Oct. 24, 1950 J. J. HEIGL ET AL 2,527,122

DETERMINATION OF OLEFINS IN HYDROCARBON MIXTURES

Filed Nov. 19, 1948 2 Sheets-Sheet 1

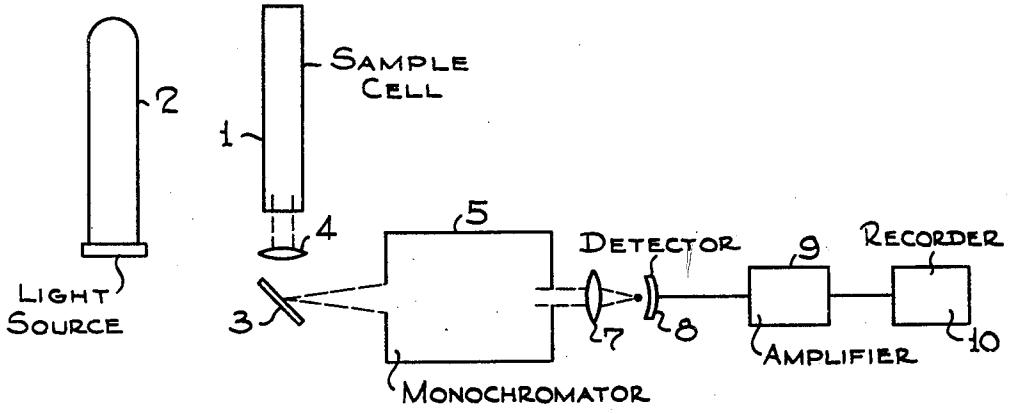


FIG.-1

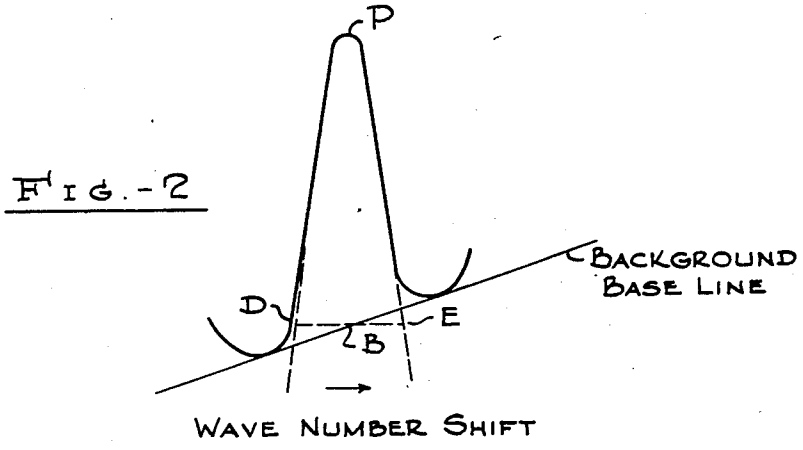


FIG.-2

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DETERMINATION OF OLEFINS IN HYDROCARBON MIXTURES

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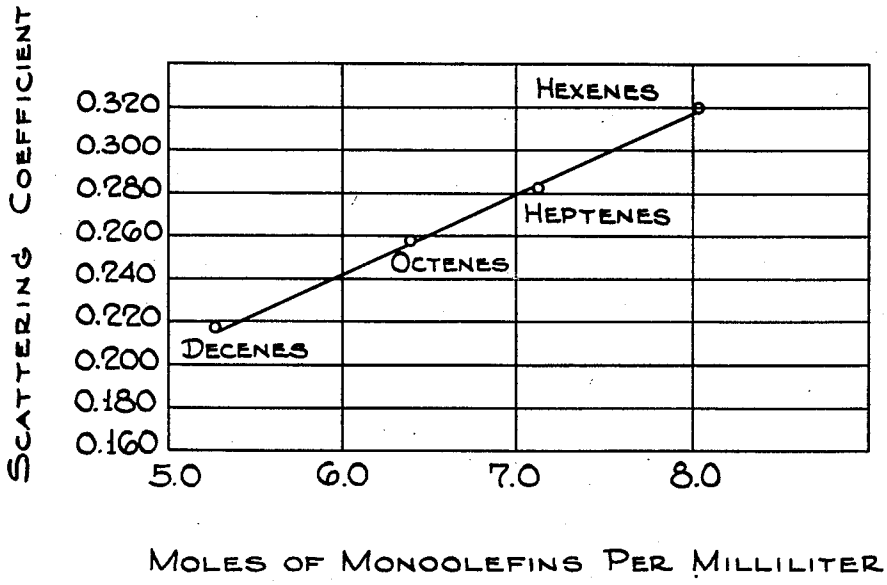


