The Analysis of Multicomponent Mixtures of Hydrocarbons in the Liquid Phase by Means of Infra-Red Absorption Spectroscopy

D. L. FRY, R. E. NUSBAUM
Research Laboratories Division, General Motors Corporation, Detroit, Michigan

AND

H. M. RANDALL
Randall Laboratory of Physics, University of Michigan, Ann Arbor, Michigan

(Received October 17, 1945)

This is a general method of applying infra-red absorption spectroscopy to the analysis of multicomponent hydrocarbon mixtures in the liquid phase. The procedure is calibrated by measuring optical densities of synthetic standard samples. A constant thickness cell is used for both standard and unknown samples. Two procedures for converting optical densities to concentrations are described. Examples are given for four- and five-component mixtures. Data are presented to show the reproducibility of repeated measurements of optical density on the same sample, and results are given to show the agreement between the infra-red analyses and the known composition of synthetic mixtures.

INTRODUCTION

A GENERAL method of applying infra-red absorption spectroscopy to the analysis of multicomponent hydrocarbon mixtures in the liquid phase has been developed and has been applied to two particular mixtures, one containing four components and the other five components. It is an empirical method based upon analytical curves prepared from absorption measurements of pure samples of the components to be found in the unknowns and of binary mixtures of these components.

A number of papers on the application of infra-red absorption spectroscopy to analytical problems have been published. Most of these have been concerned with the analysis of binary mixtures. However, two papers have described methods for the analysis of more complicated mixtures. Brattain, Rasmussen, and Cravath[1] have described a method for analyzing multicomponent mixtures in the vapor phase. This method is most useful when the components are in the vapor phase under normal conditions of temperature and pressure, but can also be used with considerably more difficulty when the compounds are liquids under normal conditions. A method for analyzing a multicomponent mixture in the liquid phase has been described by Nielsen and Smith[2] and the analysis of a three-component mixture has been discussed as an example. This method can be used only over concentration ranges for which deviations from Beer's law are negligible.

The procedures described in the present paper are used for multicomponent mixtures in the liquid phase and are applicable even though the concentrations of any of the components of the mixture vary from 0 to 100 percent.

The absorption of monochromatic radiation as it traverses an absorbing liquid is expressed by Beer's law.

$$acx = \log_{10}(I_0/I), \tag{1}$$

where I is the intensity of the radiation transmitted by x centimeters of liquid containing a concentration c of the absorbing materials; I_0 is the intensity of the radiation impinging on the liquid; and a is a constant of proportionality, known as the absorption coefficient. a is constant for any monochromatic radiation regardless of the values of c, x, or I_0.

For a mixture of two or more non-associating components, all of which selectively absorb somewhat over the whole infra-red region, Beer's law takes the following form for monochromatic radiation:

$$(a_1c_1+a_2c_2+a_3c_3+\cdots+a_nc_n)x = \log_{10}\frac{I_0}{I}, \tag{2}$$

[1] R. Robert Brattain, R. S. Rasmussen, and A. M. Cravath, J. App. Phys. **14**, 418 (1943).

[2] J. Rud Nielsen and Don C. Smith, Ind. Eng. Chem. Anal. Ed. **15**, 609 (1943).

where a is the absorption coefficient of material (1) and c_1 its concentration in the cell of thickness x; a_2, $a_3 \cdots a_n$ and c_2, $c_3 \cdots c_n$ are the corresponding values for materials 2, $3 \cdots n$.

In actual practice, however, Eq. (1) and, therefore, Eq. (2) does not hold exactly. This is shown experimentally by the fact that a curve of log I_0/I as a function of concentration with a constant thickness cell is not a straight line. This results from the fact that no spectrometer produces a monochromatic image at the receiver. Instead, there is produced an image containing a wave-length band $\Delta\lambda$.

Equation (3) is obtained by combining Eqs. (1) and (2).

$$\text{Log}\frac{I_0}{I}=\log\frac{I_0}{I_1}+\log\frac{I_0}{I_2}+\cdots+\log\frac{I_0}{I_n}. \quad (3)$$

The terms

$$\log\frac{I_0}{I_1}, \quad \log\frac{I_0}{I_2}, \quad \cdots\log\frac{I_0}{I_n}$$

are the values obtained for materials 1, $2 \cdots n$ at the chosen spectral position. In other words, the equation states that the optical density of a mixture is equal to the sum of the optical densities of the individual components of the mixture. Equation (3) does not contain the absorption coefficient and, therefore, is not subject to the same limitations as are (1) and (2).

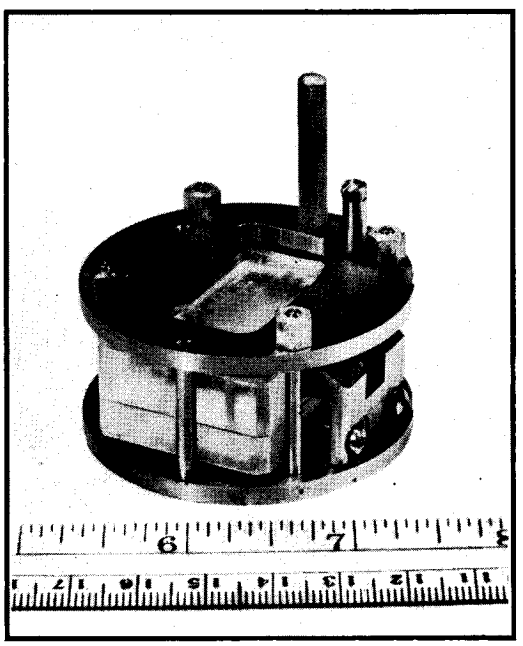

FIG. 1. An assembled cell used to obtain the infra-red absorption of liquids.

