Analysis by the Mass Spectrometer of a Liquified Hydrocarbon Mixture Containing C_3-C_5 Paraffins and Olefins[1]

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A study of two methods for removing small samples from a liquified hydrocarbon mixture of known composition has been made with a mass spectrometer. The first method, that of opening the cylinder valve and allowing the mixture to evaporate slowly into an evacuated reservoir, was shown to give varying compositions depending on the rate of evaporation. The second method employed a low-temperature bath to cool the mixture below the boiling point of all components at atmospheric pressure. A portion of the liquid was then isolated in a pipette and completely expanded into a gas reservoir. Five successive samplings agreed with the composition certified by the Phillips Petroleum Co. within the experimental error.

I. Introduction

During the last 4 years, an increasing number of mass spectrometer laboratories have participated in cooperative test programs designed to evaluate the precision and accuracy of analytical methods for light hydrocarbon analysis. Shepherd [1][2] has recently reported the results of one such cooperative test on a natural gas sample, ASTM D–3- VII–2. The sample batch was carefully prepared in the vapor phase, and all of the cylinders distributed were filled simultaneously from a common manifold. Other test programs, however, have required analysis of liquefied hydrocarbon mixtures in which the relatively minute sample used by the mass spectrometer was removed from the liquid phase, usually by evaporation. Some of the variations in reported composition of the liquefied hydrocarbon mixture may be due to real differences in the composition of the separate samples sent to different laboratories. More likely, however, is a change in composition caused by inadequate precautions taken to remove a representative sample from the liquefied contents of the cylinder. To minimize the possibility of the former, a large batch of the test sample was usually divided into a number of portions and each portion put into a cylinder using various means to maintain identical composition for each sample. Assuming such precautions to be effective, however, it should be noted that at least one case has been reported [3] in which the composition of a liquefied hydrocarbon mixture changed over a period of time due to distillation through a slowly leaking valve.

It has long been known that it is very difficult to remove a representative sample from the liquid phase of a two or more component system boiling below room temperature at atmospheric pressure. Shepherd [2] has listed the steps necessary to do this as, (1) the liquid phase is made homogeneous, (2) a portion of the liquid phase is isolated from the bulk of the liquid without change in composition (i. e., without boiling), (3) the isolated portion is completely evaporated into a suitable container again without change in composition, and (4) the vapor phase is made homogeneous.

This paper reports a series of mass spectrometric analyses made on Phillips Hydrocarbon Mixture 21, containing C_3–C_5 paraffins and olefins. The boiling range was approximately −48° to +37° C; the freezing range was approximately −188° to −105° C. The samples for analysis were withdrawn from the cylinder by two methods. First, the valve of the inverted cylinder was cautiously opened to admit a quantity of gas into an evacuated reservoir; and second,

[2] Figures in brackets indicate the literature references at the end of this paper.

[3] Phillips Hydrocarbon Mixture 6 as received by the Gas Chemistry Section, National Bureau of Standards.

a small portion of the liquid phase was isolated from the bulk of the liquid without appreciable change in composition and completely evaporated into the reservoir. For samples taken by the first method, the variation in composition was studied as a function of the flow-rate. The ap parent composition of samples taken by both methods were compared with each other and with the composition certified by the Phillips Petroleum Co.

II. Experimental Procedure

The hydrocarbon analyses were made with a Consolidated mass spectrometer [3]. The hydrocarbon mixture was blended by the Phillips Petroleum Co. as mixture No. 21 with the composition reported as accurate to ± 0.05 percent. It was received in an ICC specification steel cylinder fitted with a standard liquefied petroleum gas valve. A number of samples for analysis were removed from the liquid phase by each of the two methods described below. The data obtained by the mass spectrometer were evaluated with a Consolidated electrical computer [4] using procedures recommended by the manufacturer.

The procedures for the two methods of sampling are outlined below.