FIG.-3

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UNITED STATES PATENT OFFICE

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DETERMINATION OF OLEFINS IN HYDROCARBON MIXTURES

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Application November 19, 1948, Serial No. 60,912

1 Claim. (Cl. 88—14)

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This invention relates to an improved method for determining the percentages of mono-olefins in hydrocarbon mixtures. In accordance with this invention a suitable light source and apparatus are employed in conjunction with a sample of a hydrocarbon mixture to be analyzed, so that the Raman spectrum of the sample is produced. The Raman lines characteristic of the particular hydrocarbon mixture are then analyzed according to the process of this invention to enable the determination of the total olefin content of the hydrocarbon mixture.

In the chemical industry generally, and particularly in the petroleum refining industries, it is frequently of importance to be able to determine the percentage of olefins present in a hydrocarbon mixture. Such a determination may be made for a wide variety of purposes. For example, it may be useful in adjusting fuel quality to determine the olefinic content of a base fuel stock. Again, it may be desired to employ particular proportions of olefins in a chemical reaction, such as an alkylation reaction. In either case, the olefins are generally derived from a hydrocarbon mixture of uncertain or varying composition necessitating a determination of the olefinic content of the hydrocarbon mixture. From these general examples it is to be understood, therefore, that the present invention is of broad application to any situation wherein it is desired to establish the olefinic content of a hydrocarbon mixture.

As is well known, when a beam of light is passed through certain substances, part of the light is scattered so as to produce light of a wave length different from that of the exciting radiation. This scattered light constitutes the Raman spectrum of the substance. If the Raman spectrum of a particular substance is examined, it is found that it consists of a series of lines of extremely low intensity having both longer and shorter wave-lengths than the exciting line. A basic principle on which this invention depends is the discovery that certain Raman lines are always produced when olefins are subjected to exciting light. Thus, when a hydrocarbon mixture containing olefins is subjected to an exciting light, it will be found that Raman lines will be produced uniquely characteristic of the olefins present, even though many other Raman lines are produced by other constituents of the hydrocarbon mixture. It has furthermore been discovered that a definite relation exists between the intensity of the characteristic olefinic Raman lines and the concentration of the olefins present. Consequently, in light of these basic principles, the process of this

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invention has been developed, making possible the identification of the percentage of olefins present in a mixture from a consideration of the Raman spectrum produced from the mixture.

In order to permit a thorough understanding of this invention, the following description has been prepared directed to an explanation of the accompanying drawings wherein:

Figure 1 diagrammatically represents suitable apparatus which may be utilized in obtaining the Raman spectrum of a particular mixture in accordance with this invention, and;

Figure 2 represents a typical record resulting from scanning a portion of the Raman spectrum showing the definition of the quantities "scattering coefficient," "scattering area" and "peak base width," used in the analysis procedure of this invention, and;

Figure 3 represents a graph of the scattering coefficients of various olefinic types as determined by the method of this invention plotted against the mols of mono-olefins per milliliter in the samples employed.

Referring now to Figure 1, the numeral 1 designates a sample cell in which the hydrocarbon mixture to be analyzed may be held. The sample cell may conveniently be constructed of glass. Suitable openings are provided in the cell to permit introduction of the hydrocarbon mixture to be analyzed. While the sample may constitute either a liquid or a gas, it is to be noted, that the present invention is of greatest utility in determining the percentages of fairly high boiling olefins, not readily determinable by conventional means, so that in general the mixture to be analyzed will consist of a liquid mixture of hydrocarbons. Due to the light to which the sample cell is exposed, the sample cell may become quite hot; consequently, it is generally the practice to surround the sample cell, except for the faces thereof, with a suitable cooling jacket so as to permit maintaining the cell at a reasonable temperature. It is furthermore the general practice to suitably shield the sample cell with a medium adapted to absorb undesired light energy.