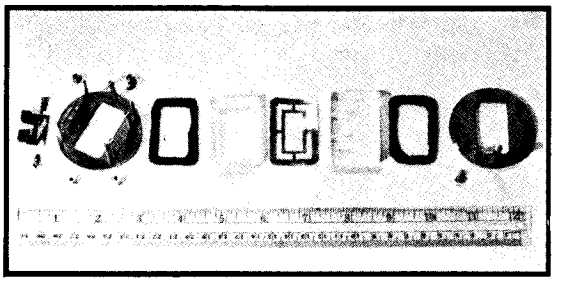

FIG. 2. Unassembled parts of a cell used in measuring the infra-red absorption of liquids.

DEVELOPMENT OF ANALYTICAL PROCEDURE

The problem in the work described here, as well as in the work of others, has been to develop a method of applying absorption spectroscopy taking into account these limitations of Beer's law. The fundamental problem of quantitative analysis in absorption spectroscopy is the determination of the log I_0/I values with sufficiently high accuracy, and the conversion of these values to percent concentration of the components in the mixture.

Absorption Cells

In the present work, optical densities are measured with a University of Michigan infrared spectrophotometer[3,4] equipped with a sodium chloride prism. Two cells are used. The background cell, consisting of a single salt plate $\frac{1}{2}''$ thick, is used to determine I_0 values. The absorption cell, shown in Fig. 1 and Fig. 2, is a modification of a cell described by Randall.[5] The frame which holds the salt plates is designed particularly for use with the University of Michigan instrument.

Starting from the left, each piece in Fig. 2 goes on top of the previous one. The salt plates of the absorption cell are $\frac{1}{4}''$ thick. They are separated by a platinum shim, the thickness of

[3] H. M. Randall and John Strong, Rev. Sci. Inst. **2**, 585 (1931).
[4] Robert A. Oetjen and H. M. Randall, unpublished thesis, University of Michigan, 1941.
[5] H. M. Randall, Rev. Sci. Inst. **10**, 195 (1939).

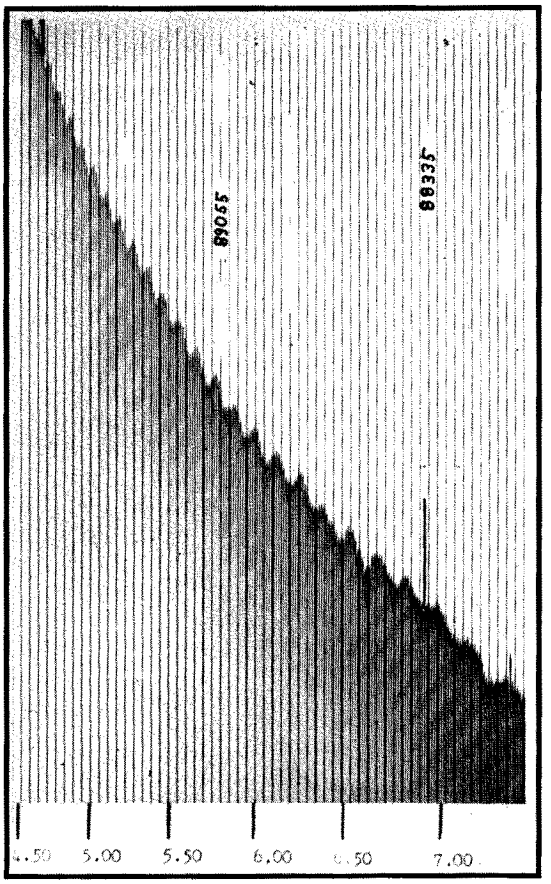

FIG. 3. A record of the interference fringe pattern obtained with a cell 0.152 mm thick.

which determines the thickness of the absorbing layer of sample. For the work described here the shim is 0.152 mm thick. The positions of the salt plates and the shim are determined by the dowl pins in the cell supports. Two rubber washers separate the salt from the stainless steel housing. After the cell is assembled, a mercury seal is established by introducing mercury into the trough in the lower plate through a hole which extends through the upper salt plate, rubber washer, and support. The liquid to be examined is introduced through one of the two holes on the side of the upper plate. Rubber pads are pressed over the holes to seal them without putting pressure on the contents of the cell. This method of sealing makes it possible to use the cell in an evacuated source box. The cell can be taken apart, cleaned, and reassembled in less than 10 minutes. However, it can be refilled in less than two minutes by expelling the liquid with an air syringe and filling with an eye dropper.

In order to use the present method successfully, it is important that the thickness of the absorption cell remain constant. The two salt plates are ground flat with corundum in ethyl alcohol, and polished on a piece of white felt stretched over a piece of plate glass. Titanium oxide is used as the abrasive for polishing, and ethyl alcohol is used to wet the titanium oxide. The finished plates are examined with an optical flat and sodium light, and if they are not flat within four diffraction fringes (i.e., 0.0012 mm) the process is repeated. The plates are examined frequently to determine whether cleaning has caused deviation from flatness.

The cells are supported in a tube directly in front of the salt window at the entrance slit of the spectrometer. The notch in the frame of the cell locates it in a given fixed position in front of the slit. The cells are handled by means of a knurled rod screwed into the upper plate.

The thickness of the cell is determined by the interference fringe method as described by Smith and Miller.[6] (See Fig. 3.) Repeat measurements made several months apart show the thickness to be 0.152 ± 0.0005 mm.

Spectral Positions

The approximate spectral positions at which optical densities are determined are selected from the records of the spectra of the pure components in the region from 3 to 13.5μ. (See Fig. 4.)