Method I. The cylinder, with a needle valve and inner member of a standard taper attached, was supported in an inverted position. The air in the needle valve connection was carefully flushed out and the cylinder attached to a 5-liter glass reservoir (A in fig. 1) by the outer standard taper, C. All volumes and connections up to the needle valve were evacuated to about 10^{-4} mm. At this point, the reservoir was isolated from the rest of the system by closing the metal sylphon valve, D. The inner surfaces of the reservoir and connections were then "conditioned" with the hydrocarbon mixture by cautiously opening the needle valve until a pressure of several centimeters was indicated on the manometer, B. The needle valve was then closed and the reservoir and connections evacuated through D to a pressure of less than 0.1 mm, as shown on B. The flushing was repeated twice at approximately the same rate. A sample for analysis was then removed from the cylinder at approximately the same rate as the flushing. by opening the needle valve until a de-

sired pressure was read on the manometer, B. The rate of flow obtained for any opening of the needle valve was calculated from the time required to introduce sufficient gas to raise the pressure in the reservoir to 15 mm. For the slowest rate measured, this required about 100 seconds, while the most rapid sampling attempted required only 15 seconds. The contents of the reservoir were mixed by convection, and a 5-ml portion isolated in the volume, G. This portion was then condensed at liquid air temperature into one of the lengths of 3-mm tubing on manifold H, and sealed off. Care was taken to adjust volumes and pressures so that the contents of the 3-mm tubing could be released directly into the inlet reservoirs of the mass spectrometer without further subdivision.

Method II. A small liquid pipette was constructed by soldering two needle valves to a sufficient length of ½-in. copper tubing to give a 3-ml volume between the valve seats. One end of the pipette was provided with a standard taper to connect to the gas reservoir (fig. 1); the other end
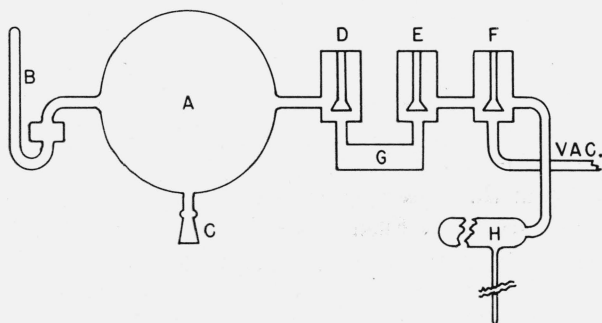

FIGURE 1.—*Schematic drawing of gas phase sampling and bottling apparatus used for methods I and II.*

was connected to the hydrocarbon cylinder by a suitable fitting. The air was flushed out of the pipette and with valve, M, closed, the unit was partially submerged in a low temperature bath ($-78°$ C) as shown in figure 2. The glass tube, L, was added before submerging to prevent contamination and to provide a means of flushing a known amount of liquid through the pipette. After 5 minutes of cooling, the unit was removed from the bath, thoroughly shaken and replaced. After this procedure was twice repeated, liquid hydrocarbon was flushed through the pipette by cautiously opening M and allowing the liquid
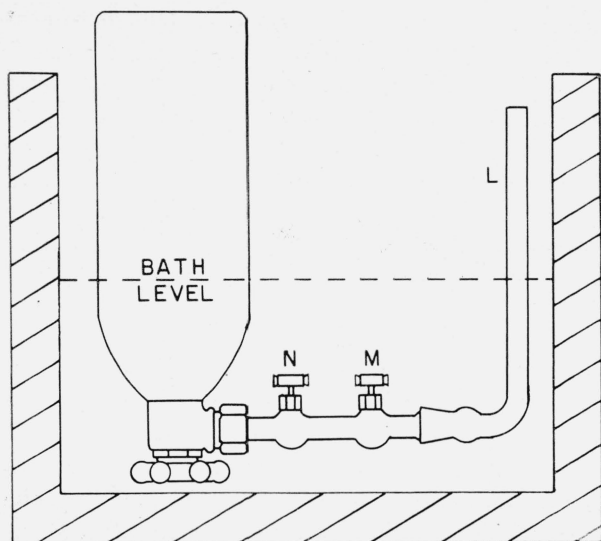
FIGURE 2.—*Hydrocarbon cylinder and liquid pipette as supported in the low temperature bath for use in method II.*