A suitable light source 2 is positioned adjacent the sample cell 1 in such a manner as to cause light to fall on the cell. If desired, a second light source may be positioned on the opposite side of sample cell 1 so that the light may be thrown on the cell from both sides thereof. It is desirable that the light source 2 be of such a character as to provide predominantly light energy of a single frequency. For example, it is suitable to employ a mercury vapor lamp or a sodium vapor lamp as

the light source 2. It is clearly important to use a light source having as great an intensity of light as is practical. In accordance with the principle discovered by Raman, when light from the source 2 falls upon the mixture of hydrocarbons in cell 1, scattered light will be produced which may be readily detected at a point outside the general path of light from the source 2. For example, scattered light will be produced from a hydrocarbon mixture contained in cell 1 which may be detected at the position occupied by the mirror 3 in Figure 1. Thus, the scattered light or the Raman lines produced from the hydrocarbon mixture may be focused by a suitable lens system 4 so as to fall on the mirror 3. The Raman lines are reflected from the mirror 3 into the entrance slit of a monochromator 5. The total Raman lines introduced to the monochromator 5 are dispersed by the monochromator into a Raman spectrum which may be observed at the focal plane of the exit slit of the monochromator. In the actual practice of this invention, a drive assembly is employed in conjunction with the monochromator so that the lines of the Raman spectrum are continuously scanned across the exit slit of the monochromator in continuous succession. Adjacent the exit slit and in the path of the light emitted therefrom, is positioned a suitable lens system 7 to cause the light issuing from the monochromator to fall on a suitable detector 8. While sensitized photographic plates, or other detecting means may be employed, it is a particular feature of this invention that a photo multiplier tube be used as the detector element. The output of the photo multiplier tube may then be amplified by a suitable amplifier 9 and this amplified output may be recorded by a high speed recorder 10. The record of the recorder 10 will consist of a continuous plot of wave length vs. intensity over the band of wave lengths for which the monochromator is adjusted to scan.

In considering the nature of the light energy detected by the detector 8, it will be found that a high intensity signal will be received at a wave length corresponding to that of the light source used and that lower intensity signals will be received at higher and lower wave lengths. Thus in the case in which the light source 2 is a mercury vapor source, the detector 8 will register a high output for 4,358 angstrom units. Longer and shorter wave length light of markedly lower intensity will also be received, falling on either side of the wave length of the exciting light. In general, the lines falling on the longer wave length side of the exciting light are conveniently employed in the practice of this invention. A sutable method of expressing the nature of the lines is to express their spectral position in terms of their distance from the exciting line expressed in wave numbers. This frequency difference may be designated as the "wave number shift" ($\Delta\nu$ cm.$^{-1}$).

If a continuous Raman spectrum, such as that emitted from a hydrocarbon mixture excited by suitable light, is examined, it will be found that above the wave length of the exciting light, the intensity of the light will vary as a function of the wave length in a manner which may be represented on a curve by peaks and valleys. This is true since all hydrocarbons have characteristic Raman spectra so that the presence of particular hydrocarbons will cause an increase in the intensity of the Raman spectra at particular frequencies. In the case of olefinic type hydrocarbons it has been found that Raman lines are obtained which are concentrated in the 1630 to 1680 wave number shift region. This effect provides a convenient manner of determining the total olefinic content of a hydrocarbon mixture. However, application of this principle in an actual analysis is subject to two principal complications.

First, in actual practice, it is found that in continuously scanning a spectrum emitted by a hydrocarbon mixture, slight shifts in the intensity at the point at which the characteristic olefinic lines appear will be encountered. This is principally due to slight fluctuations in the intensity of the light source and to variations in the output of the detector and electronic component associated therewith. To correct for this effect, it is generally the practice to utilize a suitable control standard such as carbon tetrachloride. While carbon tetrachloride will be used as an example of a suitable control standard throughout this specification it must be understood that many other standards may be employed if desired. Thus the control standard may constitute a synthetic blend of known composition, for example, having a known composition similar to that of the sample being analyzed. Again the standard chosen may be any chemical which is available in pure form and which has a distinct Raman line, preferably of about the same intensity as the lines of the sample. In order to use the control sample, such as carbon tetrachloride, it is necessary to periodically remove the sample cell containing the hydrocarbon mixture to be analyzed, and to replace the sample cell with a sample cell containing carbon tetrachloride. It is convenient to use the Raman line of the carbon tetrachloride occurring at a wave number shift of 459 ($\Delta\nu$ cm.$^{-1}$). In order to suitably correct variations of intensity of the Raman lines of the hydrocarbon mixture by this method, an expression called the "scattering coefficient" is evaluated. The scattering coefficient may be defined as the ratio of the intensity of the particular line concerned to the intensity of the chosen line of the control sample. In order to evaluate this formula, it is convenient to measure the height of the lines on the record chart produced by the recorder 10 of Figure 1, measured in millimeters above the background base line.