In order to obtain high resolution for these records the spectrograph is operated with narrow slits and slow rotation of the prism. The source of light is a Nernst glower. The light beam is interrupted by means of a shutter having a period of 3.8 seconds, and the output of the thermopile is amplified by a Firestone amplifier.[7] The recording galvanometer is five meters from the camera drum. The spectra are recorded in small sections with constant slits, and an overlapping of these sections of spectrum occurs whenever the slit widths are changed. Table I gives the maximum theoretical resolution ob-

[6] Don C. Smith and Elmer C. Miller, J. Opt. Soc. Am. **34**, 130 (1944).
[7] F. A. Firestone, Rev. Sci. Inst. **3**, 163 (1932).

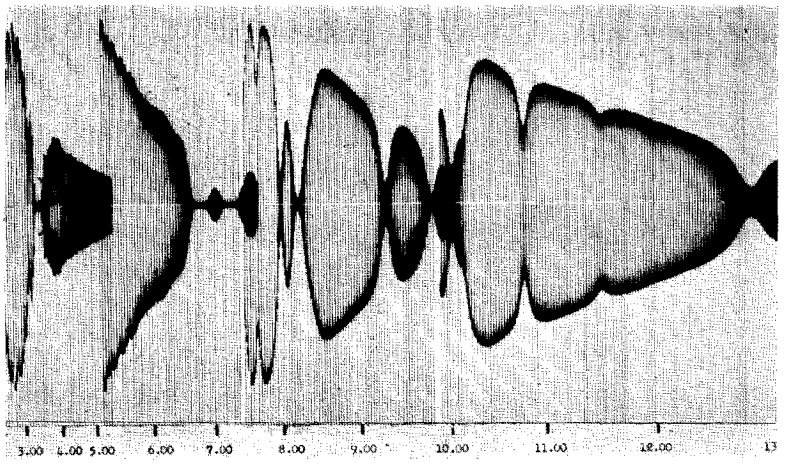

FIG. 4. The absorption spectrum of 2,2 dimethylbutane in the region 2.5 to 13.5μ.

tainable with the slit widths necessary to get half scale deflections with this amplifier.[4] Actually the resolution realized with the instrument is somewhat less than the theoretical value.

In the analysis of an n component mixture it is necessary and sufficient to determine log I_0/I values of the mixtures at n different spectral positions. When a procedure is being developed for a given mixture, the spectra of the pure components are examined and n positions are selected in such a way that a different component contributes a maximum amount of absorption at each position. It is desirable but not necessary that at each wave-length position the absorption of one component be greater than that due to any other component; and further, that the component showing major absorption be different at each of the n wave-length positions. The spectral positions which yield most accurate analyses are those at which the absorption of one component is large compared to the sum of the absorptions of all other components (assuming all components are present in concentrations similar to those in an unknown mixture). In general, this condition is found at the position of maximum absorption of a band for one component.

There are some other factors to be considered in the selection of these wave-length positions. For example, in order to reduce the time necessary to make an analysis, it may be desirable to select bands near each other. It may be desirable to select positions which are outside of the water vapor region. If one thickness of the absorption cell is to be used, the selection of the wave-length positions may depend upon the intensities of the bands; however, as far as possible, thinner absorption cells should be used when the bands are strong, and thicker ones should be used when the bands are weak. The selection of these positions is often complicated by the fact that several bands interfere with one another. This difficulty can be minimized by using the narrowest slits permitted by the sensitivity of the receiver and the available amplification of its output.

Determination of log I_0/I Values

For the measurement of log I_0/I values, the thermopile in the spectrometer is connected directly to a galvanometer with a sensitivity of one-tenth microvolt per millimeter at one meter.

TABLE I. Theoretical resolution of the spectrograph.

λ	Actual slit widths*	Effective slit widths	$\frac{\lambda}{d\lambda}$	$B\frac{dn}{d\lambda}$
2μ	0.04 mm	0.0097μ	208	640
3	0.04	0.0117	257	440
4	0.05	0.0128	314	560
5	0.06	0.0118	424	640
6	0.07	0.0117	514	800
7	0.08	0.0117	600	960
8	0.09	0.0117	686	1080
9	0.11	0.0127	711	1160
10	0.13	0.0130	768	1240
11	0.16	0.0140	787	1560
12	0.20	0.0163	738	1720
13	0.24	0.0183	711	1800
14	0.35	0.0238	589	2080
15	0.55	0.0339	443	2240

* These slit widths produce half scale deflection.

TABLE II. Resolution for operating conditions.

Spectral position $\lambda(\mu)$	Actual slit widths (mm)	Effective slit width (μ) ($d\lambda$)	Actual resolution $\lambda/d\lambda$	Prism resolution $Bdn/d\lambda$
8.23	0.55	0.071	116	1100
8.55	0.60	0.075	114	1120
8.88	0.70	0.092	96	1152
10.50	0.90	0.085	123	1400
11.28	1.10	0.096	117	1600
9.13	0.7	0.080	114	1168
10.31	0.9	0.088	117	1336
11.89	1.2	0.100	119	1704
12.30	1.3	0.116	107	1752

The scale-to-galvanometer distance for the present work is five meters. With this system it is necessary to use wider slits and therefore to accept lower resolution than that realized with the amplifier, but the accuracy of measurements is much better. The actual resolutions for the slit widths used are shown in Table II.

When the procedure for a given mixture is developed, the slit widths for each spectral position are set to give approximately 400-mm deflection when a non-absorbing material (background cell) is in the light path. Of course, after the necessary calibrations have been made for the analysis of a particular mixture, the same slit widths must always be used for this analysis.

