon per gram of sample were determined, the percentage of aromatic carbon (Ca), olefinic carbon (Co) and saturate carbon (Cs) were calculated.

CORRELATION OF THE RESULTS

To compare hydrocarbon type contents determined by the different techniques, one must make sure that the comparisons are made on the same basis. At first approximation the information obtained from MS, FIA and Br No analyses is based on the relative numbers of molecules while the results from NMR methods are based on the relative numbers of atoms.

The MS methods are straight forward when applied to the light fractions such as the samples used in this work. However, the content of olefins and of molecules containing heteroatoms must be low. Otherwise, in the case of olefins, predeterminations must be performed by other methods or estimated by reference to other samples in a series of similar analyses. This value, which is entered into the program analysing the raw MS data, markedly affects the results subsequently determined by the MS method. Failure to directly obtain the olefin content is a weakness of the MS method.

The accuracy of the olefin results derived from the Br No depends on the deviation between the experimental and the theoretical Br No values. The deviations for alkanes, cycloalkanes, aromatics, alkenes and cycloalkenes are very small (4). Fractions which contain only these hydrocarbon groups are well suited for this analysis and reliable results should be obtainable. Complications arise when dienes, S- and some N- containing compounds are present because for these there is a very large deviation between experimental and theoretical Br No values.

Results obtained by the FIA method suffer because of the incomplete separation of the hydrocarbon groups. This is easily confirmed by a MS investigation of the separated hydrocarbon fractions. For example, a series of paraffinic (saturate) hydrocarbons is clearly observed in the collected aromatic fraction, while at the same time aromatics can be detected in the collected saturate fraction. The "olefinic" fraction is even more complex. Polar (i.e. S-, N- and O- containing) compounds are eluted very slowly and are usually included in the aromatic fraction, regardless of the nature of the molecules in which they are found.

In contrast, NMR techniques do not suffer from many of these interferences. However, it is essential to acknowledge the nature and the basis of the results. The ^{13}C NMR technique gives relative percentages of

aromatic, olefinic and saturate carbon atoms (C_A , C_O and C_S), while the 1H NMR gives the percentage of aromatic, olefinic and saturate hydrogens (H_A , H_O and H_S). These results might be misleading to those who are used to thinking in molecular terms. For example, a sample having $C_A=12\%$ and $C_O=6\%$, might at first glance, seem to contain twice as many aromatics as olefins. It is important, however, to remember that it takes at least six aromatic carbons to make one basic aromatic ring, or molecule, but only two olefinic carbons to give one olefinic molecule assuming similar average molecular weight (AMW). With these factors applied to a sample with the above C_A and C_O values, the content of aromatics and of olefins on a crude molecular basis will be 2% and 3%, respectively. There are, therefore, more olefinic molecules than aromatic molecules - the reverse of what the carbon atom distribution results indicate. Small values of C_O , then, must not be ignored. To emphasize the significance and to clarify the meaning of the NMR results, the following attempt is made to convert the results from an atomic basis to a molecular basis.

Some assumptions must be made to obtain the amounts of aromatic, olefinic and saturate molecules. First, once a molecule contains an olefinic double bond or an aromatic ring it is defined as an olefinic molecule or an aromatic molecule, respectively. Second, there is only one double bond per olefinic molecule, and only one aromatic ring per aromatic molecule. Third, the remainder of the aromatic or olefinic molecule is made up of alkyl groups containing only saturate carbon and hydrogen. The boiling point range of the samples used in this study ensures that the number of molecules containing two or more aromatic rings is negligible. Fourth, a saturate molecule contains only saturate carbons and hydrogens. These assumptions become tenuous at higher olefin concentrations because of the increasing chance of finding olefinic and aromatic functions, or two or more olefinic groups, in the same molecule; whereupon a given molecule would be counted more than once.