to slowly rise in the vertical glasss tube, L.[4] When the level in L indicated a complete change of liquid in the pipette, M and N were closed and the unit connected to C (fig. 1). Thereafter it was removed from the bath, allowed to come to room temperature and the entire contents evaporated into the gas reservoir. The gas phase was then thermally mixed and sampled as described in method I.

The calibrating gases were Phillips Research Grade Hycrocarbons with the exception of *cis*-2-butene, 1-pentene and *trans*-2-pentene. The *cis*-2-butene was a Mellon-Koppers-Hinckley sample previously described by one of the authors [5]. The 1-pentene and *trans*-2-pentene were standard samples numbers 281–5S and 283–5S, respectively, available at the National Bureau of Standards.

III. Discussion of Results

The analysis of isomers in the mass spectrometer is, in general, inferior to the analysis of substances differing in molecular weight. The discrimination between butenes is particularly difficult. The following pages give complete analyses and also data for total butenes, butanes, pentenes and pentanes. Figures for the totals are usually more accurate than for separate isom-

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[4] On one or two occasions it was necessary to direct a stream of warm air on the upper end of the cylinder to initiate the flow of liquid.

ers, and are in some respects a better test of the sampling techniques.

Table 1 shows the composition of the hydrocarbon samples as a function of the sampling rate when removed from the cylinder by method I. Columns 2 to 7 inclusive are given in the order in which the samples were taken and at the flow-rate in milliliters per second indicated at the head of each column. Column 9 lists the composition reported by Phillips as accurate to ± 0.05 percent. The reproducibility of composition for the same flow-rate, as indicated by the three analyses sampled at two milliliters per second, is interesting in that it shows reproducibility to be a poor criterion of a representative sample when the sample is taken in this manner. Further evidence of this fact is given in table 2, which shows the results of six analyses made on the same hydrocarbon mixture as part of a Rubber Reserve cooperative program. In this case, the cylinder was directly attached to the mass spectrometer inlet, and vapor metered into the reservoirs. As they are obviously not representative samples, the reproducibility is unusual; although an experienced analyst will often sample at nearly the same rate several times in a row. A relatively slow rate is required to guard against breakage and observations on similar samples show the usual sampling rate in this laboratory to be about two milliliters per second.

TABLE 1.—*Mole percent composition of samples obtained by vaporizing a stream of liquid*

Component	Sample flow rate (ml/sec)[a] and mole percent							Synthetic composition
	2	5	1	2	2	3	7	
Propene	5.5	6.6	5.2	5.4	5.5	6.0	6.8	7.00
Propane	10.3	10.4	10.0	10.3	10.2	10.5	10.8	10.55
1-Butene	7.1	8.7	5.8	6.1	6.8	7.2	6.7	8.28
2-Butene	9.2	9.9	7.7	8.9	8.1	9.7	11.9	6.24
i-Butene	4.5	2.2	7.1	5.8	5.8	4.0	2.0	6.10
n-Butane	30.0	30.2	29.9	30.1	30.0	30.3	29.9	29.88
i-Butane	14.1	13.0	14.7	14.0	14.3	12.9	13.1	13.25
1-Pentene	2.4	2.5	2.2	2.4	2.2	2.5	2.1	1.65
2-Pentene	1.3	1.1	1.6	1.3	1.5	1.1	1.4	1.69
n-Pentane	8.9	8.8	9.1	9.1	9.1	8.9	8.7	8.88
i-Pentane	6.7	6.7	6.7	6.6	6.4	6.8	6.6	6.48
Total Butenes	20.8	20.7	20.6	20.8	20.7	20.9	20.6	20.62
Total Butanes	44.1	43.1	44.6	44.1	44.3	43.2	43.0	43.13
Total Pentenes	3.7	3.6	3.8	3.7	3.7	3.6	3.5	3.34
Total Pentanes	15.6	15.5	15.8	15.7	15.5	15.7	15.3	15.36