After the proper slit widths have been selected, the spectral positions are re-examined under the conditions which would be used in making the analyses, that is with wide slits and very slow rotation of the prism. These records for the hexanes are shown in Fig. 5. The upper line on each of the records shows the deflection of the galvanometer for the background cell. The bottom lines in the figures show the zero positions, and displacements along these lines in the vertical direction represent zero shift. The absorption curves lying between the background curve and the zero lines are as designated. Correct log I_0/I values can be obtained only if (1) the deflection of the galvanometer is a known function of the energy striking the thermopile and (2) all energy reaching the thermopile lies in the selected wave-length interval. In the present case, all tests have shown the galvanometer system to be linear. However, the energy reaching the thermopile actually includes some energy in addition to that from the wave-length interval, $\Delta\lambda$. This wave-length interval is determined by the slit width and the region of the spectrum for which the spectrometer is set. The radiation in this wave-length interval which passes through the absorption cell and strikes the thermopile is the radiation which should be measured. Any other energy which causes a change in the galvanometer deflection (or other measuring instrument) when the shutter is opened is called false energy and its effect must be taken into account.

Most of this false energy is probably due to scattering from various parts of the spectrometer of radiation in the region 1 to 4μ which is the region of maximum intensity incident on the

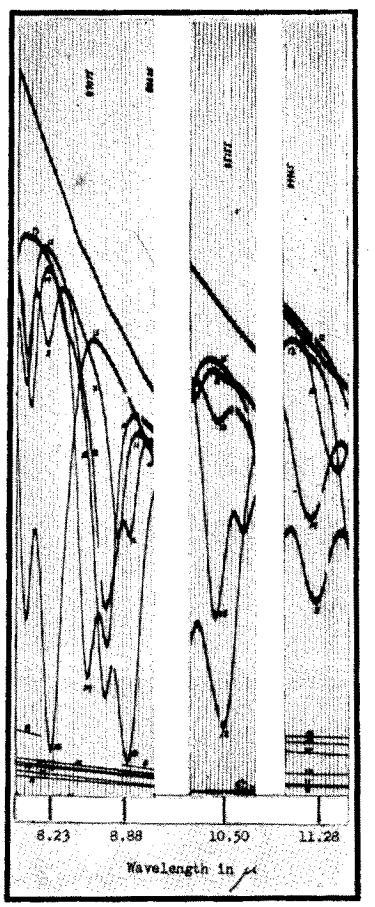

FIG. 5. Portions of the spectra of the five hexanes.

Curve no.	Component	Position of band
11	*n* hexane	11.28μ
12	3 methylpentane	10.50
13	2,3 dimethylbutane	8.88
14	2 methylpentane	8.55
15	2,2 dimethylbutane	8.23

entrance slit. This energy interferes mostly at long wave-lengths (6 to 15μ) where the true energy is small and the slits are wide. When working above 7μ most of the false energy can be cancelled out by using a mica shutter which transmits most of the radiation up to 5μ but none above 7μ. In this case the radiation below 5μ always passes into the spectrometer and is therefore included in the "zero" reading. Only the radiation of wave-lengths greater than 7μ is interrupted by the mica shutter. However, this method does not cancel out all the false energy; therefore, more refinement is necessary. A method of making partial correction for the remaining false energy has been established by using a piece of Cellophane which has two regions of 100 percent absorption, one at 9.15μ and one at 11.90μ, and obtaining the difference in the galvanometer deflections when the cells are in the light path with, first the Cellophane, and second the mica shutter. The amount of false energy when the background cell is in the light path is different from the amount when the liquid cell is in, but is practically the same for all liquids used in the liquid cell. It is proportional to I_0 at any given wave-length and therefore can be expressed as a percent of I_0. The false energy values at the two bands in the spectrum of the Cellophane film have been plotted on a graph showing wave-length *versus* false energy and a straight line has been drawn between the points. (See Fig. 6.) Curve (1) is for the background cell and curve (2) is for the liquid cell with any of the nine pure components in it. At every spectral position and given slit width, I_0 is made the same for all observations. Therefore, the false energy corrections can be converted to mm deflection and subtracted from the I and I_0 values obtained, as shown in Table III.

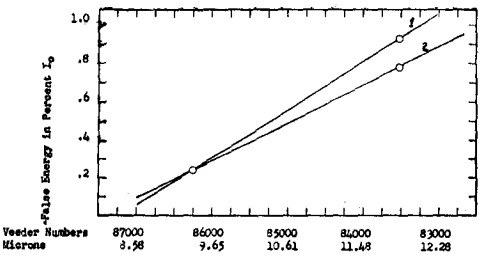

FIG. 6. False energy as a function of wave-length.

With the equipment used in this work there is some zero drift and the intensity of the light source is not perfectly controlled. For this reason the procedure in making a measurement at a given spectral position consists of making three readings as follows: (*a*) with the absorption cell alone in the light path, (*b*) with the cell plus a mica shutter in the light path, and (*c*) with the absorption cell again alone in the light path.

The averaging of (*a*) and (*c*) in general cancels out the zero drift and the subtraction of this average from (*b*) gives (*k*). This number is proportional to the difference in the energy which falls on the thermopile with the two shutter positions. In other words, (*k*) is proportional to the energy which is interrupted by a mica shutter. A similar value (*L*) is obtained with the background cell. Then because the source may have changed its intensity during this interval of time, a value similar to (*k*), called (*m*), is again obtained. (*k*) and (*m*) are then averaged to give (*n*). This should, in general, cancel out any errors due to slow changes in the source. (*n*), therefore, is I plus the false energy F and

TABLE III. False energy corrections for each spectral position and slit width.

