Mass Spectrometer Analysis of Some Liquid Hydrocarbon Mixtures

R. A. BROWN, R. C. TAYLOR, F. W. MELPOLDER, AND W. S. YOUNG
The Atlantic Refining Company, Philadelphia, Pa.

Applications of the mass spectrometer method of analysis to normally liquid hydrocarbons in the C_5 to C_8 range are discussed. Accuracies attainable for individual compounds in a number of different synthetic mixtures are given and typical analyses of several hydrocarbon fractions in gasoline boiling range are shown. It is concluded that a substantial number of the paraffins, cycloparaffins, and aromatics occurring in this region may be individually determined. Olefins and cyclo-olefins, on the other hand, may be determined individually only to a limited extent at present.

APPLICATIONS of the mass spectrometer to the analysis of normally gaseous hydrocarbon mixtures, such as those occurring in petroleum refinery practice, have been covered thoroughly in previous publications (*3, 6, 7*) where accuracies attainable with various mixtures have been experimentally established. Similar data for normally liquid mixtures in the C_5 through C_8 range, however, have been insufficient to permit an accurate evaluation of the method when applied to mixtures of practical interest. This paper presents mass spectrometer analyses of a number of known synthetic mixtures in this range for the purpose of establishing accuracy, and to illustrate by several examples the application of the method to actual mixtures.

Broadly, the hydrocarbon types which must be considered because of their known presence in petroleum products include the paraffins, cycloparaffins, mono- and diolefins, and aromatics. It would be possible, however, at present to determine only a limited number of the many compounds which might conceivably be present, even in the relatively narrow C_5 through C_8 range, for a twofold reason: The lack of pure calibrating materials of the olefinic type constitutes a serious handicap to the extension of direct mass spectrometer analysis to these compounds, and it is questionable, in view of the present status of instrumental stability and the probable similarity of olefinic mass spectra, whether many of the isomers could be identified as individuals.

In spite of the somewhat unfavorable outlook for direct olefin analysis, however, the most promising approach to the general problem at present seems to lie in the separation of olefinic compounds from a complex mixture of hydrocarbons by some means such as silica gel percolation or solvent extraction. This may be followed by hydrogenation of the olefinic portion, fractional distillation, and then identification of the resulting paraffins and cycloparaffins by the mass spectrometer method, whereupon certain branched structures may be assigned to a substantial portion of the parent olefins. This method has the obvious limitations that nothing can be learned concerning the positions of the double bonds, and that it must be presumed no rearrangement or polymerization occurs during the manipulations. By utilizing other techniques, however, such as deuteration or ozonolysis, in conjunction with the mass spectrometer method, it may be possible to assign positions to double bonds in a number of cases, thus complementing the structure data.

It is evident from the foregoing that the successful spectrometer analyses of olefins in the C_6 through C_8 range at present awaits considerable experimental investigation.

What can be done, however, with the remaining hydrocarbons may be summarized as follows:

Paraffin isomers can be identified individually except for a few pairs, which, because of pattern similarity, must be grouped occasionally in complex mixtures.

Cycloparaffin isomers can for the most part be identified individually through C_7 range, but generally must be grouped in the C_8 range.

Olefin isomers can be determined at present only in the C_5 and lower range.

Cyclo-olefins can be determined in only a few instances, primarily because suitable calibrating compounds are not available.

Aromatics such as benzene, toluene, and ethylbenzene are readily determined individually, but xylenes must be grouped, as a rule.

APPARATUS AND PROCEDURE

Mass Spectrometer Analysis. The mass spectrometer used was manufactured by the Consolidated Engineering Corp., Pasadena, Calif. The general techniques of operation and computation have been adequately described (*6, 7*).

Liquid samples and liquid calibrating compounds were introduced into the instrument by using the sintered-glass valve system previously described (*5*). The known gaseous mixtures of the C_5 hydrocarbons were prepared using manometric pressure measurements in the conventional manner, while liquid mixtures of C_6, C_7, and C_8 hydrocarbons were prepared by a semimicro-weighing method (*5*).

In addition to the synthetic mixtures, a series of alkylate fractions was analyzed (Table X), whose composition had previously been determined from fractional distillation and physical property measurements (*1*).

Generally, calibrations and mixtures were run on the same day in order to minimize errors due to pattern fluctuations. An outline of the computational method used accompanies each table.

Distillation and Preparation of Naphtha Samples. The hydrocodimer analyzed (Table II) was first separated into ten fractions on a Podbielniak high-temperature column having 60 theoretical plates operated at a reflux ratio of 100 to 1.