[a] These measurements are tabulated in the order in which they were made

TABLE 2.—*Mole percent composition of six samples evaporated directly into mass spectrometer reservoir*

Component	Sample Number and Mole Percent						Mean	Synthetic composition
	1	2	3	4	5	6		
Propene	5.2	5.2	5.5	5.5	5.5	6.0	5.5±0.2	7.00
Propane	10.3	10.3	10.3	10.3	10.4	10.5	10.4± .1	10.55
1-Butene	6.8	6.1	5.5	7.1	6.6	8.7	6.8± .7	8.28
2-Butene	8.1	8.9	9.1	9.2	8.8	9.9	9.0± .4	6.24
i-Butene	5.8	5.8	6.0	4.5	5.4	2.3	5.0±1.0	6.10
n-Butane	29.9	30.0	29.9	30.0	30.2	30.2	30.0±0.1	29.88
i-Butane	14.3	14.0	14.2	14.1	13.7	13.0	13.9± .4	13.25
Total pentenes	3.8	3.8	3.7	3.7	3.7	3.8	3.7± .1	3.34
n-Pentane	9.1	9.2	9.0	8.9	9.0	8.8	9.0± .1	8.88
i-Pentane	6.7	6.7	6.8	6.7	6.7	6.8	6.7± .1	6.48
Total Butenes	20.7	20.8	20.6	20.8	20.8	20.9	20.8± .1	20.62
Total Butanes	44.2	44.0	44.1	44.1	43.9	43.2	43.9± .2	43.13
Total Pentanes	15.8	15.9	15.8	15.6	15.7	15.6	15.7± .1	15.36

The variation of composition as a function of the rate of sampling is shown graphically in figure 3. The ordinate of a point plotted for a component represents the percent of the known composition actually found in the sample taken at the flow-rate indicated by the abscissa. For example, the amount of propene determined in a sample taken at a rate
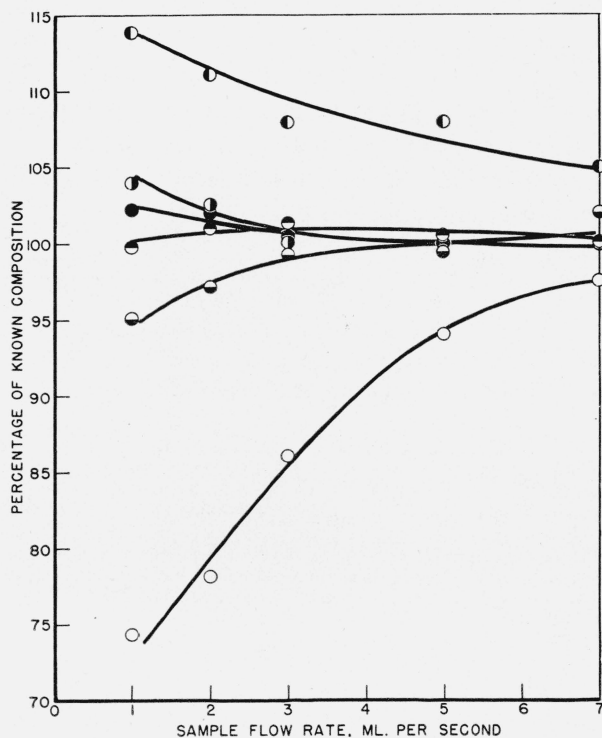

FIGURE 3.—*Percentage of known composition of the components plotted as a function of the sample flow-rate in method I.*

○, propene; ◑, propane; ◓, butenes ◑, butanes; ◐, pentenes; ●, pentanes.

of 1 ml per second was 5.2 percent. This represents only 74.3 percent of the reported concentration of propene in the original mixture. In the same sample, propane was analysed as 10.0 percent, or 95.7 percent of the known concentration. The other components are similarly plotted. Total butenes, butanes, pentenes, and pentanes are plotted because of the uncertainty of distribution between the isomers as mentioned above. The deviation from known composition is less marked with increased sampling rate. This may be the result of cooling at the valve seat, in which case, the lower boiling components pass through the valve before completely evaporating.