In Figure 2 is diagrammatically indicated the type of intensity variation recorded by the recorder 10 as a portion of the Raman spectrum is scanned. It will be noted that a peak intensity is indicated at a point identified as "P" on the curve. On either side of the peak intensity, the intensity of the signal recorded drops off sharply to a value indicated as being the "background base line." If lines are drawn along the sharply sloped portions of the curve on either side of point P, as indicated a more or less triangular area will be obtained having the base D—E and bounded by the indicated construction lines and by the sharply peaked curve. On the plot of Figure 2 the scattering coefficient may then be defined to be the distance PB of the particular intensity peak examined, divided by the similar distance PB derived from the height of the carbon tetrachloride peak. It is apparent that the area below the curve of Figure 2, may be approximately determined by finding the area of the triangle indicated, having the vertices P, D and E. This area is defined as the "scattering area" and is equal to the scattering coefficient times the base width divided by two.

As stated, a characteristic Raman line intensity

peak will be found for olefins generally, in the region of about 1630 to 1680 wave number shift ($\Delta\nu$ cm.$^{-1}$). However, for a particular olefin, the exact position within this region at which a Raman line will occur will be characteristic of that olefin and may differ for other olefins. As a result, when measuring the Raman spectrum of a sample containing a mixture of olefins, the Raman line observed in the region of 1630 to 1680 wave number shift ($\Delta\nu$ cm.$^{-1}$) is frequently a broad band rather than a sharp peak such as observed in the Raman spectrum of a pure compound. As a result of this behaviour the measurement of a scattering coefficient based upon maximum peak height can not be employed to give a true value for the olefin content since some of the olefins present contribute to widen the peak rather than to increase its height. This is the second of the complications heretofore mentioned as affecting the practice of the analytical procedure of this invention. It has been found, however, that this complication can be overcome and successful analyses performed by employing relationships based upon the total area under the Raman curve in the indicated wave number shift region.

With this brief description of the principles and general technique involved in this invention, the exact manner in which olefins may be determined can be appreciated. Indicated in Table I is pertinent Raman spectographic data concerning 29 pure olefins.

The data in Table I indicates that the magnitude of the scattering coefficient characteristic of the olefinic double bond decreases with the increasing molecular weight of the pure compound being examined. Thus, the scattering coefficient for the first 10 olefins tested, hexenes, as shown in the table was 0.301 plus or minus 0.028 and similarly the scattering coefficients for the groups of higher molecular weight olefins as indicated in the table were 0.267 plus or minus 0.034, 0.240 plus or minus 0.031, and 0.198 plus or minus 0.018. It has been established that this behavior is due to the fact that the scattering coefficients are directly proportional to the concentration of olefinic double bonds in the sample. This may readily be shown by a plot such as illustrated in Figure 3. Figure 3 shows that the scattering coefficient is directly proportional to the mols of mono olefins per milliliter. In this graph, the plotted values represent the averages of the scattering coefficients for the mono olefins of each molecular weight as given in Table I.

It has furthermore been discovered that a coefficient independent of molecular weight may be obtained by multiplying the observed scattering coefficient of each individual olefin by the molecular volume of the pure hydrocarbon. The product of this calculation may be termed the "molal scattering coefficient" and has the values represented in the third column of Table I. It will be observed that the average value of the