The three cracked naphtha samples (Tables XII and XIII) were first treated with nitrogen peroxide according to the nitrosation procedure of Bond (*2*) for the removal of olefinic materials. Aromatics and traces of nitrosates were then removed from the treated naphtha by silica gel percolation (*4*) and the resulting paraffin-cycloparaffin mixtures were distilled into 2% fractions on 100-plate columns operating at 100 to 1 reflux ratio.

Blends were then made of these near-boiling fractions, wherever possible to reduce the number of samples requiring analysis.

DISCUSSION AND RESULTS

Analysis of C_5 Hydrocarbons. Presented in Table I are three analyses of a nine-component C_5 mixture containing known amounts of iso- and *n*-pentane, cyclopentane, five pentenes, and isoprene (2-methyl-1,3-butadiene). These data show that the concentration of isoprene, 2-methyl-2-butene, and the pentanes are within a mean of 0.1 to 0.6 mole % of the known composition.

Table I. Analysis of a Synthetic C_6 Mixture

Component	Known Composition	Determined Composition 1	2	3	Mean Difference
		Mole per cent			
Isoprene	4.3	4.2	4.3	4.1	0.1
3-Methyl-1-butene	10.5	10.4	8.5	11.8	1.1
1-Pentene	10.2	11.9	9.9	7.5	1.6
2-Methyl-1-butene	9.7	6.7	10.5	9.9	1.3
trans-2-Pentene	9.6	13.3	13.4	10.0	2.6
2-Methyl-2-butene	11.1	10.9	10.2	10.5	0.6
Cyclopentane	10.3	8.2	9.4	12.7	1.8
Isopentane	19.0	19.1	18.3	18.3	0.5
n-Pentane	15.3	15.3	15.5	15.2	0.1
Total mole %	100.0	100.0	100.0	100.0	

Method of computation. Iso- and *n*-pentane were first resolved by solving two simultaneous equations based on masses 57 and 72. Isoprene, cyclopentane, and the pentenes were then resolved from seven simultaneous equations based on residual peaks at masses 39, 41, 42, 55, 68, 69, and 70.

Table II. Analysis of a Synthetic C_6 Mixture

Component	Known Composition	Determined Composition	Difference
	Mole per cent		
Cyclopentane	4.2	5.1	0.9
2,2-Dimethylbutane	4.4	4.2	−0.2
2,3-Dimethylbutane	13.3	12.3	−1.0
2-Methylpentane	28.8	29.9	1.1
3-Methylpentane	40.2	40.2	0.0
n-Hexane	9.1	8.3	−0.8
Total mole %	100.0	100.0	

Method of Computation. Six simultaneous equations based on masses 42, 43, 57, 70, 71, and 86.

Cyclopentane and the remaining pentenes agree within 1.1 to 2.6 mole %.

Although this mixture contained no cyclopentene, 1,3-pentadiene, or 1,4-pentadiene, it is believed that the presence of such compounds would introduce no additional error in the pentane, cyclopentane, or pentene analysis. It would necessitate, however, the grouping of pentadienes, cyclopentene, and other compounds of molecular weight 68.

The method of computation involves the solution of one set of two simultaneous equations and one of seven equations.

Analysis of C_6 Hydrocarbons. Table II compares the mass spectrometer analysis of a six-component C_6 hydrocarbon synthetic with its known composition, the maximum difference found being 1.1 mole %. This analysis differs from a similar mixture previously reported (*6*) by including both 2,3-dimethylbutane and cyclopentane. Although no methylcyclopentane or cyclohexane was included, a consideration of the known mass spectra of these compounds indicates that their presence would probably not affect the accuracy of the analysis for the other components. Methylcyclopentane and cyclohexane binary mixtures may be analyzed with an accuracy of approximately 0.5 mole %.

Analysis of C_7 Hydrocarbons. A ten-component mixture comprising the nine heptane isomers plus 2,2,4-trimethylpentane was analyzed by means of the mass spectrometer. The proportions of the major components in the mixture correspond approximately to those found in C_3 alkylate. The results obtained for two different analyses of this mixture are compared in Table III with the known composition. It may be seen that the mass spectrometer analysis agrees to within a mean deviation of 0.1 to 1.6 mole %. Because of the similarity in the mass spectra of 2,2-dimethylpentane and 2,2,3-trimethylbutane, however, it was found necessary to group these two compounds. Experience has shown that the average cracking pattern of these two hydrocarbons may be used for any relative concentration of the two hydrocarbons without introducing a significant error.

Based also on past experience with similar mixtures and the known behavior of the pure compounds, it is felt that the presence of cycloparaffins boiling in the C_7 paraffin range would have no adverse effect on the accuracy of the paraffin analysis. The determination of the cycloparaffins, however, would probably be limited to cyclohexane and 1,1-dimethylcyclopentane, with *trans*-1,2- and 1,3-dimethylcyclopentanes grouped in certain cases.