In 1920, A. K. Dunbar of the Harvard Cryogenic Laboratory studied the sampling of the system, liquid nitrogen+oxygen, under various conditions and at different rates of flow. His work, described in a series of reports to the U. S. Bureau of Mines, disclosed an isobaric separation yielding high nitrogen. This is in the expected direction, and the effect observed in the present work reverses this expectancy. In the effort to avoid possible misunderstanding in comparing cross-check analyses, Shepherd called attention to Dunbar's work in a 1944 report to Rubber Reserve, and at the same time added an observation he had made in 1920 with respect to the operation of a helium still. A still plate containing approximately equal parts of nitrogen and methane at 300 lb/in.[2] delivered essentially nitrogen from a needle valve located outside of the still lagging, whereas much nearer the proper mixture was delivered from a needle valve whose seat was located within the still plate itself. This experiment magnified the effect to be expected upon sampling systems like the C_{3+4+5} mixtures under pressure in cylinders delivered for Rubber Reserve cross-check analyses. As stated above, these effects are in the opposite sense to the effects shown in figure 3. An effect in the direction indicated by figure 3 could arise from an accumulation of unvaporized higher boiling components resulting from the process of conditioning the large reservoir in method I or the mass spectrometer inlet manifold in table 2. In the authors' opinion, the effect could also arise from depletion of the liquid near the needle valve with respect to the more volatile components, due to bubbles rich in these components moving under gravity in a direction opposite to the sample stream, except

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when the latter flow-rate is high. The former phenomenon has been observed in distillation apparatus while the latter is hypothetical. The important point, however, is that sampling by method I can lead to erroneous results.

Table 3 gives the composition of six samples removed from the cylinder by method II. Sample six was taken immediately after a large amount of liquid hydrocarbon was lost from the cylinder and is not included in the average values listed in column 8. For this sample, the space above the liquid in the cylinder was probably large enough to allow an appreciable change in the composition of the liquid due to a greater evaporation of the lower boiling components. Total isomers of each component are tabulated for comparison with table 1. The variation in distribution among the isomers is considerably less than in table 1 and slightly less than usually encountered in such a mixture as shown in table 2. Since the 2-butene calibration was made using the *cis*-2-butene isomer, some small error may be expected if the *trans* isomer is present in the mixture. The variation in the butenes, however, is less than that expected if ±0.5 percent pattern variation is assumed. Although the *trans*-2-pentene isomer was used to calibrate for 2-pentene, negligible error is expected since the *cis*- and *trans*-2-pentene patterns are more nearly alike than the patterns of the 2-butene isomers.

The Consolidated electrical computer was used to solve the 11 simultaneous equations. The most arduous task was the proper preparation of the matrix to assure rapid convergence in the computer. This preparation was aided by the use of 132 small wooden blocks arranged 11 by 12 in a tray and constructed in a manner that allowed any two rows or columns to be picked up and their positions exchanged. This was similar to the more elaborate checkerboard used for the same purpose in the Gas Chemistry Section of the Bureau. The coefficients and constant terms were then written on labels glued to the blocks. Several arrangements of the matrix were tried. None were more suitable than that suggested by Consolidated, except in one set of analyses in which carbon dioxide was accidentally added to the mixture. The time required for each solution was about 45 minutes. This includes time for setting in or checking the coefficients already in the computer prorated for all analyses. At first some difficulty was experienced with variable contact resistance between the helipots representing the coefficients and the contactor bar resulting in no solution or spurious results. This diminished with continued use, and under present conditions the data obtained for any of the above reported samples solved on successive trials give checks to ±0.2 percent of the value. This is much better than the reproducibility of the mass spectrometer data obtained for this mixture.

