

QUANTITATIVE LIQUID PHASE HYDROCARBON ANALYSIS BY INFRA-RED ABSORPTION.

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SUMMARY.

Part I. Sources of Error and their Correction by the Variable Path Length Absorption Cell.

The absorption spectra of pure hydrocarbons published hitherto have been peculiar to the instrument employed for their determination. An attempt is made in this paper to evaluate such factors as cell zero, the effect of scattered radiation of short wave-lengths, and the variations of absorption with thickness of absorbing material, on a quantitative basis, with the object of removing the individuality among published spectra. The advantages of using a variable thickness absorption cell for this purpose are demonstrated.

Part II. Application of the Variable Path Length Absorption Cell.

The application is discussed of a variable thickness absorbing cell to the infra-red absorption analysis of mixtures containing five hydrocarbons. The method of computation involving the corrections described in Part I is given in detail. A numerical example of the application of these corrections is given as an Appendix.

PART I.—SOURCES OF ERROR AND THEIR CORRECTION BY THE VARIABLE PATH LENGTH ABSORPTION CELL.

In recent years the demands on the petroleum industry for special products have necessitated closer control of the methods of production employed. In the last resort this control must depend on the analyses of the products, the analyses required being not so much according to molecular type as according to the individual components present. The fact that spectroscopic methods provide a means of "finger-printing" molecules, and hence provide a method of analysis, has been known for many years, and in the ultra-violet region of the spectrum such methods have been used in a quantitative manner. The use of the ultra-violet region, however, is confined to the analysis of aromatics and conjugated dienes, since the paraffins and naphthenes do not show any absorption in the readily accessible range of ultra-violet wave-lengths. This is very convenient, in that the paraffins and naphthenes do not cause interference with such aromatic and olefine analyses, but to remove the limitation recourse must be had to the infra-red.

In this region of the spectrum all types of hydrocarbons absorb radiation, so that, in order to avoid too great a complexity in the absorption spectra obtained from mixtures, it is necessary to limit the number of absorbing components to seven or eight. Unlike the ultra-violet region, however, the infra-red has not been used quantitatively until recently, chiefly owing to the experimental difficulties. That these are, or have been, formidable is reflected in the absence of a standard type of spectrometer by any of the well-known instrument-makers.

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This has had the result that each research worker has built his spectrometer according to his own ideas, and in consequence the spectra of pure materials recorded are peculiar to the instrument used with regard to the absorption intensity scale, though not, of course, with regard to the positions of the absorption maxima on the wave-length scale.

This dependence of absorption intensity on the instrument used is mainly due to the following factors :—

(a) Cell zero error. Absorption by the cell itself has the result that 100 per cent. transmission is not obtained at zero thickness of absorbing layer, and full compensation for this effect cannot be obtained by the use of a blank cell or compensating rock-salt plate.

(b) Effect of slit width on measured optical density. This is dependent on the shape of the absorption band under investigation and on the instrument characteristics.

(c) Spectral impurity at any wave-length, *i.e.*, scattered radiation in the instrument.

(d) Position of the absorption cell in the radiation path.

The existence of these factors has been recognized in the past, but very little published work has made any attempt to put them on a quantitative basis. Two of the reasons for this have been the absence of a variable-thickness absorption cell and the fact that the thickness of the fixed cells used in many cases has not been known with any great accuracy.

Another weakness of published work deriving from fixed absorption cells is that these virtually enforce the assumption of a linear relation between optical density and thickness of absorbing layer. This linearity, as is shown in this paper, has now been found not to hold for many liquids.

The sum of these individual errors is likely to be large, and the present work has set out to evaluate and remove them.

APPARATUS.

The absorption cell, which is of a continuously variable thickness type has been described elsewhere (*J. Sci. Instr.*, January 1945).

The infra-red spectrometer used was designed and built in the research laboratories of the Anglo-Iranian Oil Company at Sunbury-on-Thames, the basic optical part being a Hilger D88 infra-red spectrometer. This was removed from the tripod as normally supplied and bolted to a heavy base plate of $\frac{1}{4}$ inch steel, 3 feet \times 17 inches \times 2 inches. Under this plate a heater made from 24 feet of 24-gauge nichrome resistance wire is mounted, the heating current being controlled by a bimetal strip close to the prism. This maintains the prism at a constant temperature, so eliminating the small changes with temperature in the apparent wave-lengths of absorption maxima which have been observed in earlier instruments.

The source of radiation is the usual Nernst filament, and this has been placed inside a water-cooled jacket provided with an opening, in front of which is mounted a spring-loaded shutter.

Radiation from the Nernst falls on a concave, surface aluminized mirror, 10 cm. in diameter and of 70 cm. focal length. This mirror focuses an image of the Nernst on the entrant slit of the spectrometer.

Immediately in front of the entrant slit the variable cell is mounted on a movable trolley, together with a plane piece of rocksalt, so that either can be placed in front of the slit by moving the trolley, this being controlled by compressed air and vacuum. The purpose of the plane rocksalt plate is to compensate for the loss of radiation by reflection from the face of the absorption cell, thus allowing a true measure to be made of the amount of radiation before absorption occurs. The arrangement also serves to eliminate the effects of atmospheric absorption within the instrument.

The apparatus for amplifying the thermopile current is of the conventional twin photo-cell type. A photograph of the spectrometer is shown in Fig. 1.

EXPERIMENTAL PROCEDURE.

When the absorption spectra of the individual pure components of a mixture are examined, it is observed that certain bands of a given substance stand clear of those due to the other components. The wave-lengths of the maxima of such bands are referred to as "key" wave-lengths for that particular component. The experimental procedure consists in determining for each component the optical density at the selected "key" wave-lengths for the mixture being analysed.* This procedure is repeated for a series of thicknesses of the absorbing layer for each component, and from the results calibration curves are drawn of optical density against thickness. Once these curves have been obtained the cell is filled with the sample to be analysed, the thickness of absorbing layer being chosen so that the major absorption peaks give optical densities lying between the values 0.20 and 0.60. These limits are chosen since the accuracy of determining the optical density falls off rapidly both above and below these values. In general, for hydrocarbon analyses, thicknesses of 0.114 mm. and 0.216 mm. have been found satisfactory for major and minor absorption peaks, respectively.

The sources of error enumerated above are then dealt with in the following manner.

(a) *Determination of Cell Zero.*

In order to compensate for energy losses by reflection at the absorption cell end plates, for atmospheric absorption in the instrument, and for long wave-length absorption by rocksalt itself, a rocksalt compensating plate is used, which ideally would enable the energy transmitted by the variable cell and its liquid to be exactly corrected to that transmitted by the liquid alone.

This compensation cannot, of course, be made exact, and if it could, the exactness could not be maintained, owing to the slow deterioration of the rocksalt windows of the absorption cell. This deterioration is caused by the action of atmospheric moisture and by the action of moist samples, these causing the windows to "fog" in the course of time. It is of no

* The optical density is defined as $\log_e \frac{I_0}{I}$, where I_0 and I are the intensities of the incident and transmitted radiation, respectively. In practice it is more usual to use common logarithms.

advantage to replace the compensating plate by a second cell filled with a non-absorbing liquid and to compare the transmission with that of the sample cell filled with the same liquid, since the amount of light scattered by the slightly fogged windows of the latter will still have its effect.

Two methods of determining the instrument zero have been employed. In the first method the cell is filled with a non-absorbing liquid and the zero error recorded as a percentage of the energy transmitted by the compensating plate. For this purpose carbon tetrachloride, which has been found to have no absorption in thicknesses up to 1.05 mm. at 7.4μ , has been used for the shorter wave end of the spectrum, and methylcyclopentane, the absorption of which is negligible in a thickness of 0.114 mm., in the 10.7μ region. The second method is somewhat more laborious, and is used only as a periodic check on this first method. It consists of determining the optical density at a peak of absorption for a series of cell thicknesses, preferably on a band which is known to have a nearly linear relationship between optical density and thickness, the optical densities being calculated assuming that the transmission through the cell is 100 per cent. of that through the compensating plate. It is then found that the line so obtained cuts the axis of optical density, the percentage transmission corresponding to this being the cell zero.

These two methods have been found to give the same result to within 1 per cent. in transmission. A confirmatory point is that when the curves of transmission against wave-length are corrected for this zero they do not cross the line of 100 per cent. transmission.

This process of zero determination is carried out weekly during routine work, a check on the cell thickness being obtained simultaneously by choosing another wave-length where there is an absorption band.

Effect of Slit Width and Spectral Impurity.

It was observed during the course of the work that the calibration curves of thickness of absorbing material against optical density showed a very pronounced curvature. Moreover, the curvature was not uniform, but fell into three parts, corresponding to low optical densities (between 0.2 and 0.3), medium optical densities (0.31–0.60), and high optical densities. This behaviour can be ascribed to the influence of two factors—Slit Width and Spectral Impurity.

(b) Effect of Slit Width.