Analysis of C_8 Hydrocarbons. Octanes in the 99.2° to 115.6° C. Range. Tables IV and V show the results obtained on three different blends of nine octane isomers. Nine simultaneous equations were solved based on mass spectra data at masses 42, 43, 56, 57, 70, 71, 85, 99, and 114. Pattern coefficients are so similar for many of these isomers that stability of the mass spectrometer appears to be an important factor in obtaining reproducibility. In several cases it was necessary to group two isomers in order to stay within a reasonable limit of error. Thus in Table IV,

Table III. Analysis of a Synthetic C_7 Mixture

Component	Known Composition	Determined Composition 1	2	Mean Difference
		Mole per cent		
2,2-Dimethylpentane	3.5 } 5.7	5.8	5.7	0.1
2,2,3-Trimethylbutane	2.2			
2,4-Dimethylpentane	50.7	48.9	49.3	1.6
3,3-Dimethylpentane	1.9	1.9	1.8	0.1
2,3-Dimethylpentane	31.7	33.0	33.6	1.6
2-Methylhexane	1.7	1.3	0.9	0.6
3-Methylhexane	3.8	4.6	3.0	0.8
3-Ethylpentane	1.8	1.6	2.5	0.5
n-Heptane	1.3	1.6	2.0	0.5
2,2,4-Trimethylpentane	1.4	1.3	1.2	0.2
Total mole %	100.0	100.0	100.0	

Method of Computation. Nine simultaneous equations based on masses 42, 43, 55, 57, 70, 71, 85, 99, and 100. 2,2-Dimethylpentane and 2,2,3-trimethylbutane were grouped by using an average cracking pattern.

Table IV. Analysis of a Synthetic C_8 Mixture Boiling between 99.2° and 115.6° C.

Component	Known Composition	Determined Composition 1	2	3	4	5	Mean Difference
		Mixture 1A, Mole Per Cent					
2,2,4-Trimethylpentane	7.7 } 26.6	4.2			10.5	15.0	
2,2-Dimethylhexane	18.9 }	23.2	24.0	25.7	18.0	13.4	1.6
2,2,3-Trimethylpentane	9.9	9.8	10.8	10.0	10.5	9.6	0.4
2,5-Dimethylhexane	17.1	15.7	19.8	16.2	16.1	16.1	1.4
2,4-Dimethylhexane	8.0	7.9	11.3	14.9	7.0	4.8	2.9
3,3-Dimethylhexane	15.7 } 22.3	17.5	2.5	1.7	15.9	22.2	
2,3,3-Trimethylpentane	6.6 }	4.3	20.6	17.9	6.0	0.9	1.1
2,3,4-Trimethylpentane	7.0	7.1	10.4	13.5	6.2	4.2	2.7 } 2.2
2,3-Dimethylhexane	9.1	10.3	0.6	0.1	9.8	13.8	4.8 }
Total mole %	100.0	100.0	100.0	100.0	100.0	100.0	
		Mixture 1B, Mole Per Cent					
2,2,4-Trimethylpentane	12.3 } 20.4	12.4	{ 18.7	5.6	{ 25.1	7.0	{ 1.9
2,2-Dimethylhexane	8.1 }	7.6		12.7		13.2	
2,2,3-Trimethylpentane	12.5	13.6	13.6	14.2	13.1	13.2	1.0
2,5-Dimethylhexane	8.6	9.1	10.5	8.4	9.1	7.9	0.8
2,4-Dimethylhexane	7.2	5.6	6.7	9.1	12.8	9.3	2.3
3,3-Dimethylhexane	17.5 } 29.3	16.0	13.0 } 31.6	10.8 } 30.1	{ 23.5 } 28.1	11.1	{ 2.7
2,3,3-Trimethylpentane	11.8 }	16.4	18.6 }	19.3 }		17.0 }	
2,3,4-Trimethylpentane	9.1	8.6	8.9	10.9	14.7	12.4	2.3 } 2.8
2,3-Dimethylhexane	12.9	10.7	10.0	9.0	1.7	8.9	4.8 }
Total mole %	100.0	100.0	100.0	100.0	100.0	100.0	

Method of Computation. Nine simultaneous equations based on masses 42, 43, 56, 57, 70, 71, 85, 99, and 114.

Table V. Analysis of a Synthetic C_8 Mixture (1C) Boiling between 99.2° and 115.6° C.