Principal absorber	$\lambda(\mu)$	cm^{-1}	Slit widths (mm.)	I_0 (mm)	False energy correction I_0 (mm)	False energy correction I (mm)
2,3 dimethylbutene−1	9.13	1096	0.70	320.0	0.5	0.5
2,3 dimethylbutene−2	10.31	970	0.90	345.0	2.0	1.5
2,2,3 trimethylbutene	11.89	841	1.30	390.0	3.5	3.0
Methylpentenes	12.30	813	1.40	375.0	4.0	3.5
2,2 dimethylbutane	8.23	1215	0.55	450.0	0.5	0.5
2 methylpentane	8.55	1170	0.60	420.0	0.5	0.5
2,3 dimethylbutane	8.88	1126	0.70	495.0	0.5	0.5
2 methylpentane	10.50	952	0.90	430.0	2.0	2.0
n hexane	11.28	886	1.10	430.0	3.0	2.5

TABLE IV. Standard deviations of log I_0/I values for two samples.

Sample 223		Sample 756	
0.549	0.549	0.153	0.154
.550	.554	.153	.154
.548	.545	.153	.150
.548	.547	.152	.151
.548	.548	.150	.150
.549	.548	.152	.149
.547	.544	.149	.153
.551	.548	.155	.148
.550	.546	.153	.147
.552	.548	.145	.150
.551	.552	.149	.151
.547	.550	.150*	.150
.549	.550	.151	.152
.546	.551	.151	.149
.548	.548	.149	.151
Average	.548		.151
Max. dev. from the mean	.004		.006
Std. dev.	.0022		.0023

(L) is I_0 plus the false energy F_0. These observations are written in a data sheet as follows:

Absorption cell			Background cell		
Shutter open	Shutter closed	Shutter open	Shutter open	Shutter closed	Shutter open
(a)	(b)	(c)	(d)	(e)	(f)
(g)	(h)	(j)			

The values of I_0+F_0 and $I+F$ are obtained from the above readings in the following manner:

$$(b)-\left[\frac{(a)+(c)}{2}\right]=(k), \quad (e)-\left[\frac{(d)+(f)}{2}\right]=(L),$$

$$(h)-\left[\frac{(g)+(j)}{2}\right]=(m), \quad \frac{(k)+(m)}{2}=(n),$$

$$(L)=I_0+F_0, \quad (n)=I+F.$$

F and F_0 are the false energy values which are subtracted to determine I_0 and I (see Table III).

It is essential in this method that changes in optical densities due to unavoidable changes in the two cells be known. It is, therefore, desirable to have a standard absorbing material which can be checked daily. This check is made with a "pure" sample of 2,2,3 trimethylbutene at 11.89μ at the beginning and end of each day. When the log I_0/I deviates from the standard value (0.600) by more than 0.003, all values of log I_0/I determined on that day are corrected by adding or subtracting the indicated amount.

Reproducibility in Determining log I_0/I Values

Thirty determinations of log I_0/I values at one spectral position for two samples have been made over a period of three months. These values are listed in Table IV.

The standard deviations for the two sets of data are essentially the same even though the amount of absorption differs. For this particular case a change of 0.002 in log I_0/I represents a change of 0.3 percent in the concentration of the component sought. For a cell twice as thick it would represent 0.15 percent, for one-half as thick, 0.6 percent. Likewise the deviation in terms of percent concentration would be more or less, depending on whether the principal absorber absorbs more or less at this wave-length.

Analytical Curves

In making infra-red analyses it is necessary to convert values of log I_0/I to concentrations. The conversion may be made by means of analytical curves each of which shows log I_0/I as a function of concentration of a particular compound. In the present work with liquids, the data for such a curve are obtained by measuring log I_0/I with binary mixtures in the absorption cell.

The amount of absorbing material in the path is varied by using a cell of constant thickness and diluting the absorber with one of the compounds which has a high transmission at the wave-length in question. Three series of binary mixtures were made for the four-component mixture and four series were made for the hexane mixture. These solutions have concentrations as shown in Table V. It will be seen that for the four-component problem, one of the components of all the mixtures is 2,3 dimethylbutene−2. This was selected because it absorbs strongly at only one of the spectral positions. At all the other positions it absorbs very little. In the case of the hexane series 2,2 dimethylbutane was selected as the common component.

The preliminary analytical curves are obtained by plotting, for each spectral position, a curve showing percent concentration of the material diluted, which is 100 percent in the "a" solution (Table V), *versus* the log I_0/I for each of the binary mixtures (a through h) in the series. For the four-component problem, this means three

TABLE V. Compositions of binary mixtures used for analytical curves.

Mixture series no.	Components	Amounts by percent volume							
		a	*b*	*c*	*d*	*e*	*f*	*g*	*h*
		Four component mixtures							
1	Methylpentenes	100	64	32	16	8	4	2	0
	2,3 dimethylbutene−2	0	36	68	84	92	96	98	100
2	2,3 dimethylbutene−1	100	64	32	16	8	4	2	0
	2,3 dimethylbutene−2	0	36	68	84	92	96	98	100
3	2,2,3 trimethylbutene	100	64	32	16	8	4	2	0
	2,3 dimethylbutene−2	0	36	68	84	92	96	98	100
		Hexane mixtures							
11	Normal hexane	100	80	60	30	15	7	4	0
	2,2 dimethylbutane	0	20	40	70	85	93	96	100
12	3 methylpentane	100	80	60	40	20	10	5	0
	2,2 dimethylbutane	0	20	40	60	80	90	95	100
13	2,3 dimethylbutane	100	80	60	40	20	10	5	0
	2,2 dimethylbutane	0	20	40	60	80	90	95	100
14	2 methylpentane	100	80	60	40	20	10	5	0
	2,2 dimethylbutane	0	20	40	60	80	90	95	100

curves at each of the four spectral positions, and for the hexanes, four curves at each of the five spectral positions.