This may be explained as follows. When the degree of absorption is high, the absorption band is wide and has a comparatively flat peak which fills the whole of the slit. The absorption is then more or less uniform across the whole slit. As the thickness of absorbing material is reduced, the shape of the absorption band changes and begins to show a definite peak. At a certain point, depending on the shape of the absorption band, the slit width becomes relatively greater than the wave-band at the peak of absorption. When this occurs, since the slit transmits not truly monochromatic radiation but a small range of wave-lengths, the observed absorption decreases more rapidly than before, since only one wave-length is truly at the peak of absorption, and the other transmitted wave-lengths are absorbed to a less extent. This causes the line repre-

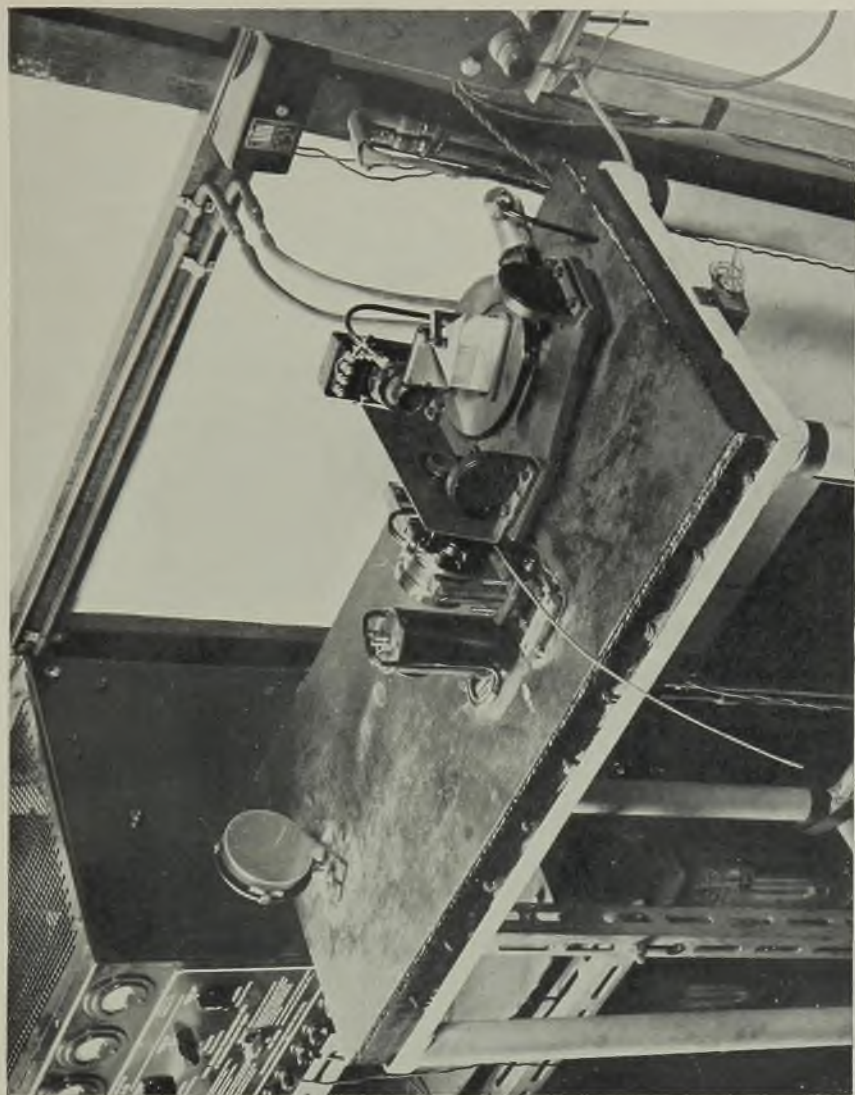


FIG. 1.
INFRA-RED SPECTROMETER FOR ANALYSIS OF LIQUID MIXTURES.

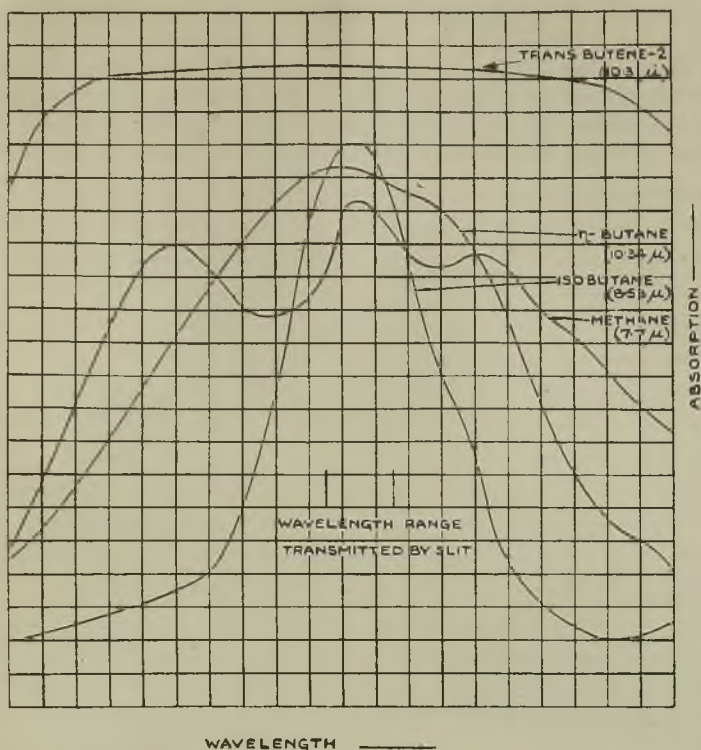
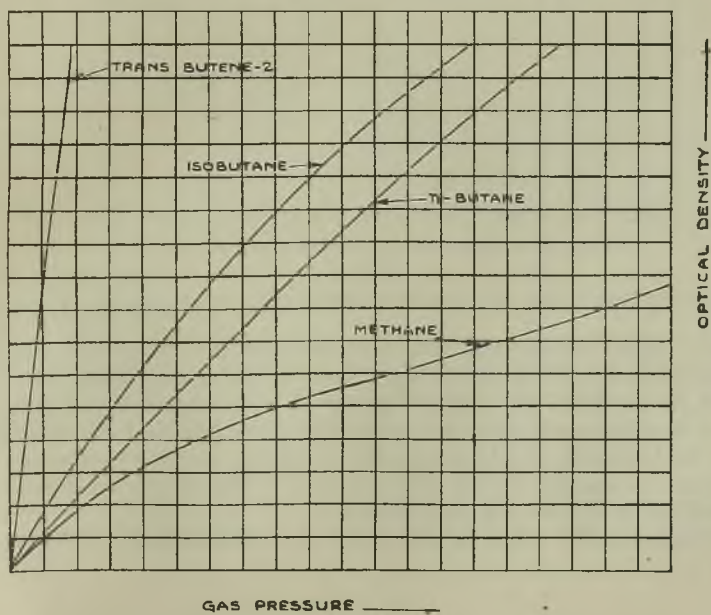


Fig. 2.
COMPARISON OF WIDTH OF ABSORPTION PEAKS.



senting change of optical density with change of thickness to become curved.

This effect of band shape on the curvature of the calibration curves may be best illustrated by referring to Figs. 2 and 3 and the corresponding calibration curves in which absorption bands due to methane (7.7μ), isobutane (8.58μ), *n*-butane (10.34μ), and *trans*-butene-2 (10.35μ) are

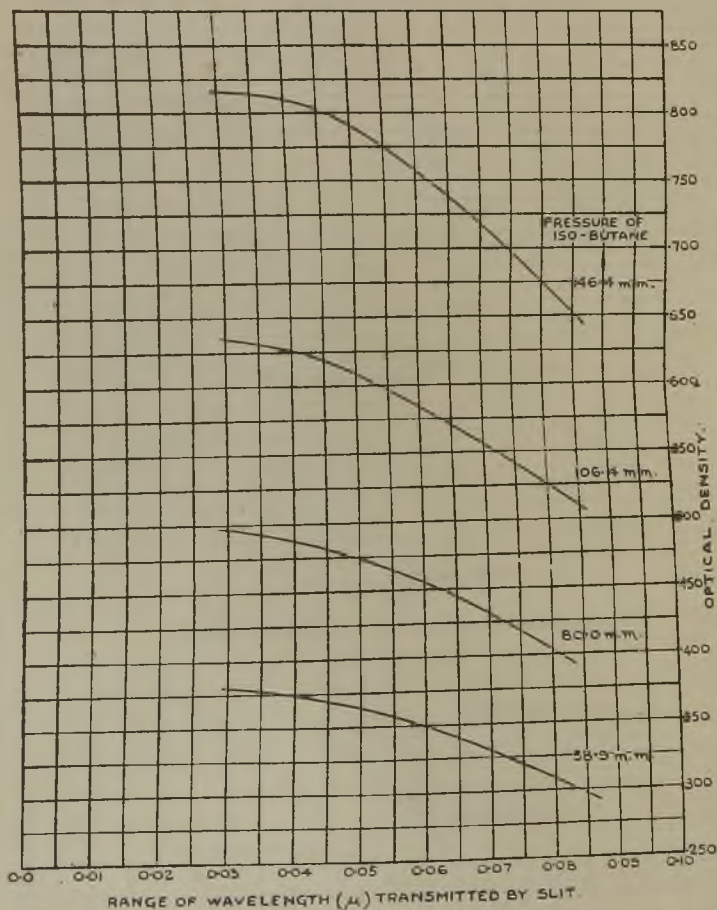


FIG. 4.

EFFECT OF SLIT WIDTH ON OPTICAL DENSITY FOR 8.58μ BAND OF *iso*-BUTANE.

shown. These curves show that the narrower the top of the absorption band relative to the slit width, the greater the curvature observed.

This curvature of the calibration curves is an experimental fact which cannot be eliminated, since the use of slits so narrow that the above effect would be negligible would reduce the available energy to amounts which could not be measured with any accuracy. The effect can, however, be allowed for by the use of a variable cell.