Component	Known Composition	Determined Composition 1	Determined Composition 2	Mean Difference
		Mole Per Cent		
2,2,4-Trimethylpentane	38.0	41.0	39.7	2.4
2,2-Dimethylhexane	0.7	0.8	1.3	0.4
2,2,3-Trimethylpentane	4.0	0.2	0.3	3.8
2,5-Dimethylhexane	12.8	12.7	13.9	0.6
2,4-Dimethylhexane	14.2	14.3	17.1	1.5
3,3-Dimethylhexane	2.1	1.1	0.0	1.6
2,3,3-Trimethylpentane	8.1	8.7	9.0	0.8
2,3,4-Trimethylpentane	16.4	17.4	18.7	1.7
2,3-Dimethylhexane	3.7	3.8	0.0	1.9
Total mole %	100.0	100.0	100.0	

Method of Computation. Nine simultaneous equations based on masses 42, 43, 56, 57, 70, 71, 85, 99, and 114.

runs 2, 3, 4, and 5 were reported with 2,2,4-trimethylpentane and 2,2-dimethylhexane, and 3,3-dimethylhexane and 2,3,3-trimethylpentane grouped. It also was found desirable to group 2,3,4-trimethylpentane and 2,3-dimethylhexane in order to improve accuracy in most cases. Table V indicates, however, that no such grouping was necessary in a mixture of somewhat different relative concentrations. It is felt that this difference in composition had little effect on the accuracy, the improvement being due to more stable operation of the mass spectrometer during these runs. The errors reported in Table IV are attributed to a 1% fluctuation in the octane patterns. On this basis a satisfactory analysis of all the isomers requires that fluctuations in the mass spectrometer cracking patterns shall not exceed 1%.

OCTANES IN THE 106.8° TO 113.5° C. RANGE. Table VI shows the analysis of four mixtures containing six components. Here an appreciable increase in over-all accuracy was obtained as a result of reducing the number of components from nine to six. In two cases out of six, however, it was necessary to group 2,2-dimethylhexane and 2,2,3-trimethylpentane, presumably because of unstable mass spectrometer operation.

OCTANES IN THE 111.9° TO 115.6° C. RANGE. Four different synthetic mixtures of four components each were analyzed. The data in Table VII show that it was unnecessary to group any isomers and also that the average difference between the known and mass spectrometer analysis was approximately 1 mole %.

OCTANES IN THE 113.5° TO 125.7° C. RANGE. The data in Table VIII show the analysis of three different blends containing eight components. These data indicate that it was necessary to group 2,3,4-trimethylpentane, 2,3-dimethylhexane, and 4-methylheptane. The resulting agreement between known and mass spectrometer compositions is from 0.5 to 1.6 mole %. Reference to Table VIII also shows that the ratio of 2,3,4-trimethylpentane to 2,3-dimethylhexane can be approximated by assuming that 4-methylheptane is absent from a given mixture. This was permissible, since most samples of interest were found to contain little or no 4-methylheptane.

ANALYSIS OF HYDROCARBONS OCCURRING IN ALKYLATE. The alkylate analyzed was one submitted to this laboratory by the A.P.I. Project 6 for cooperative spectrographic analysis. The distillation analysis of the alkylate was determined by A.P.I. Project 6 from distillation and physical property measurements (*1*). Table IX shows the mass spectrometer analysis of 39 cuts

Table VI. Analysis of Four Synthetic C_8 Mixtures Boiling between 106.8° and 113.5° C.

	Sample 3A, Mole Per Cent				Sample 3B, Mole Per Cent			Sample 4A, Mole Per Cent				Sample 4B, Mole Per Cent		
Component	Known composition	Determined composition 1	Determined composition 2	Mean difference	Known composition	Determined composition	Difference	Known composition	Determined composition 1	Determined composition 2	Mean difference	Known composition	Determined composition	Difference
2,2-Dimethylhexane	1.3	0.9	1.4	0.3	1.7	11.9	0.3	6.5	5.8	8.2	1.2	7.4	24.0	1.1
2,2,3-Trimethylpentane	12.0	13.2	11.7	0.8	9.9			31.5	33.6	30.8	1.4	15.5		
2,5-Dimethylhexane	34.6	33.5	34.9	0.7	31.9	30.7	1.2	14.1	14.1	13.2	0.5	22.1	20.4	1.7
2,4-Dimethylhexane	30.1	29.1	30.3	0.6	35.3	37.3	2.0	31.1	29.7	30.1	1.2	29.7	31.8	2.1
3,3-Dimethylhexane	3.6	4.4	2.8	0.8	3.0	1.1	1.9	5.0	5.3	5.6	0.5	6.4	4.0	2.4
2,3,4-Trimethylpentane	18.4	18.9	18.9	0.5	18.2	19.0	0.8	11.8	11.5	12.1	0.3	18.9	19.8	0.9
Total mole %	100.0	100.0	100.0		100.0	100.0		100.0	100.0	100.0		100.0	100.0	

Method of Computation. Six simultaneous equations based on masses 56, 57, 70, 85, 99, and 114.