The final analytical curves are obtained from these preliminary curves by a procedure which will now be described. First, the final analytical curve of the component which has the least absorption at the spectral position being considered is drawn as a straight line from the (0.0) point to the point at 100 percent concentration. This is illustrated by Fig. 7 which is a graph of the preliminary and final analytical curves at 9.31μ for the four-component mixture. At this spectral position 2,2,3 trimethylbutene (*C*, Fig. 7) is the least absorbing pure compound. The contribution of this component to the log I_0/I value of the binary mixtures of this compound with 2,3 dimethylbutene−2 is determined from this final curve for 2,2,3 trimethylbutene. This contribution (lower *C* curve, Fig. 7) is subtracted from the preliminary curve of the binary mixture of these two components (upper *C* curve, Fig. 7) at a convenient number of points. These differences are the contribution to the log I_0/I values of 2,3 dimethylbutene−2 in each binary mixture and, when plotted against the concentration of 2,3 dimethylbutene−2, represent the final analytical curve of this component. As 2,3 dimethylbutene−2 is the common component in binary mixtures of each of the other compounds, the final analytical curves for the remaining two compounds can be obtained by a series of subtractions similar to that described above. (Subtract difference between upper and lower *C* curves from upper *A* and *D* curves to obtain lower *A* and *D* curves). In this way an analytical curve for each of the components in the four-component mixture has been obtained

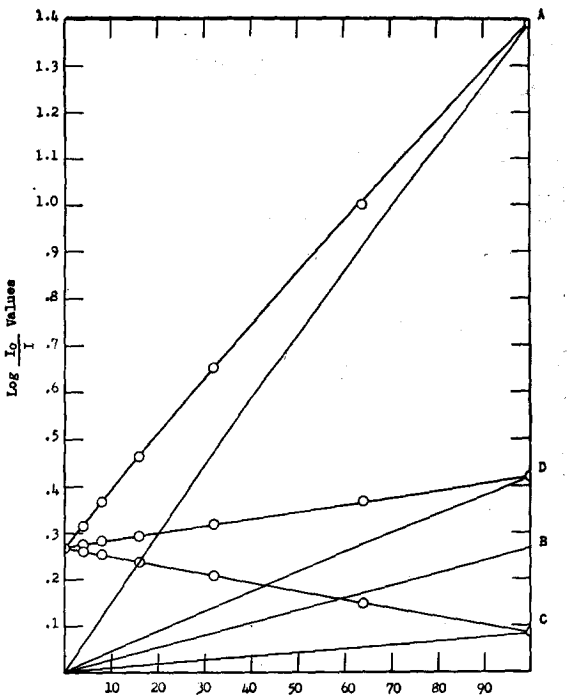

FIG. 7. Analytical curves at 9.31μ. Curves with circles are preliminary curves.

A. 2,3 dimethylbutene−1
B. 2,3 dimethylbutene−2
C. 2,2,3 trimethylbutene
D. methylpentene

at each of the four spectral positions (16 curves). For the hexane mixtures there are five curves at each of five spectral positions or a total of 25 curves.

After the analytical curves are obtained, it is possible to analyze mixtures which contain any or all of the components in any possible concentration. To do this, it is necessary only to obtain the log I_0/I values at all the spectral positions (n, if an n component mixture) and to convert them to concentrations by use of one of the two methods described below.

Two Methods of Converting Optical Densities to Concentrations

One method of converting optical densities to concentrations is a method of graphical approximation. In this case the analyses are arrived at by successive approximations based upon the final analytical curves. (See Fig. 7.) This method presupposes that the optical density of the mixture is equal to the sum of the optical densities of the component parts of that mixture as expressed in Eq. (3).

In converting optical densities to concentrations by this method, the log I_0/I value at one spectral position is applied to the analytical curve of the material which has its major absorption at that wave-length, and the first approximation of percent concentration for that component is read from the curve. The log I_0/I value at a second spectral position is corrected by subtracting the contribution of the first component at this wave-length. The corrected log I_0/I value is applied to the analytical curve of the material which has its major absorption at this position to obtain the first approximation for this component. The log I_0/I value at a third spectral position is corrected for the contribution of the first and second components and the corrected log I_0/I value is applied to the appropriate curve to obtain the first approximation for this third component. This procedure is continued until the first approximation is obtained for all components of the mixture. Successive approximations are obtained by repeating this process for each component, always using the latest approximate concentration of the other components. This is continued until two consecutive sets of approximations are the same. The last set of values is the analysis of the mixture.

The analytical curves can be used graphically, as just described, or they can be used to obtain mathematical expressions to make the same approximations. In this paper the latter will be called a method of applied corrections. The analytical curves, in general, are not straight lines (see Fig. 7). However, a straight line drawn between the points on the curve corresponding to concentration = 0 and concentration = 50 percent does not deviate far from the analytical curve at any point. Each of these straight lines is represented by an equation such as (1). The slopes of the straight lines are the approximate absorption coefficients, so that the optical density (log I_0/I) of a mixture at a given spectral point can be written from Eq. (2) as:

$$(\log I_0/I)_{\lambda_j} = b_{1_j}c_1 + b_{2_j}c_2 + b_{3_j}c + \cdots b_{n_j}c_n, \quad (4)$$

where b_{i_j}, $b_{2_j}\cdots n_{n_j}$ are the slopes of the straight lines referred to above for components 1, $2\cdots n$ at wave-length λ_j, and c_1, $c_2\cdots c_n$ are the concentrations. There is one of these equations for each of the 1, 2, $3\cdots n$ wave-lengths.