Calculating Procedure of NMR Results

Using the weight percent of carbon (C_T) and of hydrogen (H_T) as determined by elemental analysis and the percentages of carbon and hydrogen atoms, corresponding carbon contents (C'_A , C'_O and C'_S) and hydrogen contents (H'_A , H'_O and H'_S) on a weight basis are derived from the formula:-

$$X'_i = X_T \times X_i / 100$$

where $X = C \text{ or } H$

$$i = A, O, S$$

The sum of $C'_A + H'_A$ reflects, then, the amount of carbon and hydrogen in aromatic rings, while $C'_O + H'_O$ is the amount of carbon associated with double bonds and of hydrogen attached to these carbons. The sum of $C'_S + H'_S$ represents the amount of carbon and hydrogen associated with the saturated alkyls, as well as including the alkyl substituents on aromatic rings and olefinic double bonds.

Because the NMR technique does not include alkyl substituents on the aromatic rings, the following formula has to be applied to obtain the content of aromatic molecules:

$$\% \text{ Aromatics} = (C'_A + H'_A) \times \frac{AMW}{C_6H_{6-n}}$$

where AMW is an average molecular weight of the sample and n the number of ring hydrogens substituted by alkyl groups. The value of n can be derived from the equation.

$$(C'_A + H'_A) / C'_A = C_6H_{6-n} / C_6 = \frac{72 + 6-n}{72} =$$

$$n = 78 - \frac{72(C'_A + H'_A)}{C'_A}$$

The amount of olefinic molecules is obtained in a similar manner with the formula:

$$\% \text{ Olefinics} = (C'_O + H'_O) \times \frac{AMW}{C_2H_2}$$

The C_2H_2 (gram molecular weight of 26) in the equation reflects the assumption that one double bond per molecule and one hydrogen atom being attached to each olefinic carbon.

The amount of alkyl substituents attached to aromatic molecules and olefinic molecules (as indicated in the definitions and assumptions above) must be subtracted from the $C'_S + H'_S$ sum to get the content of saturate molecules. The following formula is used:

$$\% \text{ Saturates} = (C'_S + H'_S) - \% \text{ Arom.} - (C'_A + H'_A) - \% \text{ Olef.} - (C'_O + H'_O)$$

The results of these calculations performed on the three samples are summarized in Table 1.

The assumptions introduced during these calculations inevitably affect the final results. For example, the average molecular weight is not necessarily the same for the aromatic, olefinic or saturate hydrocarbons. Also as previously discussed and illustrated, the NMR determination of olefinic carbon is based on the assumption that there is only one olefinic hydrogen attached to each olefinic carbon. As compensation for these it is important to remember that while other techniques are limited to light fractions with low olefin and heteroatom contents, the NMR analysis is suitable even for as heavy samples as coals. To minimize the number of assumptions used in an NMR analysis it might be desirable to use the carbon and hydrogen contents at an atomic basis for correlation with the properties of the various samples.

DISCUSSION

The results of the hydrocarbon content analyses as determined by the different methods are presented in Table II.

From the chemical composition point of view, sample 1 is representative of many commercial products in that it is a refined fraction. Species which would interfere with the analyses are not present and thus an estimate of the content of each hydrocarbon type can be performed relatively easily by MS as well as NMR techniques. Also, the absence of olefin and the very small amounts of S-, O- and N- containing compounds makes this sample ideal for FIA analysis. However, a MS investigation of the fractions from the FIA separation clearly shows the same overlap of aromatic and saturate molecules previously mentioned. Therefore, the FIA method may only be a useful tool in establishing trends within a series of samples rather than in determining exact values of hydrocarbon types content.

In the case of sample 2, some complications may arise for FIA and MS methods because of the presence of olefins and S- and N- containing compounds. For the MS analysis, a predetermination of the olefins must be made by another technique. The amount of olefins obtained from the Br No is believed to be a maximum value because an additional consumption of bromine by S- and N- containing compounds cannot be excluded. In comparison with the other methods, FIA gives a lower content of saturates, and this suggests that an incomplete separation (i.e., an overlap of saturate fraction with the olefinic fraction) is the reason for the higher olefin value determined by the FIA. Depending on whether the FIA or Br No olefin content is used in the MS analysis, the results will be subsequently affected and the accuracy of the MS method becomes questionable. In the case of sample 2, an olefin content of 20% was assumed for the MS calculations.