Table VII. Analysis of Four Synthetic C_8 Mixtures Boiling between 111.9° and 115.6° C.

	Sample 2A, Mole Per Cent			Sample 2B, Mole Per Cent				Sample 5A, Mole Per Cent				Sample 5B, Mole Per Cent		
Component	Known composition	Determined composition	Difference	Known composition	Determined Composition 1	Determined Composition 2	Mean difference	Known composition	Determined Composition 1	Determined Composition 2	Mean difference	Known composition	Determined composition	Difference
3,3-Dimethylhexane	2.9	3.1	0.2	13.4	12.9	12.8	0.6	3.0	4.4	3.5	1.0	5.5	6.2	0.7
2,3,4-Trimethylpentane	50.5	49.6	0.9	37.0	36.4	38.0	0.8	42.5	43.5	42.7	0.6	57.2	55.7	1.5
2,3,3-Trimethylpentane	35.3	36.4	1.1	32.2	33.5	32.4	0.8	37.5	35.5	36.1	1.7	25.1	26.1	1.0
2,3-Dimethylhexane	11.3	10.9	0.4	17.4	17.2	16.8	0.4	17.0	16.6	17.7	0.6	12.2	12.0	0.2
Total mole %	100.0	100.0		100.0	100.0	100.0		100.0	100.0	100.0		100.0	100.0	

Method of Computation. Four simultaneous equations based on masses 70, 71, 85, and 114.

Table VIII. Analysis of Three Synthetic C_8 Mixtures Boiling between 113.5° and 125° C.

	Sample 6A, Mole Per Cent				Sample 6B, Mole Per Cent				Sample 6C, Mole Per Cent			
Component	Known composition	Determined composition 1	Determined composition 2	Mean difference	Known composition	Determined composition 1	Determined composition 2	Mean difference	Known composition	Determined composition 1	Determined composition 2	Mean difference
2,2,3-Trimethylpentane	12.1	14.9	11.5	1.7	6.9	6.7	4.0	1.5	2.4	1.9	2.2	0.4
2,3,4-Trimethylpentane	25.2		29.6		8.0		14.6		0.0		0.3	
2,3-Dimethylhexane	35.6	65.6	35.0	1.6	10.9	28.0	13.4	1.6	9.3	6.9	7.9	1.9
4-Methylheptane	5.9		[a]		10.7		[a]		0.0		[a]	
3,4-Dimethylhexane	10.5	11.9	9.6	1.2	8.9	8.4	7.1	1.2	19.5	19.0	18.7	0.7
2-Methylheptane	5.8	5.2	7.0	0.9	10.8	12.8	13.5	2.4	5.0	7.2	7.1	2.2
3-Methylheptane	5.4	2.4	4.9	1.8	6.6	7.0	8.2	1.0	27.1	27.0	26.8	0.2
n-Octane	0.0	0.0	2.4	1.2	37.2	37.1	39.2	1.1	36.7	38.0	37.0	0.8
Total mole %	100.0	100.0	100.0		100.0	100.0	100.0		100.0	100.0	100.0	

Method of Computation. Six simultaneous equations based on masses 56, 71, 84, 85, 99, and 114 with 2,3,4-trimethylpentane, 2,3-dimethylhexane, and 4-methylheptane grouped by using an average pattern.

[a] The approximate ratio of 2,3,4-trimethylpentane to 2,3-dimethylhexane was determined by assuming the absence of 4-methylheptane. Method of computation involved seven simultaneous equations based on mass 70 in addition to those listed above.