For the four-component mixtures the equations are:

$$\begin{aligned}
\left(\log \frac{I_0}{I}\right)_{\lambda_1} &= 0.01442c_1 + 0.00270c_2 \\
&\quad + 0.00840c_3 + 0.00499c_4, \\
\left(\log \frac{I_0}{I}\right)_{\lambda_2} &= 0.00193c_1 + 0.00391c_2 \\
&\quad + 0.00136c_3 + 0.00601c_4, \\
\left(\log \frac{I_0}{I}\right)_{\lambda_3} &= 0.00155c_1 + 0.00082c_2 \\
&\quad + 0.00622c_3 + 0.00757c_4, \\
\left(\log \frac{I_0}{I}\right)_{\lambda_4} &= 0.00080c_1 + 0.00125c_2 \\
&\quad + 0.00092c_3 + 0.02792c_4,
\end{aligned} \quad (5)$$

where the λ's and c's are as follows:

$\lambda_1 = 9.12\mu$ c_1 is the concentration of 2,3 dimethylbutene−1,

$\lambda_2 = 10.31\mu$ c_2 is the concentration of 2,3 dimethylbutene−2,

$\lambda_3 = 11.89\mu$ c_3 is the concentration of 2,2,3 trimethylbutene,

$\lambda_4 = 12.30\mu$ c_4 is the concentration of methylpentenes.

With considerable effort the above four equations can be solved for the concentrations, giving Eqs. (6).

$$
\begin{aligned}
c_1 &= 76.28\left(\log\frac{I_0}{I_1}\right) - 52.72\left(\log\frac{I_0}{I_2}\right) \\
&\quad + 1.335\left(\log\frac{I_0}{I_3}\right) - 0.7350\left(\log\frac{I_0}{I_4}\right), \\
c_2 &= -32.10\left(\log\frac{I_0}{I_1}\right) + 304.0\left(\log\frac{I_0}{I_2}\right) \\
&\quad - 55.45\left(\log\frac{I_0}{I_3}\right) - 45.47\left(\log\frac{I_0}{I_4}\right), \\
c_3 &= -14.48\left(\log\frac{I_0}{I_1}\right) - 12.52\left(\log\frac{I_0}{I_2}\right) \\
&\quad + 171.7\left(\log\frac{I_0}{I_3}\right) - 41.67\left(\log\frac{I_0}{I_4}\right), \\
c_4 &= -0.2710\left(\log\frac{I_0}{I_1}\right) - 11.69\left(\log\frac{I_0}{I_2}\right) \\
&\quad - 3.214\left(\log\frac{I_0}{I_3}\right) + 39.19\left(\log\frac{I_0}{I_4}\right).
\end{aligned}
\tag{6}
$$

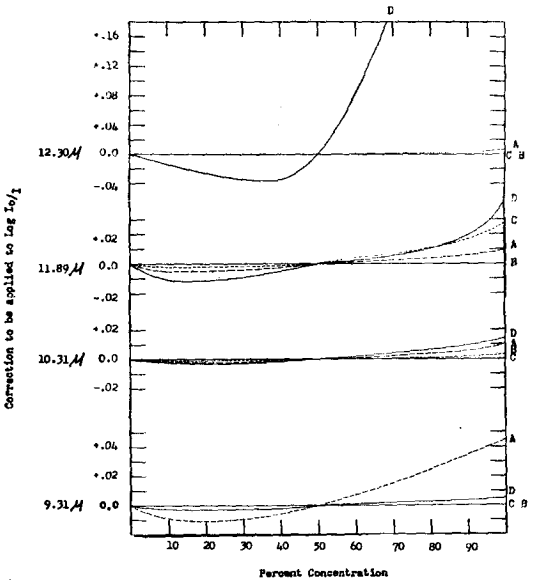

FIG. 8. Correction curves for four-component mixture used with method of applied corrections. (See Fig. 7 for explanation of *A*, *B*, *C*, and *D*.)

Equations (6) are used in connection with a series of correction curves which are obtained in the following manner: the differences between the $\log(I_0/I)$ values as obtained from the analytical curves and the straight lines mentioned above are plotted against the concentrations of each component at each wave-length. For the four-component mixture, these are shown in Fig. 8.

TABLE VI. Results of analyses of synthetic mixtures of four components.

Sample no.	2,3 dimethylbutene−1 Actual	2,3 dimethylbutene−1 Spec.	2,3 dimethylbutene−2 Actual	2,3 dimethylbutene−2 Spec.	2,2,3 trimethylbutene Actual	2,2,3 trimethylbutene Spec.	Methylpentenes Actual	Methylpentenes Spec.
U–1	25.0%	25.2%	25.0%	23.2%	25.0%	25.7%	25.0%	24.9%
U–2	30.0	30.4	20.0	18.5	30.0	31.4	20.0	19.9
U–3	20.0	20.1	30.0	29.3	35.0	36.9	15.0	15.1
U–5	33.3	33.2	33.3	33.9	33.3	33.6	0.0	0.0
U–6	33.3	34.0	33.3	33.5	0.0	0.0	33.3	33.3
U–7	0.0	0.0	33.3	34.0	33.3	34.3	33.3	33.6
U–8	33.3	33.5	0.0	0.0	33.3	34.3	33.3	33.7
O–1	25.0	24.6	25.0	23.9	25.0	24.4	25.0	25.2
O–2	12.5	11.5	62.5	63.5	12.5	11.2	12.5	12.3
O–3	42.0	42.8	18.0	17.3	20.0	19.0	20.0	19.4
O–4	36.0	35.6	18.0	16.9	26.0	25.1	20.0	20.5
O–5	33.3	33.6	33.3	31.9	33.3	32.6	0.0	0.0
O–6	33.3	33.6	0.0	0.0	33.3	33.5	33.3	33.0
O–8	33.3	33.1	33.3	33.0	0.0	0.3	33.3	33.0
O–9	50.0	50.7	0.0	0.0	50.0	50.1	0.0	0.0
O–10	0.0	0.0	0.0	1.1	50.0	49.7	50.0	49.9
O–11	2.5	1.9	3.0	3.0	90.0	88.8	4.5	4.9
Av. dev.	0.36%		0.72%		0.77%		0.25%	
Max. dev.	1.0		1.8		1.9		0.6	

TABLE VII. Results of analyses of synthetic mixtures of five components.