The quantitative effect of slit width on optical density has not so far

been ascertained on the instrument described above, but Fig. 4 shows the effect on a spectrometer of identical design used for gas analysis. In Fig. 4 the horizontal scale represents the slit width in terms of the range of wave-lengths transmitted as calculated from the geometry of the spectrometer. The experimental accuracy in determining the optical density is 0.005, and it follows that to maintain this accuracy in the range

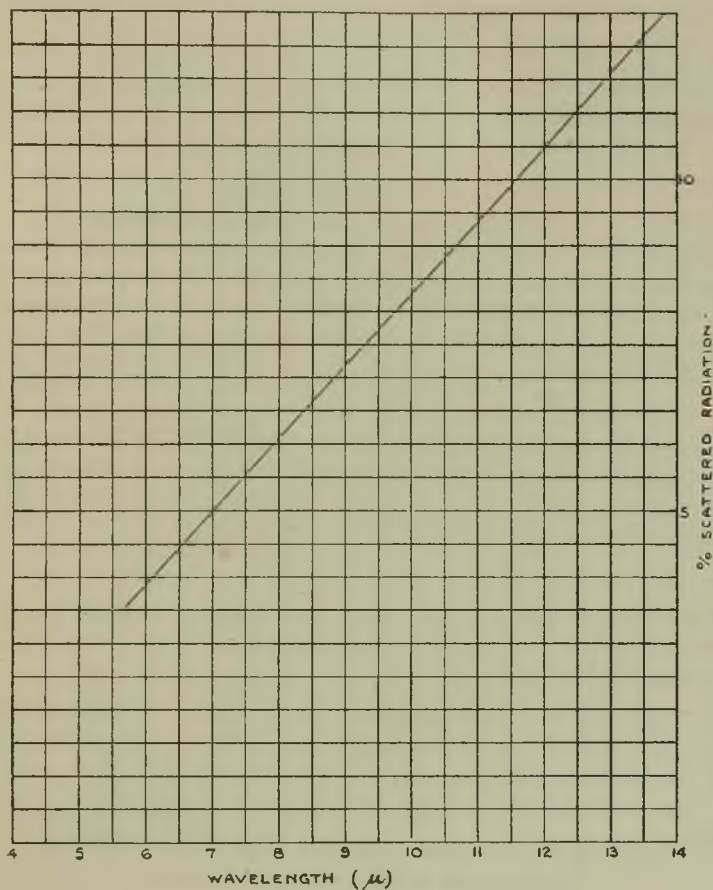


FIG. 5.
PERCENTAGE SCATTERED RADIATION *v.* WAVE-LENGTH.

of the band used for illustration (*isobutane* at 8.58μ) the slit width must not vary by more than 0.01μ . On the present instrument this corresponds to a difference of three divisions on the slit width scale, seven being the normal scale reading in this range of the spectrum.

(c) *Effect of Scattered Radiation.*

This effect arises from the fact that when the prism is set in a position to transmit the longer wave-lengths, the radiation actually falling on the

exit slit includes a small proportion of radiation of short wave-length ($1-2 \mu$) which has been scattered within the instrument—*e.g.*, by internal reflections in the prism. This scattered radiation is a property of the spectrometer rather than of the absorption cell, so that the amount received by the thermopile at a given wave-length is the same whether the absorption cell or the plane rocksalt plate is in the radiation path. While the

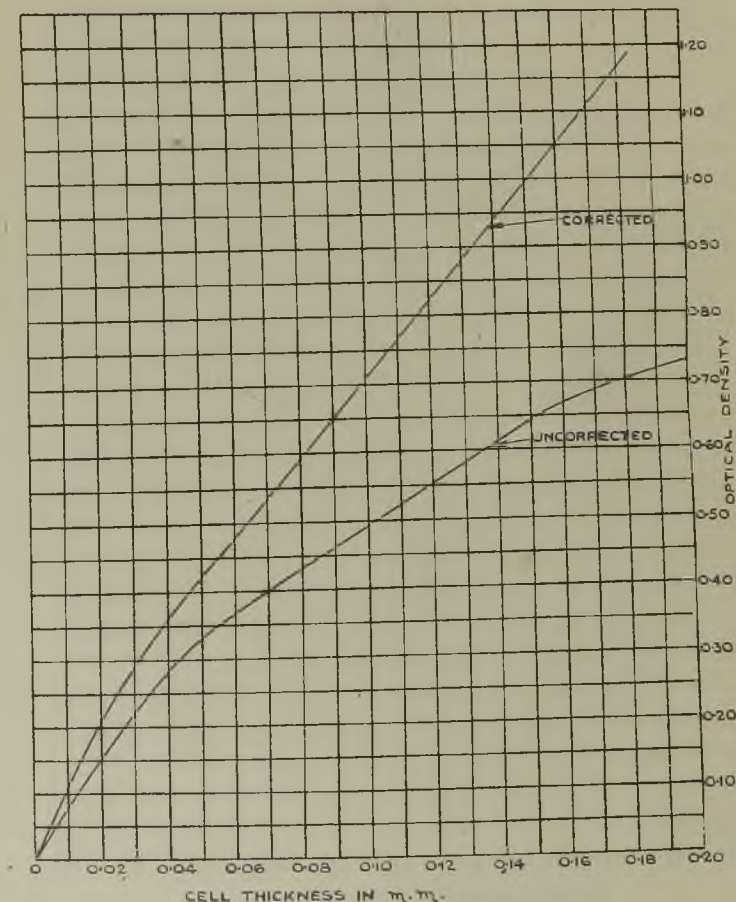


FIG. 6.

EFFECT OF CORRECTING FOR SCATTERED RADIATION. η -HEXANE CALIBRATION CURVE AT 13.80μ .

actual amount of this scattered light is very small, its effect can be considerable, owing to its high energy content. The observed absorption, therefore, is false, since the incident radiation includes some wave-lengths which are not absorbed, giving a figure for the optical density lower than the true figure. The amount of this scattered radiation present at different wave-lengths may be determined by using large thickness of highly absorbing materials. Any radiation then transmitted as measured by the galvano-

meter deflections is taken as false energy. The materials used to determine the scattered radiation were *n*-hexane and *cyclohexane* for the 7 μ region, benzene for the region around 9.64 μ , *cyclohexane* for 11 μ , *m*-xylene and *n*-hexane for the region between 13 μ and 14 μ .

A graph of percentage scattered radiation against wave-length, determined by the procedure illustrated in the Appendix, is shown in Fig. 5. Using this graph, the optical density observed at any wave-length is corrected for scattered radiation to give the true value. The effect on the calibration curves of making this correction at each thickness is illustrated in Fig. 6 for the *n*-hexane band at 13.80 μ . It can be seen from this curve that by making this correction there will be a considerable gain in accuracy in the upper region of optical density.

(d) Position of Cell in Radiation Path.

It is important that the absorption cell should return to exactly the same position in the path of the radiation, otherwise there is no certainty that the instrument zero is the same. In the present apparatus this is ensured by making the trolley carrying the absorption cell and compensating plate act as a switch between fixed stops connected in series with two pilot lights operated from a 4-volt transformer. Unless the pilot lights are operating fully, no galvanometer readings are taken.

It is also advisable to place the absorption cell so that it is always oriented in the same manner in the radiation path. This precaution should be taken on account of the fact that there is a temperature gradient from the bottom to the top of the Nernst filament source. From measurements with an optical pyrometer this is estimated to be equivalent to an energy difference of 10 per cent. in output.

PART II.—APPLICATION OF THE VARIABLE PATH LENGTH ABSORPTION CELL.

The problem of analysing mixtures containing benzene, *n*-hexane, methylcyclopentane, 3-methylpentane and 2 : 2-dimethylpentane is treated in some detail below. The essential preliminary was to decide on the best "key" wave-lengths for the analyses, and this involved the determination of the absorption spectra of the pure hydrocarbons over the wave-length range 3–14 μ .

TABLE I.
Physical Properties of Hydrocarbon Used.

Component.	B.P., ° C.	F.P., ° C.	d_4^{20} .	n_D^{20} .	Bank No.	Purity, %.
<i>n</i> -Hexane	68.75	— 95.45	0.6593	1.3751	1025	99.3
Benzene	80.20	5.48	0.8792	1.5012	1062	99.95
Methylcyclopentane	71.85	—142.63	0.7489	1.4099	1036	99.7
3-Methylpentane	63.35	Glass	0.6642	1.3768	1010	—
2 : 2-Dimethylpentane	79.20	—123.65	0.6735	1.3821	1069	99.75

The physical properties of the materials used are given in Table I, the absorption spectra, fully corrected for the sources of error discussed in Part I, being shown in Figs. 7–11. These curves have been determined

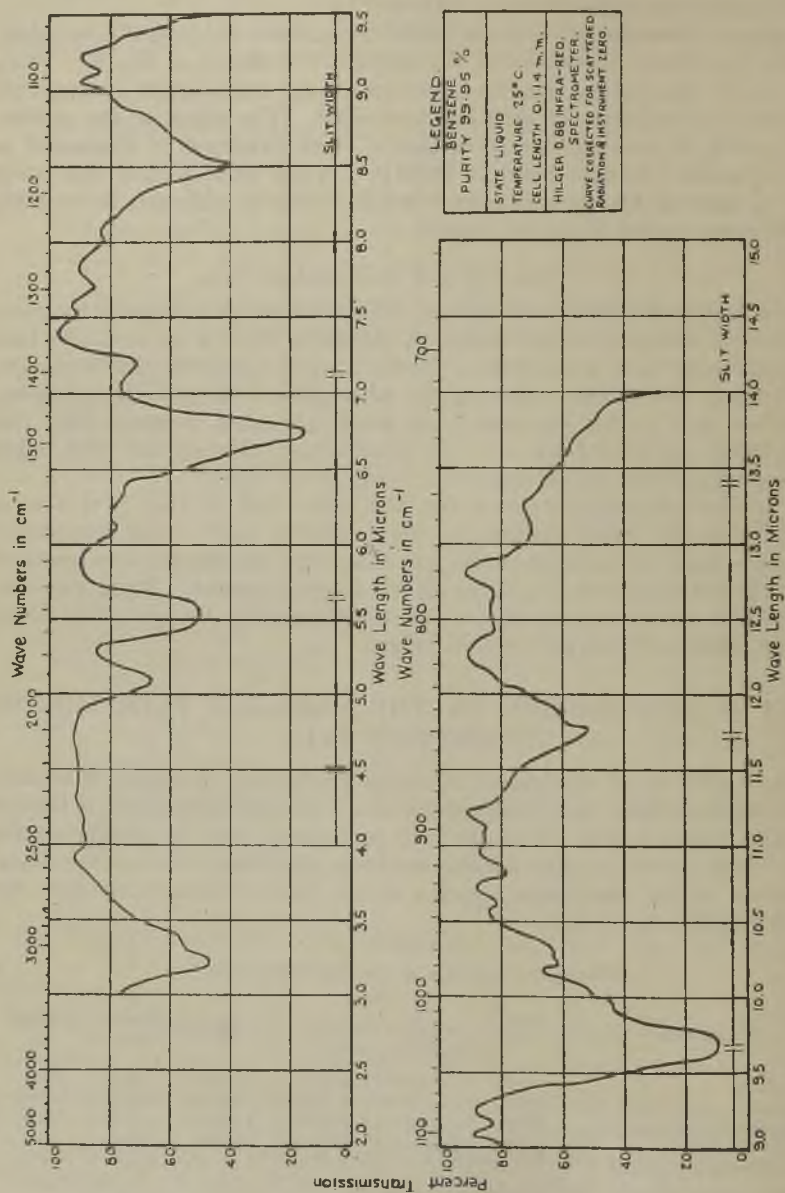


Fig. 7.