Table IX. Analysis of an Alkylate from 39 Distillate Fractions

Component	Distillation Analysis (1)	Mass Spectrometer Analysis	Difference
	Volume Per Cent		
Isobutane		....	
n-Butane	8.3 ± 0.5	0.34	0.1
Neopentane		0.06	
Isopentane		8.02	
Pentenes	.....	0.09	..
n-Pentane	0.6 ± 0.3	0.35	0.2
2,2-Dimethylbutane	0.0	0.0	0.0
2,3-Dimethylbutane	4.7 ± 0.8	4.84	0.1
2-Methylpentane	1.1 ± 0.5	1.02	0.1
3-Methylpentane	0.4 ± 0.2	0.42	0.0
2,2-Dimethylpentane	0.2 ± 0.2	....	..
2,4-Dimethylpentane	3.4 ± 0.9	3.55	0.2
2,2,3-Trimethylbutane	0.2 ± 0.2	0.25	0.1
2,3-Dimethylpentane	2.3 ± 0.6	2.32	0.0
2-Methylhexane	0.3 ± 0.2	0.18	0.0
3-Methylhexane		0.15	
2,2,4-Trimethylpentane	24.3 ± 0.9	24.4	0.1
2,2-Dimethylhexane	0.2 ± 0.2		
2,5-Dimethylhexane	6.6 ± 1.4	4.48	0.6
2,4-Dimethylhexane		2.70	
2,2,3-Trimethylpentane	1.2 ± 0.6	1.21	0.0
2,3,4-Trimethylpentane	13.0 ± 1.8	12.4	0.8
2,3,3-Trimethylpentane	12.3 ± 1.8	12.3	0.0
2,3-Dimethylhexane	3.0 ± 1.4	3.0	0.0
3,4-Dimethylhexane	0.4 ± 0.3		
4-Methylheptane		17.92	0.0
2-Methylheptane	17.5		
3-Methylheptane and higher			
Total vol. %	100.0	100.0	

after the individual results had been combined into an over-all analysis. The agreement between the "known" composition and mass spectrometer analysis in general is within a few tenths of 1 mole %.

ANALYSIS OF HYDROCARBONS AND CRACKED NAPHTHAS. To illustrate the applicability of the mass spectrometer method to actual unknown mixtures, the data in Table X show an analysis of a typical hydrocodimer in the boiling range of 79° to 119° C. Here the analysis of ten cuts is shown combined on the basis of the total sample. It can be seen that the only compounds present in measurable amounts are the paraffin hydrocarbons.

As pointed out previously, the cracked naphthas were treated prior to distillation to remove olefinic and aromatic material, in order to eliminate interference caused by the presence of a large number of olefins for which pure calibrating compounds are not available. The aromatic fraction in the boiling range covered would not interfere with the analysis and was only removed incidentally.

Table XI shows the analyses of the paraffin-cycloparaffin portions of two cracked naphthas. The analysis of each of the six individual cuts into which the treated naphthas were split by distillation are included to show the overlap in concentrations of individual compounds between successive cuts. In all cases it was necessary to group the di- and trimethylcyclopentanes.

Table XII gives the same data for a third cracked naphtha over a somewhat wider temperature range. Here, too, most of the cycloparaffins had to be grouped, although some of the dimethylcyclopentanes could be individually determined.

CONCLUSIONS

A review of the application of mass spectrometer analysis to the determination of C_5, C_6, C_7, and C_8 hydrocarbons in known and unknown mixtures is given. From the accumulated data it was concluded:

All the C_6 and C_7 paraffin and cycloparaffin hydrocarbons for which pure standards are available may be individually determined, with the exception of 2,2-dimethylpentane and 2,2,3-trimethylbutane which normally must be grouped and the 1,2- and 1,3-dimethylcyclopentanes which frequently must be grouped.

Various octanes must be grouped according to the complexity of the sample and/or stability in operation of the mass spectrometer. Under ideal conditions for narrow boiling fractions, however, it is necessary to group only 4-methylheptane with 2,3,4-trimethylpentane and 2,3-dimethylhexane. In the absence of 4-methylheptane each of the remaining isomers can be resolved individually.

In general, most of the C_8 cycloparaffin isomers must be grouped, because of similarity in their cracking patterns.

Benzene, toluene, ethylbenzene, and grouped xylenes may be resolved from most hydrocarbon mixtures.

Table X. Analysis of a Hydrocodimer from Eight Distillate Fractions Boiling between 79° and 119° C.

Component	Volume Per Cent
2,2-Dimethylpentane	0.39
2,4-Dimethylpentane	0.15
2,2,3-Trimethylbutane	0.0
2,3-Dimethylpentane	1.07
2-Methylhexane	0.04
3-Methylhexane	0.22
2,2,4-Trimethylpentane	30.6
2,2-Dimethylhexane	
2,5-Dimethylhexane	1.28
2,4-Dimethylhexane	2.28
2,2,3-Trimethylpentane	15.1
3,3-Dimethylhexane	....
2,3,4-Trimethylpentane	32.9
2,3,3-Trimethylpentane	5.52
2,3-Dimethylhexane	4.68
4-Methylheptane	0.15
3,4-Dimethylhexane	1.51
2-Methylheptane	0.13
3-Methylheptane	0.22
Higher boiling compounds	3.76
Total volume %	100.00

Table XI. Paraffin and Cycloparaffin Hydrocarbon Content of Thermal Cracked Naphtha Boiling between 80° and 105° C.