Sample no.	2,2 dimethylbutane Actual	Spec.	2,3 dimethylbutane Actual	Spec.	2 methylpentane Actual	Spec.	3 methylpentane Actual	Spec.	*n* hexane Actual	Spec.
H–1	20.0%	20.4%	20.0%	19.8%	20.0%	19.2%	20.0%	19.6%	20.0%	19.8%
H–2	10.0	10.4	10.0	10.1	10.0	9.7	10.0	9.6	60.0	59.2
H–3	5.0	5.4	5.0	5.3	5.0	5.0	55.0	54.0	30.0	28.4
H–4	2.5	2.8	52.5	51.8	2.5	2.2	27.5	27.1	15.0	15.1
H–5	1.2	1.6	26.3	25.9	51.2	50.3	13.8	13.1	7.5	7.8
H–6	50.6	50.7	13.1	13.3	25.6	24.7	6.9	6.8	3.8	4.4
Av. dev.	0.33%		0.32%		0.54%		0.50%		0.60%	
Max. dev.	0.4		0.7		0.9		1.0		1.6	

To make an analysis the log (I_0/I) values of the mixture are determined at each of the selected spectral positions and are substituted in Eqs. (6). The first approximate concentrations are obtained from these equations. The correction to be applied to the experimentally determined log (I_0/I) at each wave-length position is determined by subtracting the sum of the values obtained from the correction. These new log (I_0/I) values are then used in Eq. (6) and second approximate concentrations are determined. This process is carried on until the concentrations are the same for two consecutive approximations. The last set of values is the analysis. In the present work, three approximations have been sufficient.

DISCUSSION OF DATA

In order to check the methods, synthetic mixtures have been made and analyzed. The results are shown in Table VI for the four-component mixture and in Table VII for the hexanes. It will be seen that in no case does the analysis obtained deviate from the actual composition

TABLE VIII. Comparison of results by two methods.

Sample no.	2,3 dimethylbutene –1 Graphical approximation	Applied correction	2,3 dimethylbutene –2 Graphical approximation	Applied correction	2,2,3 trimethylbutene Graphical approximation	Applied correction	Methylpentenes Graphical approximation	Applied correction
O–3	20.1%	19.8%	29.3%	29.1%	36.9%	37.0%	15.1%	15.1%
O–4	35.6	35.5	16.9	16.6	25.1	24.7	20.5	20.4
O–5	33.7	33.6	32.2	31.9	32.5	32.6	0.0	0.0
O–11	2.0	1.9	2.9	3.0	89.2	88.8	5.0	4.9

TABLE IX. Data showing the effects of extraneous elements.

Sample		2,3 dimethyl-butene –1	2,3 dimethyl butene –2	2,2,3 trimethyl-butene	Methyl-pentene	2 methyl butene –2	Octene cut
U–5	As made	33.3%	33.3%	33.3%	0.0%	0.0%	0.0%
	Analysis	33.2	33.9	33.6	0.0	Assumed Absent	
	As made	32.5	32.5	32.5	0.0	2.5	0.0
	Analysis	33.4	35.8	28.1	2.4	Assumed Absent	
U–7	As made	0.0	33.3	33.3	33.3	0.0	0.0
	Analysis	0.0	34.0	34.3	33.6	Assumed Absent	
	As made	0.0	32.5	32.5	32.5	0.0	2.5
	Analysis	0.0	33.5	33.5	32.6	Assumed Absent	
U–8	As made	33.3	0.0	33.3	33.3	0.0	0.0
	Analysis	33.5	0.0	34.3	33.7	Assumed Absent	
	As made	31.5	0.0	31.5	31.5	2.5	2.5
	Analysis	35.9	0.0	34.4	34.0	Assumed Absent	

by more than 2.0 percent of the total mixture. The average error for all components in all mixtures shown in the two tables is 0.5 percent.

All the synthetic mixtures have been analyzed by the graphical approximation method, and some have been analyzed by both methods. Results obtained by the two methods for four samples are compared in Table VIII.

The complete analysis of a four-component mixture can be made in 45 minutes with the method of graphical approximations, and in 30 minutes with the method of applied corrections.

It should be pointed out that the presence in the unknown mixture of compounds for which analyses are not made will cause large or small errors depending upon whether the extraneous materials absorb strongly or weakly at any of the spectral positions. It has been found in the case of the four-component mixture that many of the unknowns submitted for analysis have contained two extraneous compounds. Synthetic mixtures including 2.5 percent of each of these components were prepared and analyzed, assuming the extraneous components absent. The results of this study are shown in Table IX. It will be noticed that these concentrations of the extraneous components cause errors up to 4.0 percent in the analyses. If the approximate amount and effect of the extraneous components can be determined, and they frequently can, errors such as those shown in the example can be eliminated or at least minimized by making appropriate corrections.

SUMMARY

A method has been described for analyzing multicomponent mixtures of hydrocarbons in the liquid phase by means of their infra-red absorption spectra. A constant thickness absorption cell is used, and analytical curves are established on the basis of synthetic binary mixtures of the different components in the multicomponent mixtures to be analyzed. Two procedures for using the analytical curves to convert optical densities to concentrations by means of successive approximations have been described. Four- and five-component mixtures are completely analyzed in less than 45 minutes per sample and the average error is 0.5 percent of the total sample.