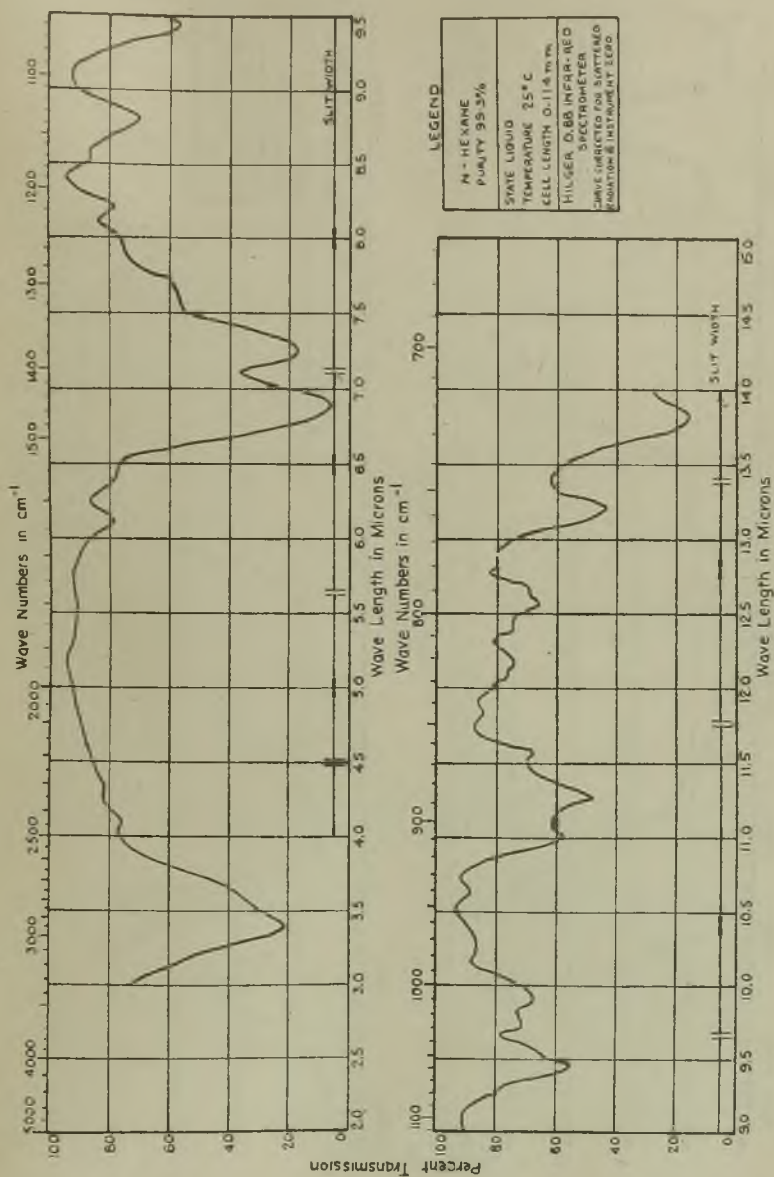


FIG. 8.

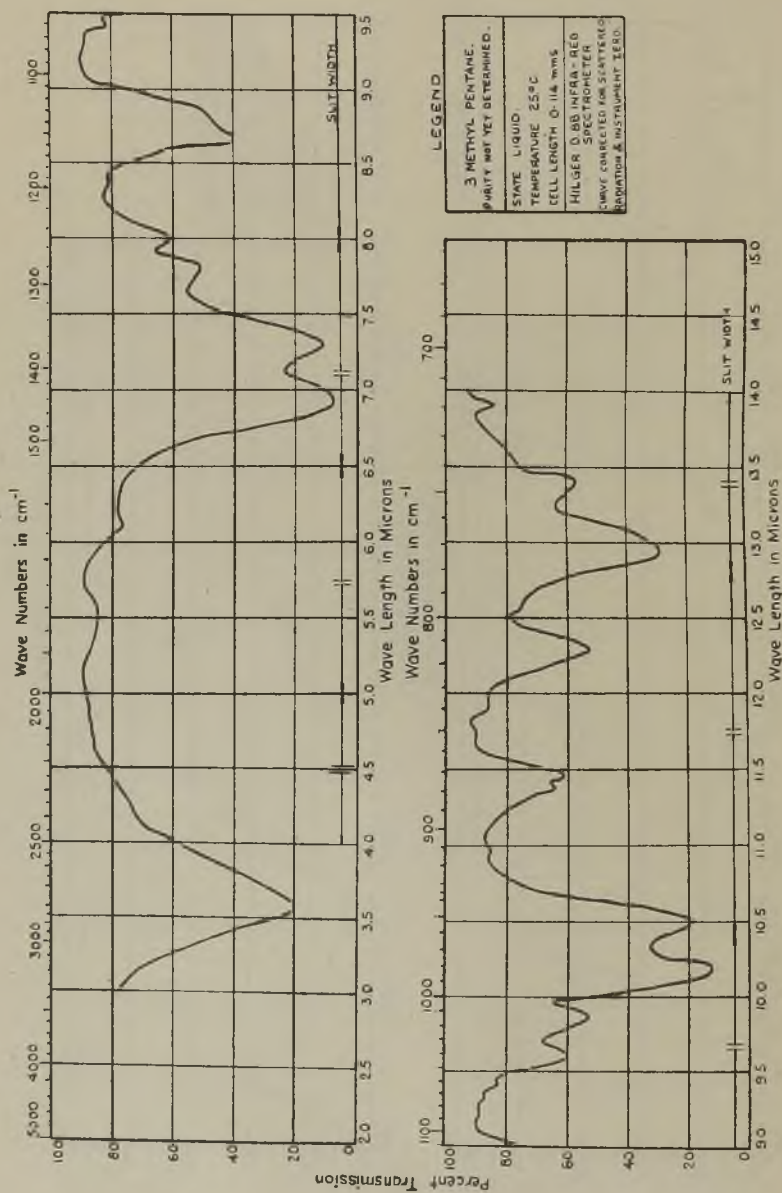


Fig. 9.

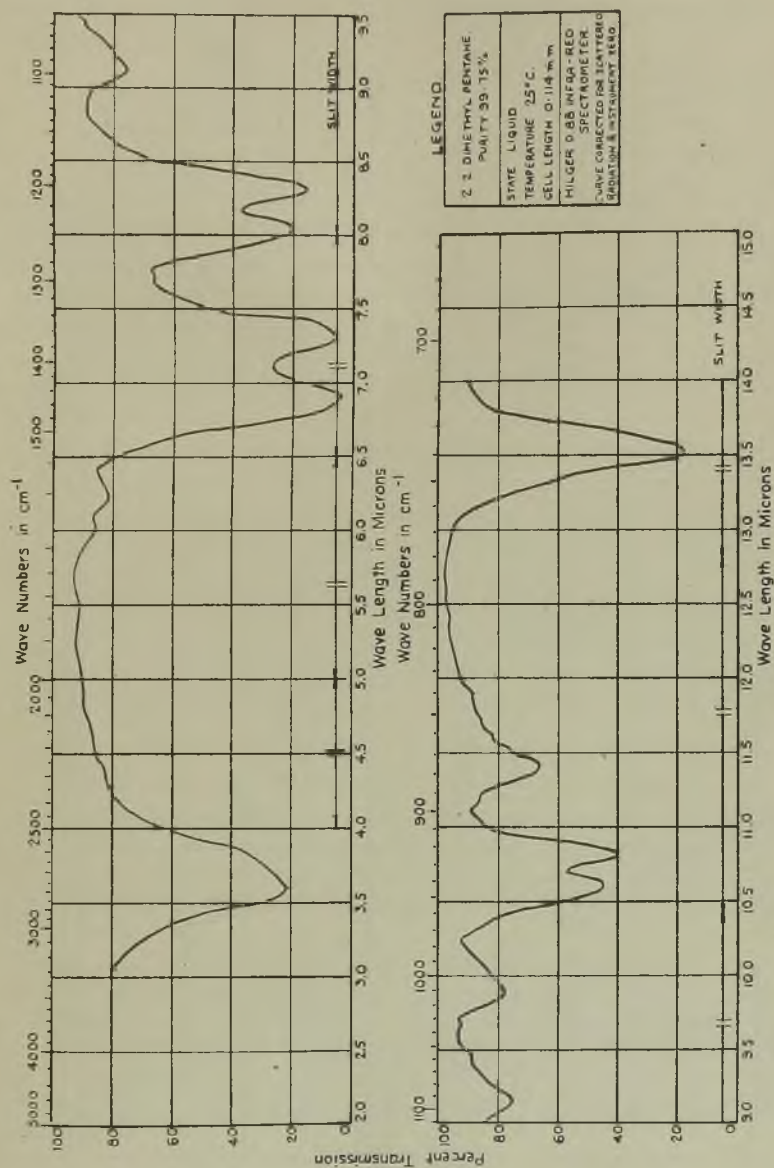


FIG. 10.