	Fraction No.							Fraction No.						
	1	2	3	4	5	6	Total	1	2	3	4	5	6	Total
	Boiling Point, ° C.							Boiling Point, ° C.						
Hydrocarbon	80–90	90–92	92–96	96–99	99–101	101–105	80–105	80–90	90–92	92–96	96–99	99–101	101–105	80–105
	Naphtha A, Volume Per Cent							Naphtha B, Volume Per Cent						
2,4-Dimethylpentane	0.37	...	..	...	...	..	0.37	0.08	..	..	...	...	..	0.08
3,3-Dimethylpentane	0.53	...	..	...	...	..	0.53	0.21	..	..	...	...	..	0.21
2,3-Dimethylpentane	0.89	2.47	0.24	...	...	..	3.60	1.82	0.28	0.73	...	...	..	2.83
2-Methylhexane	1.64	6.26	0.50	...	...	..	8.40	2.24	2.78	1.25	...	...	..	6.27
3-Methylhexane	..	6.06	1.76	2.94	...	..	10.76	..	4.74	3.57	1.10	...	..	9.41
3-Ethylpentane	..	...	0.26	...	...	..	0.26	..	..	0.82	...	...	..	0.82
n-Heptane	..	...	1.62	11.92	3.56	0.48	17.58	..	..	2.26	12.78	15.31	0.15	30.50
2,5-Dimethylhexane	..	...	..	...	...	0.23	0.23	..	..	..	...	...	0.25	0.25
2,4-Dimethylhexane	..	...	..	...	...	0.22	0.22	..	..	..	...	...	0.23	0.23
Cyclohexane	7.25	0.08	..	...	...	..	7.33	5.25	0.14	..	...	...	..	5.39
Dimethylcyclopentanes	1.91	10.60	2.85	2.39	...	..	17.75	1.73	5.22	6.24	0.69	...	..	13.88
Methylcyclohexane	..	...	..	2.22	17.55	7.76	27.53	..	..	..	0.45	12.08	10.98	23.51
Ethylcyclopentane	..	...	..	...	1.40	2.69	4.09	..	..	..	...	1.41	4.15	5.56
Trimethylcyclopentanes	..	...	..	...	0.39	0.96	1.35	..	..	..	0.03	...	1.03	1.06
							100.00							100.00

Table XII. Paraffin and Cycloparaffin Hydrocarbon Content of Catalytic Cracked Naphtha Boiling between 28° and 120° C.

Hydrocarbon	Fraction No. 1	2	3	4	5	6	7	8	9	Total
	Boiling Point, °C. 28–49	49–67	67–82	82–93	93–99	99–103	103–111	111–118	118–120	28–120
	Volume Per Cent									
2,2-Dimethylbutane	0.14	0.14	..	..	..	..	..	...	..	0.28
2,3-Dimethylbutane	0.72	4.57	..	..	..	..	..	...	..	5.29
2-Methylpentane	..	18.07	0.11	..	..	..	..	...	..	18.18
3-Methylpentane	..	10.52	..	..	..	..	..	...	..	10.52
n-Hexane	..	1.13	3.81	..	..	..	..	...	..	4.94
2,2,3-Trimethylbutane	..	...	1.03	0.11	..	..	..	...	..	1.14
2-Methylhexane	..	..	..	5.81	..	..	..	...	..	5.81
3-Methylhexane	..	..	..	6.02	1.53	..	..	...	..	7.55
n-Heptane	..	...	..	..	1.43	0.94	..	...	..	2.37
2,2,4-Trimethylpentane	..	...	..	..	0.20	0.05	..	...	..	0.25
2,5-Dimethylhexane	..	...	..	..	..	..	0.47	...	..	0.47
2,4-Dimethylhexane	..	...	..	..	..	..	0.58	..	..	0.58
2,2,3-Trimethylpentane	..	...	..	..	..	..	0.26	...	..	0.26
2,3,4-Trimethylpentane / 2,3-Dimethylhexane / 4-Methylheptane	..	...	..	..	..	..	0.10	0.81	..	0.91
3,4-Dimethylhexane	..	...	..	..	..	..	..	1.06	..	1.06
2-Methylheptane	..	...	..	..	..	..	..	1.58		
3-Methyl-3-ethylpentane	..	...	..	..	..	..	..	0.04	3.06	4.68
3-Ethylhexane	..	..	..	..	..	..	..			
Cyclopentane	0.47	0.52	..	..	..	..	..	...	..	0.99
Methylcyclopentane	0.18	0.80	9.48	1.24	..	..	..	...	..	11.70
Cyclohexane	..	...	0.67	0.06	..	..	..	...	..	0.73
1,1-Dimethylcyclopentane	..	...	0.56	0.71	..	..	..	...	..	1.27
1,3-Dimethylcyclopentane / 1,2-Dimethylcyclopentane	..	...	..	6.75	1.90	0.79	0.36	...	..	9.80
Methylcyclohexane	..	...	..	..	0.28	2.58	1.47	...	..	4.33
Ethylcyclopentane	..	...	..	..	0.10	0.80	1.04	0.38	..	2.32
Trimethylcyclopentane	..	...	..	..	..	0.06	1.31	...	..	1.37
Other C_8 cycloparaffins	..	...	..	..	..	..	1.37	1.83	..	3.20
										100.00