IV. Conclusions

The foregoing experiments indicate that a common technic of sampling volatile liquid mixtures, namely, permitting a slow stream of liquid to evaporate into an evacuated volume, can lead to large systematic errors in the analysis. In the Phillips hydrocarbon mixture 21, samples introduced into previously flushed reservoirs at slow rates were deficient in propene and rich in butanes and pentenes. Other components showed smaller effects. The error was reduced if the sampling rate was increased. The error was minimized, however, by withdrawing a small liquid sample from the cylinder without change in composition at the point of withdrawal. This can be done within the limits of error of the present mass spectrometer by lowering the temperature of the cylinder and contents in the vicinity of the valves to a temperature sufficiently below the boiling point of all components at atmospheric pressure and a sample removed as described above.

TABLE 3.—*Analyses of samples removed in the liquid phase*

Component	Sample number and mole percent						Mean 1 to 5	Synthetic composition
	1	2	3	4	5	[a]6		
Propene	7.1	7.0	7.2	6.7	7.1	6.3	7.02±0.14	7.00
Propane	10.7	10.5	10.6	10.7	10.6	10.5	10.62± .06	10.55
1-Butene	7.6	8.8	8.4	8.0	8.0	8.3	8.12± .34	8.28
2-Butene	6.3	6.0	6.1	5.9	5.8	6.4	6.02± .14	6.24
i-Butene	6.5	5.8	5.9	6.5	6.7	5.8	6.28± .34	6.10
n-Butane	30.2	30.2	29.4	29.4	29.7	29.3	29.78± .22	29.88
i-Butane	13.1	13.1	13.6	14.0	13.5	14.3	13.46± .29	13.25
1-Pentene	1.6	1.6	1.8	1.6	1.6	1.6	1.64± .06	1.65
2-Pentene	1.8	1.8	1.7	1.8	1.8	1.8	1.78± .03	1.69
n-Pentane	8.6	8.7	8.8	8.6	8.5	8.4	8.64± .09	8.88
i-Pentane	6.5	6.5	6.5	6.8	6.7	7.3	6.60± .12	6.48
Total butenes	20.4	20.6	20.4	20.4	20.5	20.5	20.46± .07	20.62
Total butanes	43.3	43.3	43.0	43.4	43.2	43.6	43.24± .11	43.13
Total pentenes	3.4	3.4	3.5	3.4	3.4	3.4	3.42± .03	3.34
Total pentanes	15.1	15.2	15.3	15.4	15.2	15.7	15.24± .09	15.36

[a] Sample 6 was drawn from a nearly empty cylinder.

Mass Spectrometer Hydrocarbon Analysis

The analysis of a volatile mixture on the basis of a liquid sample involves the assumption that a negligible amount of the mixture is in the gas phase. As the ratio of liquid to gas density at atmospheric pressure is 200–300 to 1, the gas phase clearly can be neglected if the liquid nearly fills the container. If it is nearly empty, the liquid is no longer representative of the mixture within the precision of the analyses. It has been noted before that sample 6 of table 3 is measurably depleted in propene for this reason. Samples 1 to 5 of table 3 obtained from a nearly full container show in general a mean composition agreeing with the synthetic composition within the range of experimental uncertainty. For propene, propane, total butenes, butanes, pentenes, and pentanes, this uncertainty is of the order of 0.1 percent of the total amount. The discrimination between isomers is considerably less accurate than this.

Recent modifications of the Consolidated mass spectrometer that were not used in this work may reduce the experimental error somewhat. They will, however, emphasize the importance of improved sampling procedure.

V. References

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