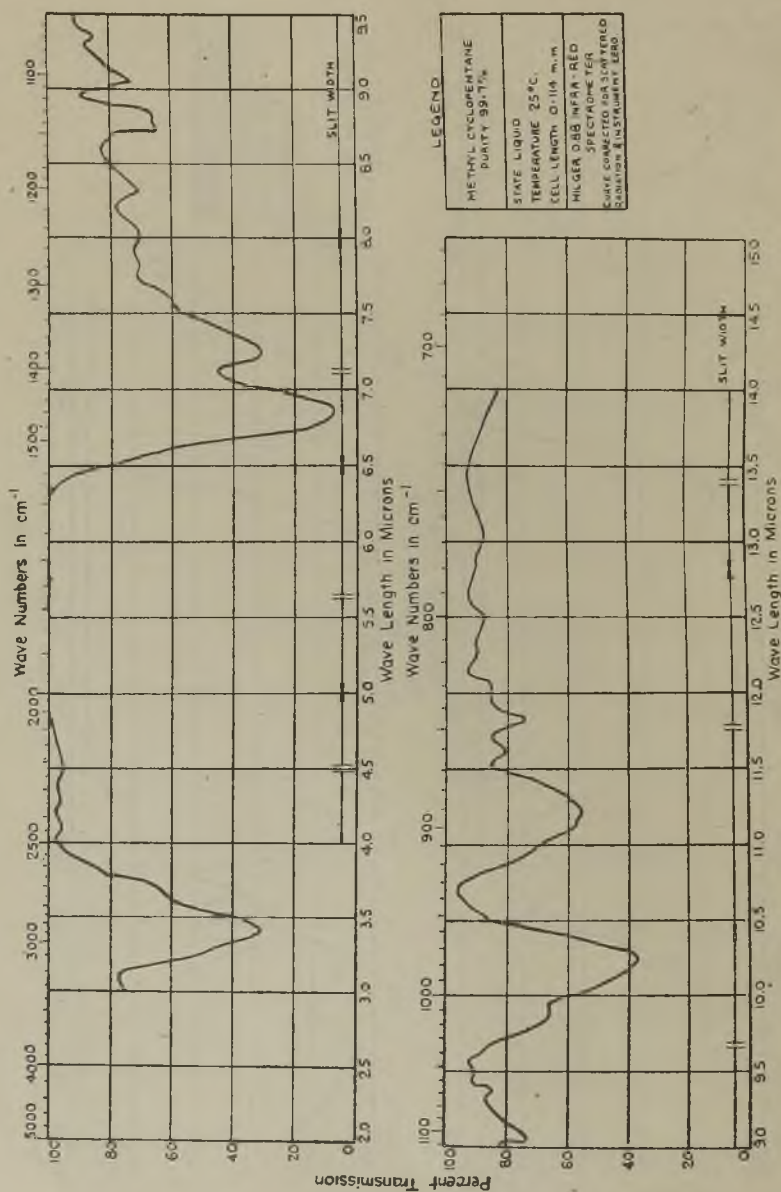


FIG. 11.

using an absorbing layer 0.114 mm. thick, but analyses have been carried out also at a cell thickness of 0.216 mm.

Referring to the hydrocarbons listed in Table I and the transmission curves shown in Figs. 7-11, the "key" wave-lengths for mixtures of these materials are:—

Hydrocarbon.	Key Wave-length (μ).
Benzene	9.64
<i>n</i> -Hexane	13.80
3-Methylpentane	10.5 and 13.0
Methylcyclopentane	10.24
2 : 2-Dimethylpentane	13.50

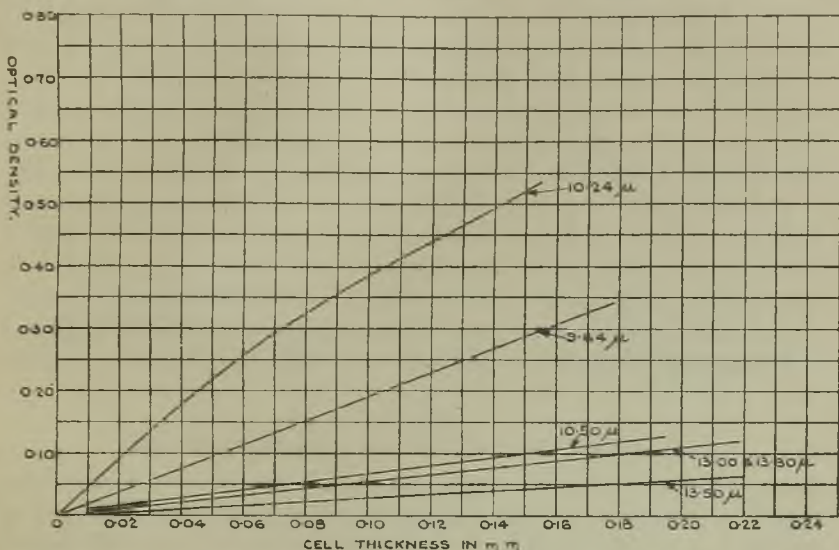


FIG. 12.

OPTICAL DENSITY *vs.* THICKNESS FOR METHYLCYCLOPENTANE.

The figures obtained for the transmission at each of these wave-lengths are corrected for cell zero and scattered radiation as described in Part I, and a corrected optical density deduced (see example in Appendix). The results of repeating this procedure for a series of thicknesses are shown in Figs. 12-16.

COMPUTATION OF RESULTS.

The fact that for many hydrocarbon liquids the relation between optical density at a "key" wave-length and thickness of absorbing layer is a curve, introduces a certain amount of difficulty into the computation, in that it is not possible to use a system of simultaneous equations to obtain the final analysis. The method adopted, therefore, is that of successive approximation.

From the corrected measured optical densities, and using the appropriate transmission curves for the pure components (Figs. 7-11), it will be obvious in the simplest case that at one wave-length one component is responsible for most of the absorption. To a first approximation we assume that all the absorption at this wave-length is due to this hydrocarbon, and using

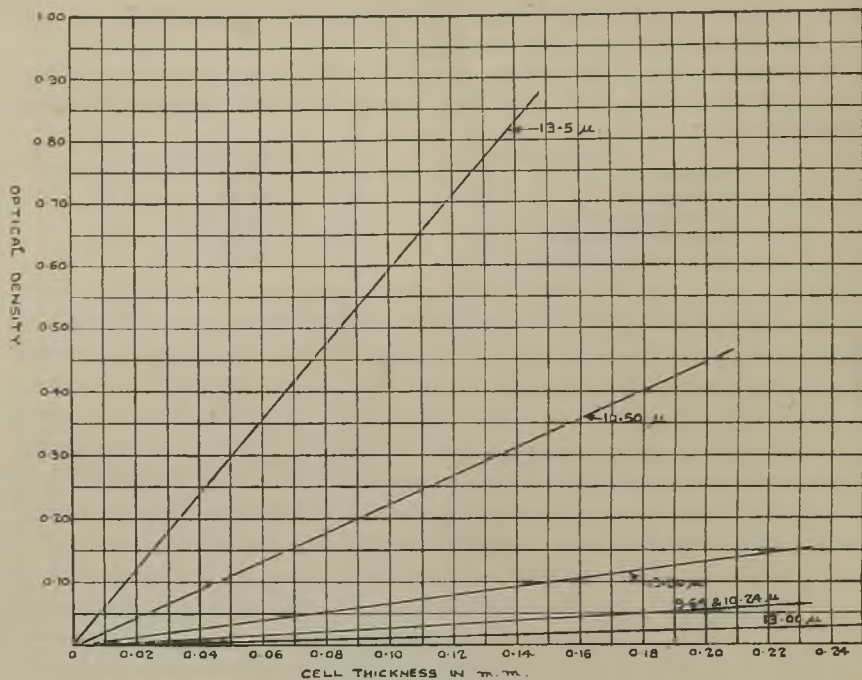


FIG. 13.

OPTICAL DENSITY vs. THICKNESS FOR 2:2-DIMETHYLPENTANE.

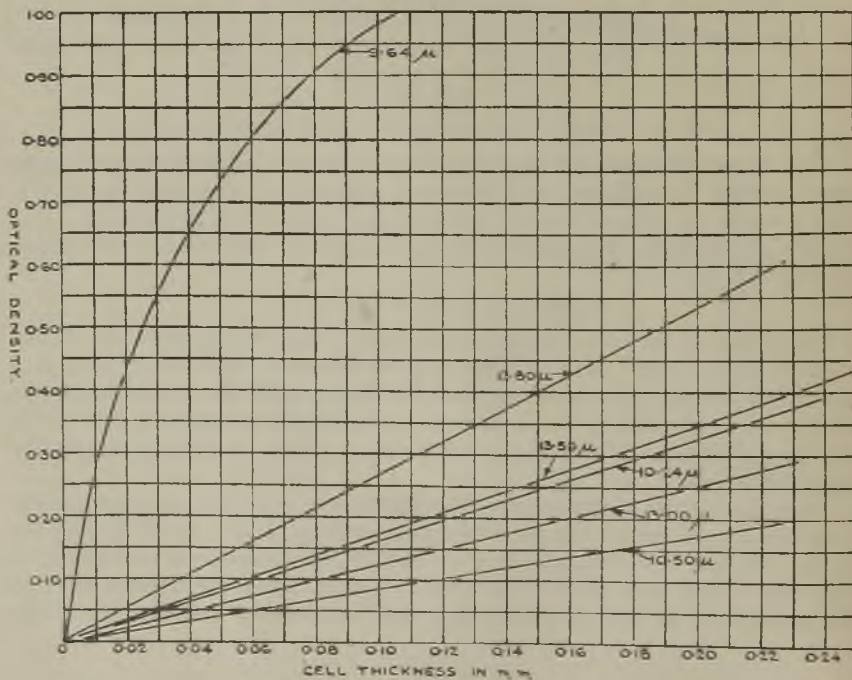


FIG. 14

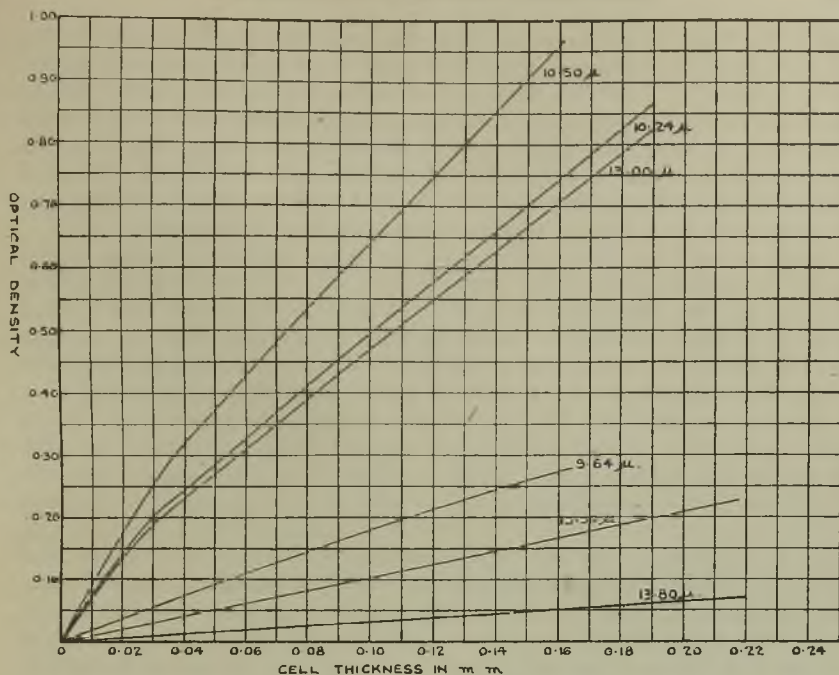


Fig. 15.
OPTICAL DENSITY vs. THICKNESS FOR 3-METHYLPENTANE.