C_6 and heavier olefins and cyclo-olefins cannot be analyzed directly on the mass spectrometer because of pattern similarity and unavailability of pure calibrating samples.

LITERATURE CITED

(1) Am. Petroleum Inst., A.P.I. Project 6 Report, "Analysis of Alkylates and Hydrocodimers" (August 31, 1946).

(2) Bond, G. R., Jr., IND. ENG. CHEM., ANAL. ED., **18**, 692 (1946).

(3) Brewer, A. K., and Dibeler, V. H., *J. Research Natl. Bur. Standards*, **35**, 125 (1945).

(4) Mair, B. J., and Forziati, A. F., *Ibid.*, **32**, 165 (1944).

(5) Taylor, R. C., and Young, W. S., IND. ENG. CHEM., ANAL. ED., **17**, 811 (1945).

(6) Washburn, H. W., Wiley, H. F., and Rock, S. M., *Ibid.*, **15**, 541 (1943).

(7) Washburn, H. W., Wiley, H. F., Rock, S. M., and Berry, C. E., *Ibid.*, **17**, 74 (1945).

RECEIVED March 28, 1947. Presented before the Division of Petroleum Chemistry at the 111th Meeting of the AMERICAN CHEMICAL SOCIETY, Atlantic City, N. J.

Infrared Analytical Techniques for Analyzing C_5 Mixtures

VERNON THORNTON AND ANNETTE E. HERALD, *Phillips Petroleum Company, Bartlesville, Okla.*

Mixtures of C_5 hydrocarbons have been analyzed in the vapor phase rapidly and with sufficient precision for plant control. The analytical techniques were greatly simplified by the discovery that the extinction per unit pressure was constant over a pressure range of 50 to 650 mm. of mercury at 30° C. for the two C_5 paraffins and six C_5 olefins under consideration. Small variations in the concentrations of components appearing in fractionation products were quickly measured by infrared method, even though the components possessed relatively weak absorption bands, by comparing with a reference mixture.

WHEN the problem of applying infrared analytical techniques to the control of plant operations was considered for streams containing mixtures of C_5 hydrocarbons, the literature had little to offer in the way of developed methods.

The difficulty of confining these volatile samples in conventional liquid absorption cells is evident and most laboratories have spent considerable effort toward building a satisfactory liquid cell capable of containing samples under small pressures (*1–4*).

In view of this difficulty it was decided to investigate the possibility of analyzing C_5 mixtures in the vapor phase. To this end highly purified samples of each hydrocarbon listed in Table I were scanned at desirable pressures in conventional type gas absorption cells of suitable length over the rock salt range of a Perkin-Elmer Model 12-A spectrometer equipped with photoamplifier and Brown recorder.

From these scannings, extinctions were measured at twenty-three wave lengths, corresponding to key absorption bands of the components. These extinctions, measured at several pressures, were plotted against uncorrected pressures and in every case a straight line through the origin resulted. Figure 1 shows this linear relationship for a paraffin, *n*-pentane at the 8.7-micron band, for an olefin, 2-methyl-1-butene at the 8.2-micron band, and for a mixture of 2-methyl-1-butene(52%) and 1-pentene (48%), at the 8.2-micron band. This linear relationship was the most that could be hoped for and somewhat surprising to one who had analyzed C_4 mixtures by a similar procedure.

Key wave lengths were chosen from the spectrograph records and pressure-extinction curves plotted for each of the eight materials shown in Table I at each of the key wave-length positions.

From the slope of these curves the extinction coefficients needed to set up the usual set of simultaneous equations were obtained. Table II shows one such set of extinction coefficients. The underscored extinction coefficients are those of the principal absorber at the spectral positions indicated. The most unfavorable

Table I. Components of a C_5 Cut

Compound	Boiling Point, °C.	Compound	Boiling Point, °C.
3-Methyl-1-butene	18.8	*trans*-2-Pentene	35.85
Isopentane	27.89	*n*-Pentane	36.0
1-Pentene	30.1	*cis*-2-Pentene	37.0
2-Methyl-1-butene	31.05	2-Methyl-2-butene	38.49