TABLE I

Raman data used for determination of total mono-olefins

Olefin Hydrocarbon	Wave Number Shift ($\Delta\nu$cm.$^{-1}$)	Scattering Coefficient	Scattering Coefficient Times Molecular Volume	Peak Base Width (mm.)
3-Methyl-1-pentene	1,640	0.294	36.9	25.0
4-Methyl-1-pentene	1,643	0.332	41.8	24.5
c-4-Methyl-2-pentene	1,663	0.338	42.3	23.0
2,3-Dimethyl-1-butene	1,647	0.265	32.8	23.5
t-4-Methyl-2-pentene	1,647	0.260	32.5	23.5
2-Methyl-1-pentene	1,650	0.261	32.1	23.5
1-Hexene	1,650	0.338	42.2	24.0
t-3-Hexene	1,670	0.314	38.9	23.5
c-2-Hexene	1,660	0.288	35.3	23.5
2,3-Dimethyl-2-butene	1,680	0.323	38.3	23.5
Average for Hexenes		0.301±0.028	37.3±3.4	
2,4-Dimethyl-2-pentene	1,675	0.298	41.9	24.5
4,4-Dimethyl-1-pentene	1,643	0.216	30.2	27.0
1-Heptene	1,645	0.306	43.0	23.0
3-Ethyl-2-pentene	1,665	0.317	43.0	25.0
t-2-Heptene	1,660	0.226	31.5	27.0
c-2-Heptene	1,660	0.253	35.0	25.5
3-Heptene	1,660	0.255	35.7	27.0
Average for Heptenes		0.267±0.034	37.2±4.7	
2,4,4-Trimethyl-1-pentene	1,647	0.212	33.1	25.0
2,4,4-Trimethyl-2-pentene	1,675	0.230	35.2	24.5
6-Methyl-1-heptene	1,643	0.235	36.9	24.0
2-Methyl-1-heptene	1,650	0.277	43.0	24.0
2-Ethyl-1-hexene	1,647	0.230	35.5	24.0
1-Octene	1,640	0.293	45.9	25.0
4-Methyl-3-heptene	1,665	0.297	45.8	24.0
t-2-Octene	1,670	0.198	30.9	25.0
c-2-Octene	1,670	0.192	29.7	28.0
Average for Octenes		0.240±0.031	37.3±5.0	
3,4,4,5-Tetramethyl-2-hexene (L.B.)[1]	1,655	0.225	42.6	23.0
3,4,4,5-Tetramethyl-2-hexene (H.B.)[1]	1,655	0.190	35.9	23.0
Decene-1	1,643	0.178	33.7	24.5
Average for Decenes		0.198±0.018	37.4±3.5	
Overall average			37.3±4.2	23.8±1.0

[1] These olefins are distinguished as low-boiling and high-boiling isomers.

It will be noted that for each of the olefins tested, the table gives the wave number shift encountered for the particular olefin. The "scattering coefficient" and "peak base width" or DE in Figure 2, as formerly defined, are also given in the table. In the third column of the table a new value is given, identified as the scattering coefficient times the molecular volume of the particular olefin. molal scattering coefficient is the slope of the line represented in Figure 3 and is substantially constant over the entire molecular weight range. The constancy of the molal scattering coefficient with molecular weight is further indicated by the data of Table II. It will be observed that for the olefins in each of the molecular weight ranges, the molal scattering coefficient is 37.3 plus or minus 0.1.

TABLE II

Constancy of molal scattering coefficient with molecular weight

Molecular-Weight Range	Number of Isomers Studied	Molal Scattering Coefficient
Hexenes	10	37.3
Heptenes	9	37.2
Octenes	7	37.3
Decenes	3	37.4
Average		37.3

A simple and direct method for converting the measured scattering coefficient into mols of unsaturates per milliliter of sample may be derived by using the molal scattering coefficient. It will be observed that the line plotted in Figure 3 must by definition pass through zero scattering coefficient at zero mols of unsaturates per milliliter of sample. Consequently, a scattering coefficient is equal to the mols of unsaturates per milliliter times the slope of the line, or in other words, is equal to the mols of unsaturates per milliliter times 37.3. Conversely, an observed scattering coefficient divided by 37.3, is equal to the mols of unsaturates per milliliter. As developed, this relationship is valid regardless of the molecular weight of the mono olefins in the sample.

In accordance with these considerations in actually determining the mols of mono olefin present in a sample, the scattering coefficient of the olefin peak in the region of 1630 to 1680 ($\Delta\nu$ cm.$^{-1}$) is determined. The observed base width of the olefin peak is measured from the plot in millimeters. The concentration of the mono olefins in the sample may then be determined by the formula:

$$\text{Moles of mono-olefins per milliliter} = \frac{\text{Scattering coefficient} \times \text{base width}}{(37.3)(23.8)}$$

In this formula, it will be noted that since millimeters were used as the unit for determining the average base width (23.8) that therefore millimeters should be the units employed for measuring the base width of the particular olefin peak.

As an example of the application of this invention, several synthetic samples were prepared containing olefins of all the types represented in Table I. These olefins were heptene-1, octene-1, 2 - methyl - 1-pentene, cis-4-methyl-2-pentene, 2,3-dimethyl-2-butene, and 2,2,4-trimethyl-2-pentene. Samples were prepared by mixing arbitrary proportions of each of the specified olefins to give the compositions indicated in Table III.