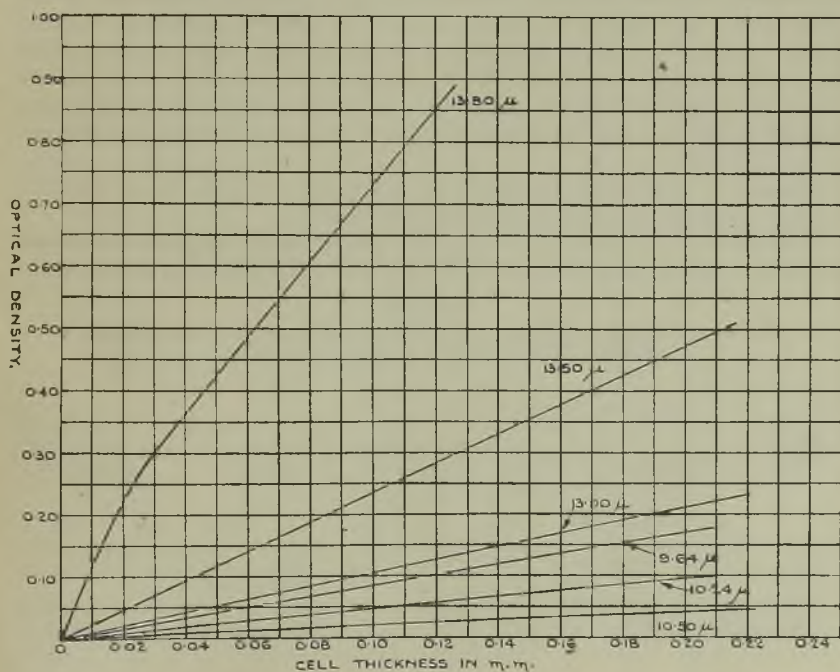


Fig. 16.

NESS FOR n-HEXANE,

one of the Figs. 12-16, we deduce for this wave-length what would be the effective absorbing thickness of this hydrocarbon alone, to give the measured optical density. From the same set of curves the optical density due to this layer of the individual hydrocarbon, at each of the other wave-lengths concerned, is read off. These optical densities are subtracted from the appropriate measured densities for the mixture, and from the results, in a similar manner, the assumption is made that all the residual absorption at one wave-length is due to another (predominating) component.

Again using Figs. 12-16, we deduce the layer thickness for this second major component at its "key" wave-length, and derive a resulting optical density at the other wave-lengths. At each wave-length this optical density is again subtracted from the measured value less the amount already deducted on account of the first component: leaving a series of residual densities to be accounted for by the remaining components.

Working in this way through all the components present, we should arrive at a series of layer thicknesses (one per component) which will add up to the cell thickness used in the analysis (say, 0.114 mm.): and the "residual" or unaccounted optical density should be zero. A first approximation will not achieve this result in general, but inspection will show in what direction the approximation is in error, and enable due allowance to be made in the assumed layer thicknesses of the major absorbing components. The process is then repeated until (1) the sum of the calculated layer thicknesses agrees with the cell thickness used within the error of setting of the cell (0.0029 mm.), and (2) the sum of the optical densities at any wave-length due to all components is equal, within experimental error, to the observed total optical density. A check may be required at another (thicker) cell setting, particularly where some of the components are present in small amounts, in order to establish whether small "residual" optical densities are due to inaccurate estimation of the minor components, or are due to experimental errors in measurement (an optical density of 0.2 is considered to be the minimum which can be reliably measured, and the experimental error at this density is estimated to be ± 0.005).

Finally, a check may be made at some wave-length other than the "key" wave-lengths used in the approximations.

It has been found that, as a rule, only two successive approximations are required: and the process may be illustrated by the following example:—

TABLE II.

Analyses of Synthetic Mixtures of Benzene, n-Hexane, 3-Methylpentane, Methylcyclopentane and 2:2-Dimethylpentane.

Blend No.	Vol.-%.									
	Benzene.		n-Hexane.		3-Methylpentane.		Methylcyclopentane.		2:2-Dimethylpentane.	
	Act.	Obs.	Act.	Obs.	Act.	Obs.	Act.	Obs.	Act.	Obs.
1	7.5	7.7	70.0	72.5	15.0	14.2	7.5	5.6	—	—
2	7.5	7.8	70.0	71.0	7.5	6.8	15.0	14.4	—	—
3	10.3	11.9	59.0	59.0	5.1	5.4	15.4	15.1	10.2	8.6
4	23.4	23.9	20.8	21.0	1.3	2.7	20.8	20.5	33.7	31.9

Using Blend 3 of Table II, the experimental data corrected for cell zero and scattered radiation by the procedure illustrated in the Appendix are as follows :—

Component.	Wave-length (μ).	Corrected Optical Density.	Cell Thickness, mm.
Benzene	9.64	0.436	} 0.114
Methylcyclopentane	10.24	0.190	
3-Methylpentane	10.50	0.124	
3-Methylpentane	13.00	0.150	
2 : 2-Dimethylpentane	13.50	0.252	
<i>n</i> -Hexane	13.80	0.610	
Methylcyclopentane	10.24	0.330	} 0.216
3-Methylpentane	10.50	0.204	
3-Methylpentane	13.00	0.270	
2 : 2-Dimethylpentane	13.50	0.482	

1. Assuming as a first approximation that all the absorption at 13.80 μ is due to *n*-hexane, and, using Fig. 16, an optical density of 0.610 is equivalent to 0.0813 mm. of *n*-hexane.

2. The optical density at 9.64 μ due to this amount of *n*-hexane is 0.070, the difference between this and the observed figure of 0.436 being 0.366. Taking this difference to be due entirely to benzene gives a thickness of 0.0178 mm. (Fig. 14).

3. The optical densities at 13.0 μ due to these amounts of *n*-hexane and benzene are 0.085 and 0.020, respectively, and subtracting the sum of these from the observed figure of 0.150 leaves 0.045. This is equivalent to 0.0063 mm. of 3-methylpentane (Fig. 15).

4. The contributions at 10.24 μ are now calculated, the sum being 0.115, which, when subtracted from the observed figure of 0.190, leaves 0.075 equivalent, from Fig. 12, to 0.0165 mm. of methylcyclopentane.

5. The contributions at 13.5 μ are now calculated, the sum being 0.229, which, when subtracted from the observed figure of 0.252, leaves 0.023 equivalent, from Fig. 13, to 0.0038 mm. of 2 : 2-dimethylpentane.

6. The total optical densities due to these calculated amounts of the five components are now calculated, and the sums compared with the observed figures as below :—

Component.	Estimated Thickness, mm.	Wave-length of Max. Absorption.	Wave-length (μ).					
			9.64.	10.24.	10.50.	13.00.	13.50.	13.80.
Benzene	0.0178	9.64	0.376	0.030	0.015	0.020	0.032	0.050
<i>n</i> -Hexane	0.0813	13.80	0.070	0.040	0.020	0.085	0.190	0.610
3-Methylpentane	0.0063	10.5 and 13.0	0.010	0.045	0.055	0.045	0.007	—
Methylcyclopentane	0.0165	10.24	0.030	0.075	0.010	0.010	0.004	0.010
2 : 2-Dimethylpentane	0.0038	13.50	—	—	0.008	—	0.023	0.002
Total optical density	(calc.)	—	0.486	0.190	0.108	0.160	0.256	0.672
Optical density	(obs.)	—	0.436	0.190	0.124	0.150	0.252	0.610

7. From an inspection of these calculated optical densities it is evident that the *n*-hexane content is too high, as evidenced by the optical density at 13.8 μ . The same applies to the benzene figure at 9.64 μ . The excess optical density of 0.062 at 13.8 μ corresponds to a thickness of 0.0122 mm. of *n*-hexane, and the corresponding excess of benzene at 9.64 μ is 0.0038 mm. These amounts are subtracted from the thicknesses obtained by the first approximation, the resulting thicknesses being 0.0691 mm. of *n*-hexane and 0.0140 mm. of benzene.

8. The remaining wave-lengths—*viz.*, 10.24, 10.5, 13.0, and 13.50 μ —are now corrected using these revised figures. The calculated optical densities are now 0.180, 0.108, 0.149, 0.219, respectively.

9. Comparison of these figures with the observed optical densities indicates that more methylcyclopentane and 2:2-dimethylpentane are required, but the amount of 3-methylpentane is very close to the true figure. The new thicknesses required to balance the optical densities at 10.24 and 13.50 μ are 0.0178 mm. and 0.0102 mm. of methylcyclopentane and 2:2-dimethylpentane, respectively.