From an analytical point of view sample 3 is an example of a very complex fraction, with special problems arising because of the presence of dienes. The estimate of olefins from the Br No is affected in particular.

If one attempts a recalculation of the NMR results from an atomic to a molecular basis (vide supra), logical results are not obtained. For example, the molecular olefin content (Table II) from the NMR analysis is unquestionably

too high. The value may be affected, by the assumption that each double bond is on a separate molecule, which is not the case for a diene. Also, aromatic ring substituents containing double bonds, if present, are counted twice, once as an aromatic molecule and once as an olefinic molecule.

The interference of the dienes can be corrected and accounted for by estimating the diene content. However, the diene correction will only add to the uncertainty of the NMR results expressed on a molecular basis because of the number of previous and current assumptions and corrections needed for the calculation. The presence of dienes will markedly affect MS results as well. The tendency of dienes to be strongly adsorbed on a solid surface will result in a slow elution during the FIA analysis and most likely lead to their inclusion in the aromatic fraction.

It appears that a quantitative analysis on molecular basis for hydrocarbon types in refined, low olefin content products can be performed quickly and accurately by MS techniques. The evaluation of samples containing dienes or large amounts of olefins and heterocyclic compounds can be performed by MS and NMR methods but with a sacrifice in accuracy as is clearly illustrated by sample 3.

The NMR results at the atomic level, i.e., the percentages of aromatic, olefinic and saturate carbons and hydrogens, appear to be the least affected by various interferences and involve the fewest assumptions. The ease with which these results can be obtained and their accuracy makes the NMR method a promising one. The ability to analyze the heaviest fractions, including coals, is of an extraordinary importance as well. Correlating these NMR results with various parameters and properties of the products may therefore be very helpful. The marked difference in properties of the three samples analyzed in this work can for example, be clearly recognized from either the NMR's atomic carbon or hydrogen distributions shown in Table I.

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TABLE I

RECALCULATIONS OF NMR RESULTS TO MOLECULAR BASIS

	SAMPLE		
	#1	#2	#3
C _T , %	84.9	85.0	85.5
H _T , %	14.0	13.9	12.2
S, %	0.09	0.58	1.72
N, ppm	1	0.083	0.01
Br No	0	42	121
AMW	110	111	102
C _A , %	8.5	8.6	15.4
C _O , %	0.0	4.0	20.8
C _S , %	91.5	87.4	63.8
H _A , %	2.2	2.5	6.3
H _O , %	0.0	2.0	11.1
H _S , %	97.8	95.5	82.5
C _A , %	7.2	7.3	13.2
C _O , %	0.0	3.4	17.8
C _S , %	77.7	74.3	54.5
H _A , %	0.31	0.35	0.77
H _O , %	0.0	0.28	1.35
H _S , %	13.69	13.30	10.06
Aromatics, %	11.0	11.3	18.7
Olefins, %	0.0	15.7	75.1
Saturates, %	89.0	73.0	3.9

TABLE II

HYDROCARBON GROUP CONTENTS AS DETERMINED BY THE DIFFERENT METHODS %

	SAMPLE		
	#1	#2	#3
Aromatics from FIA	9.6	8.4	25.7
NMR	11.0	11.3	18.7
MS	8.6	7.7	14.0
Olefins from FIA	0.5	25.1	57.1
NMR	0.0	15.7	75.1
MS	0*	20*	50.0*
BrNo	0	20.9	58.8
Saturates from FIA	89.9	66.5	17.2
NMR	87.9	72.0	3.9
MS	91.3	72.3	36.0

* The MS technique is incapable of independently determining an olefin concentration. These reported values (which were also used in the program for calculating the aromatics and saturates from the MS data) are estimates made with knowledge of the sample's history and its FIA and Br No analyses.