As stated in the table, sample A consisted of a 100% mixture of all of the indicated olefins while samples B and C respectively consisted of 76.9 and 51.2% olefins by volume of the sample, The residual portion of samples B and C consisted of the diluent 2,2,4-trimethyl-pentane. As indicated in Table III, the analytical procedure of this invention was capable of establishing the olefin content of the samples with a deviation from 2.4 to 8.0% resulting in an average deviation of 4.5% of the actual value.

As a further example of this invention, samples were analzyed for total olefins in the presence of paraffins, naphthenes, and aromatics. A sample was prepared containing 23.7% of 9 carbon atom aromatics, 46.3% of mono olefins, 25% of naphthenes, and 5% of paraffins. Indicated in Table IV are the analytical results that were obtained by applying the procedure of this invention. It will be noted that the olefins were identified with a percentage deviation of 5.2%.

TABLE IV

Analysis for total olefins by Raman spectrometry

Sample: Blend of 23.7% C_9 aromatics, 46.3% mono-olefins, 25% naphthenes, and 5% paraffin

Molecular Type	Composition		Deviation from Reported Value, Per Cent
	Known	Found	
Olefins, millimoles per milliliter	0.327	0.310	5.2

Further tests were made in which the total olefins were determined in a naphtha produced by hydrocarbon synthesis processes. The test results of the method of this invention were compared with the results obtained by a bromine number determination and by an infrared analysis using conventional methods. It will be noted from the data of Table V that the Raman method of this invention gave results for the percent of total olefins closely agreeing with results obtained by the two conventional analyses procedures.

TABLE V

Analyses for total olefins in a hydrocarbon synthesis naphtha

Analytical Method	Millimoles Mono-olefins Per Milliliter		
	Raman	Bromine-Addition	Infrared
Sample Description			
Total naphtha	4.36	5.06	4.62
135— to 250—° F. fraction	5.45	5.28	5.73
250— to 350—° F. fraction	3.16	3.78	2.75

TABLE III

Analysis for total mono-olefins by Raman spectrometry

[Blends of Olefins of All Types [1] Diluted with 2,2,4-Trimethylpentane]

	Sample "A"		Sample "B"		Sample "C"	
	Contains 100 Per Cent Olefins by Volume		Contains 76.9 Per Cent Olefins by Volume		Contains 51.2 Per Cent Olefins by Volume	
	Millimoles Olefin Per Milliliter	Deviation, Per Cent	Millimoles Olefin Per Milliliter	Deviation, Per Cent	Millimoles Olefin Per Milliliter	Deviation, Per Cent
Blended composition	7.06		5.43		3.61	
Found:						
Run No. 1	7.07	0	5.30	2.4	3.45	4.4
Run No. 2	6.60	6.5			3.32	8.0

[1] Heptene-1, octene-1; 3 ethyl-1-pentene, 2 methyl-1-pentene; cis-4-methyl-2-pentene; 2,3 dimethyl-2-butene; 2,4,4 trimethyl-2-pentene.

It will be apparent to those skilled in the art that the broad method of this invention may be refined and modified in many ways. For example, electrical computing devices and various charts may be employed to facilitate the analytical determinations. Again it may be desirable to utilize a Raman spectograph which is provided with slits of a suitable width to just cover the 1630 to 1680 wave displacement region of the spectrum.

What is claimed is:

The method of quantitatively determining the total olefin content of a liquid sample consisting of the steps of scanning the Raman spectrum of the said sample in the 1630 to 1680 wave number shift region, producing a curve expressing the variation of intensity within this region, and measuring the peak intensity and the peak base width of the curve of intensity within this region above the base background intensity whereby the total area beneath the intensity curve above the background intensity within this region may be determined and whereby the total olefin content of the sample may be obtained.

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REFERENCES CITED

The following references are of record in the file of this patent:

Rank et al., Article in the Journal of the Optical Society of America, vol. 36, June 1946, pp. 325 to 334 inclusive.

Rank, Article in the Journal of the Optical Society of America, vol. 37, June 1947, pp. 798 to 801 inclusive.

Dunstan et al., Text—The Science of Petroleum, vol. 2, 1938, pp. 1206 to 1210, 1213 and the plate with figures 1 to 3 opposite page 1206. Published Oxford University Press, London.