Using the thicknesses now obtained, a final check is made of the optical densities, with the results shown below:—

Component.	Estimated Thickness, mm.	Wave-length of Max. Absorption.	Wave-length (μ).					
			9.64.	10.24.	10.50.	13.00.	13.50.	13.80.
Benzene	0.0140	9.64	0.330	0.023	0.011	0.015	0.026	0.040
<i>n</i> -Hexane	0.0691	13.80	0.060	0.035	0.018	0.071	0.161	0.550
3-Methylpentane	0.0063	10.50 and 13.00	0.010	0.046	0.055	0.046	0.008	0.001
Methylcyclopentane	0.0178	10.24	0.031	0.080	0.010	0.009	0.003	0.010
2:2-Dimethylpentane	0.0102	13.50	0.001	0.001	0.021	0.001	0.060	0.008
Total optical density	(calc.)	—	0.432	0.185	0.115	0.142	0.258	0.609
Optical density	(obs.)	—	0.436	0.190	0.124	0.150	0.252	0.610

It is observed that at the wave-lengths 10.5 and 13.0 μ , which are both for 3-methylpentane, the observed optical densities are lower than 0.2, which is considered to be the lower limit of accurate determination. Also the calculated values are both lower than the observed values. Whether this is due to having too little 3-methylpentane, or due to errors in the measurement of the optical densities, may be checked by using a greater cell thickness at these wave-lengths.

Using the quantities of the various components as determined above, the optical densities at 10.24, 10.5, 13.0, and 13.50 μ are calculated for a thickness of 0.216 mm. and compared with the experimental values as below.

Optical Density.	Wave-length (μ).			
	10.24.	10.50.	13.00.	13.50.
Obs.	0.330	0.204	0.270	0.482
Calc.	0.340	0.210	0.268	0.481

The agreement between the observed and calculated optical densities is now within the experimental error of determination, thus indicating that the analysis for the components present in small amounts is correct.

The final analysis is therefore :—

Component.	Thickness, calc.	Vol.-%.	
		Obs.	Act.
Benzene	0.0140	11.9	10.3
<i>n</i> -Hexane	0.0691	58.9	59.0
3-Methylpentane	0.0063	5.4	5.1
Methylcyclopentane	0.0178	15.2	15.4
2 : 2-Dimethylpentane	0.0102	8.6	10.2
		100.0	100.0
Total thickness, calc.	0.1174		
" " obs.	0.1143		

It should be noted that the sum of the calculated thicknesses is greater than that deduced from the cell setting. The accuracy with which the cell thickness can be adjusted is approximately 0.0029 mm. in 0.114 mm.—*i.e.*, 2 per cent.—and therefore the calculated thicknesses are divided by the observed total thickness to obtain the percentage composition. This spreads any small error which may be present in the observed optical densities over all the components.

The procedure of working in thicknesses also provides a useful check on the analysis. For example, in the analysis of an *iso*heptane fraction which had supposedly been freed from 3-methylpentane it was found that the total calculated thickness was too low. The "key" wave-lengths for 3-methylpentane were then examined, and it was found that some 8 per cent. of this material was present. The total thickness was still too low, but rose to the cell setting figure when, on examining the optical densities at 13.50 μ , it was found that some 3 per cent. of 2 : 2-dimethylpentane was present. The optical densities calculated at six wave-lengths checked with the observed values for the five component mixture.

The results of four synthetic mixtures calculated by the above procedure are given in Table II.

The total time required for each of these analyses is about 1½ hrs. This includes instrument time as well as computation.

DISCUSSION OF RESULTS.

The analyses given in Table II show that a high degree of accuracy can be attained, and the usefulness of having a variable cell is demonstrated in checking small amounts present of certain components. It must be understood, however, that the accuracy attained applies only to mixtures similar to those examined and may not apply to mixtures containing other components. The accuracy of analysis depends to a large extent on suitable "key" wave-lengths being available for each component, and

this condition cannot always be satisfied as it has been in the analyses quoted.

ACKNOWLEDGMENT.

The experimental work described above was carried out in the research laboratories of the Anglo-Iranian Oil Company, Ltd., Sunbury-on-Thames, Middlesex, and the authors express their thanks to the Chairman for permission to publish this paper.

APPENDIX.—APPLICATION OF THE CORRECTIONS FOR SCATTERED RADIATION AND CELL ZERO.

With radiation of wave-length 13.1μ passing through the plane rocksalt plate, a galvanometer deflection of 13.2 cm. was observed. The corresponding deflection observed with a thickness of 0.406 mm. of *m*-xylene in the radiation path was 1.5 cm. Since on increasing the thickness of absorbing layer no further diminution of the galvanometer deflection was observed, this 1.5 cm. must be due to wave-lengths which are not absorbed—*i.e.*, they represent scattered radiation amounting to $1.5/13.2 \times 100 = 11.3$ per cent. of that transmitted through the rocksalt plate, and the true transmission through the plate is proportional to a deflection of $13.2 - 1.5 = 11.7$ cm.

The graph shown in Fig. 5 was derived by repeating this process at other wave-lengths using the appropriate absorbing materials.

As an example of the application of this correction the absorption band at 13.80μ due to a layer of *n*-hexane 0.150 mm. thick is considered.

The galvanometer deflections observed were 9.0 and 1.75 cm. for the radiation passing through the rocksalt plate and absorption cell, respectively. This corresponds to a transmission of 19.45 per cent. uncorrected for scattered radiation. From Fig. 5 the amount of scattered radiation at 13.80μ is 12.5 per cent., corresponding to a galvanometer deflection of 9.0×12.5

$\frac{100}{100} = 1.1$ cm. The true amount of radiation of 13.80μ wave-length passing through the plane rocksalt plate is therefore proportional to $9.0 - 1.1 = 7.9$ cm. These corrected deflections give a transmission of $\frac{0.65}{7.9} \times 100 = 8.25$ per cent.

Had the cell zero been 100 per cent.—*i.e.*, if the cell had transmitted when empty exactly the same amount of energy as the rocksalt plate, these deflections would have corresponded to an optical density of $\log \frac{100}{8.25} = 1.083$. At this wave-length, however, the cell zero as determined was 84.5 per cent., and the optical density corrected for this figure is $\log \frac{84.5}{8.25} = 1.008$.

AMMONIA—A FUEL FOR MOTOR BUSES.

By EMERIC KROCH,* D.Sc. (Member).

THE first utilization of liquid anhydrous ammonia as a fuel for motor-buses took place in Belgium during the year 1943.

The first motor-bus was equipped and put into service in April 1943, and since then eight buses operating on three lines have covered several tens of thousands of miles, leaving and arriving on schedule, thus maintaining an important public service for the Belgian civilian population.

Before describing the principal features of this new development in alternative motor fuels and the results obtained during the first twelve months of exploitation, it appears opportune to give the reasons why this particular alternative motor fuel was chosen for the service described above.

In October 1942 the management of the S.N.C.F.V. (Société Nationale des Chemins de Fer Vicinaux—the Belgian State-supervised system of suburban and countryside transportation by rail and road) was informed that no more diesel oil would be available for motor buses.

The engineers of the S.N.C.F.V., together with Belgian specialists, made a rapid survey of the then existing possibilities of replacing diesel oil by an alternate fuel. As no liquefied petroleum gas (propane/butane) or so-called "rich" gas (with a B.T.U. content of 750–1000/cu. ft.) in sufficient quantities were available, the choice was restricted to compressed coal gas (B.T.U. content less than 550/cu. ft.) or producer gas.

Neither of the two solutions appeared satisfactory to the experts of the S.N.C.F.V. The engines by which the buses were powered were barely sufficient to assure the service, which, owing to war-time conditions, was strained to the limit. The number of passengers had increased by at least 30 per cent. per bus, and the load was therefore much higher than in pre-war days.

Both anthracite and wood-gas producers entailed a loss of power of 25–40 per cent. Compressed coal gas appeared to be a better proposition, but, in the case of two bus lines, both the quality and the quantities of the gas available were deficient. The relatively low B.T.U. content of the then-produced coal gas (around 400/cu. ft.) would have made it necessary to equip the buses with a large number of steel cylinders in order to carry sufficient fuel for at least one round trip. This would have further reduced the carrying capacity of the buses which was already strained to the limit.

There appeared, therefore, to be a deadlock, and the service was discontinued in November 1942, thereby causing great inconvenience to the population, which had to rely on these lines as their sole means of communication.

The engineers of the S.N.C.F.V. then approached the writer and his

* Managing Director of Comprigaz, Ltd. (Brussels).

associates for the purpose of examining the possibilities of adapting for the motor buses the new system based on the patents of Ammonia Casale and J. L. Restieau and E. Kroch (known as the Gazamo process), and which has been first presented to the Belgian public at the Alternate Fuel Exhibition organized by the Association of the University of Brussels Engineers in June 1942 (Fig. 1).

AMMONIA AS FUEL FOR INTERNAL-COMBUSTION ENGINES.

It would be beyond the scope of this article to describe in detail the development of the use of anhydrous ammonia as motor fuel, but letters patent and other indications can be traced as far back as 1905. It seems, however, that the first practical application on a limited scale was due to Ammonia Casale, Ltd., who took out patents in Italy in 1935 and 1936. The Casale system was characterised by partial thermal decomposition of ammonia in a catalytic reaction chamber heated with exhaust gases from the motor.

The Gazamo process, which has been tested on the road principally during the severe winter of 1941-42, appears to be the first application on a fairly large scale, as about 100 vehicles were equipped for use of ammonia as fuel.

Without going into details or any lengthy theoretical considerations, a brief summary of the characteristics of anhydrous ammonia, as well as a short discussion of the principles underlying the Gazamo system, are necessary for the further comprehension of the subject.

TABLE I.

Properties of Anhydrous Liquid Ammonia.

Chemical formula : NH_3 .

Molecular weight : 17.

Percentage composition : N = 81.5%, H = 17.5%.

Specific gravity (gas) (air = 1) at 60° F. and 30 in. Hg = 0.596.

Specific gravity (liquid) at 60° F. = 0.639.

Boiling point at 30 in. Hg. = -28° F.

Freezing point -108° F.

Vapour pressure in lb./sq. in. abs. at various temperatures.

° F.	-28°	0°	32°	50°	60°	80°	100°	122°
Lb./sq. in. abs.	14.7	30.4	64.3	89.2	107.6	153.0	211.9	294.8

Heating value (lower) B.T.U. per lb. : 8060.

Heating value (lower) B.T.U. per cu. ft. (60° F. and 30 in. Hg) : 380.

Specific heat (liquid) at 60° F. : 1.12 B.T.U./lb.

Latent heat of vaporization in B.T.U. per lb. at various temperatures.

° F.	-28°	0°	32°	50°	60°	80°	100°	122°
B.T.U./lb.	589	612	621	625	627	631	633	634

Solubility in water.

1300 vol. NH_3 in 1 vol. H_2O at 32° F.

Mean liquid expansion coefficient between 32° F. and 122° F. : 0.0027.

Limits of inflammability (ammonia + air at 60° F. and 30 in. Hg) : lower 17% ; higher 30% of ammonia in air,

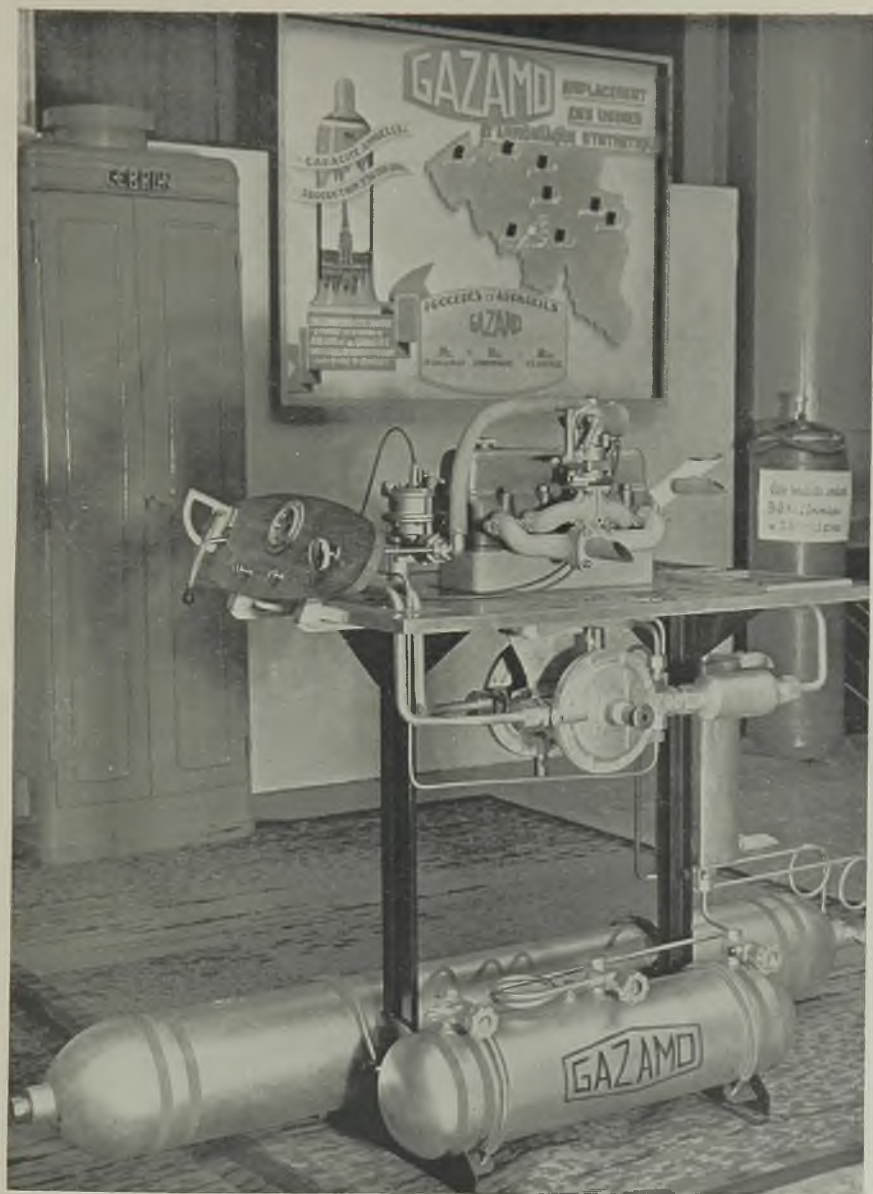


FIG. 1.

GAZAMO STAND AT THE ALTERNATE FUEL EXHIBITION, BRUSSELS, 1942. THE FRONT CYLINDER CONTAINS ANHYDROUS LIQUID AMMONIA AND THE REAR ONE COMPRESSED COAL GAS. A STANDARD 110-LB. AMMONIA CONTAINER IS SEEN IN THE RIGHT-HAND CORNER. THE MAP ON THE BOARD INDICATES THE LOCATION OF EIGHT SYNTHETIC AMMONIA PLANTS IN BELGIUM—BRUSSELS, TERTRE, HOUDENG-GOEGNIES, WILBROECK, ZANDVOORDE, SELZAETE, RENORY, TILLEUR—CAPABLE OF PRODUCING 230,000 TONS OF ANHYDROUS AMMONIA PER YEAR.

[To face p. 214.]



FIG. 3.

AMMONIA-EQUIPPED MOTOR BUS. AMMONIA CONTAINERS ARE FIXED ON THE FRONT OF THE VEHICLE AND THE GAS CYLINDERS ON THE TOP.

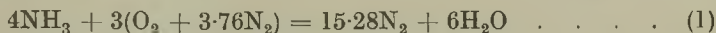
Anhydrous ammonia (NH_3), as produced by direct synthesis in large quantities in most of the industrial countries, is, under ordinary conditions, a colourless gas with characteristic odour, very soluble in water, with which it forms the common household ammonia.

Ammonia is easily liquefied under moderate pressure, and can be kept in liquid state in appropriate steel cylinders, tank cars, motor trucks, and storage tanks. Vapour-pressure characteristics of ammonia are similar to those of propane and containers for propane are also suitable for handling, transportation, and storage of ammonia, provided no copper or copper alloys are present.

The various physical and chemical characteristics of anhydrous ammonia are given in Table I.

COMBUSTION OF AMMONIA.

While it has been known since the beginning of the nineteenth century that ammonia could be made to burn, the combustion reaction and its conditions were examined in detail much later. Assuming a simplified formula for the composition of air, *viz.* 21 per cent. oxygen and 79 per cent. nitrogen (without inert gases), the theoretical combustion of ammonia in air can be stated as follows :



Fear has been expressed (and still is in some quarters) that another reaction can also take place :



with formation of nitrogen oxide leading to appearance of nitrous acid and eventually of nitric acid in the combustion gases.

It can be stated emphatically that after using ammonia as motor fuel for many thousands of miles no trace of corrosion was apparent on the parts of the motor in contact with the combustion gases. In fact no more and perhaps less, than ordinary wear and tear was apparent on the cylinders, valves and exhaust manifolds.

The amount of heat produced by reaction (1) based on 1 g.-mol. of ammonia with water non-condensed (lower heat value) is 75.7 cal. Thus the lower B.T.U. value of gaseous ammonia is approximately 380 B.T.U./cu. ft., or rather lower than that of a good pre-war manufactured gas. The question arises quite naturally why it should be expedient to substitute ammonia for coal gas and what, if any, advantages might be derived from its use.

There are many good reasons why ammonia is an excellent motor fuel, and although the scope of this article does not permit the discussion of details, a short description of the various favourable features is given.

(1) *Less Air Required for Combustion.*

Most of the liquid motor fuels used up to the present are of the hydrocarbon type, and their complete combustion yields as end-products water and carbon dioxide. While one atom of carbon requires two atoms of oxygen for complete combustion, hydrogen requires but one half atom of oxygen per atom.

Taking as an example the lowest saturated paraffin hydrocarbon, methane, which is present in coal gas, a simple reasoning shows that it requires for complete combustion 2.66 times as much air as does ammonia. Thus even with a rather lower heating value the mixture ammonia-air compares favourably with mixtures of the richer fuel gases and vapours.

(2) *Expansion through Combustion.*

The principle of all internal-combustion engines is the combustion in a confined space of an explosive mixture with a rise in pressure due to the high temperatures obtained. In the case of the combustion of ammonia, there is a further increase in pressure which is used for the same purpose. If we compare the total volumes on both sides of reaction (1) we see that $4 + 14.28 = 18.28$ volumes on the left side become $13.28 + 6 = 19.28$ volumes on the right side. This ratio or expansion coefficient is thus $19.28 : 18.28$ or 1.057. The calculated final pressure after the combustion should therefore be multiplied by the above coefficient—the highest for any known fuel. Incidentally, gasoline shows neither expansion nor contraction, while hydrogen leads to a considerable contraction, which decreases its already moderate value as fuel.

(3) *Anti-knock Value of Ammonia.*

At the time of this writing no reliable figures are available as to the relative anti-knock value of ammonia as motor fuel but, judging from the high compression ratios which ammonia tolerates, it may safely be assumed that the comparative octane number of ammonia as fuel is rather higher than 100. The actual compression ratio of the motor bus engines described hereafter was 8.5 : 1. In this case it was not the question of raising the compression ratio but, on the contrary, of decreasing it to a safe level, since it must be remembered that the power units were diesel engines which had an original compression ratio of around 16 : 1.

The three factors favouring the use of ammonia as motor fuel made it likely that good results could be expected from its use as motor fuel for high compression engines. Figures from actual operating experience bear out this assumption. Before going into that part, however, a somewhat detailed description of the Gazamo equipment will illustrate its general features and also its particular application to motor buses.

THE GAZAMO PRINCIPLE AND EQUIPMENT.

The flow-sheet (Fig. 2) illustrates the Gazamo principle as applied for use on mobile internal-combustion engines. Coal gas containing roughly 50 per cent. hydrogen is used to promote the ignition of the air-ammonia mixture. The process, based on the patents of Ammonia Casale (French Patents 799,610 and 802,905; Belgian Patents 412,814 and 413,637), is also covered by patents of Emeric Kroch and J. L. Restieau (Belgian Patent 446,844).

On the right-hand side of the flow-sheet is shown that part of the equipment which supplies the necessary hydrogen in the form of coal gas. The gas is stored in metal cylinders which, according to Belgian practice

and Government regulations, are built for an operating pressure of 200 kg./cm.². Incidentally, it should be mentioned that in France pressures up to 250 kg./cm.² are admitted. The cylinders (usually from two to six in number) are manifolded by means of forged steel tees and seamless steel tubing of 25/60 in. O.D. and 15/64 in. I.D. On one side of the manifold

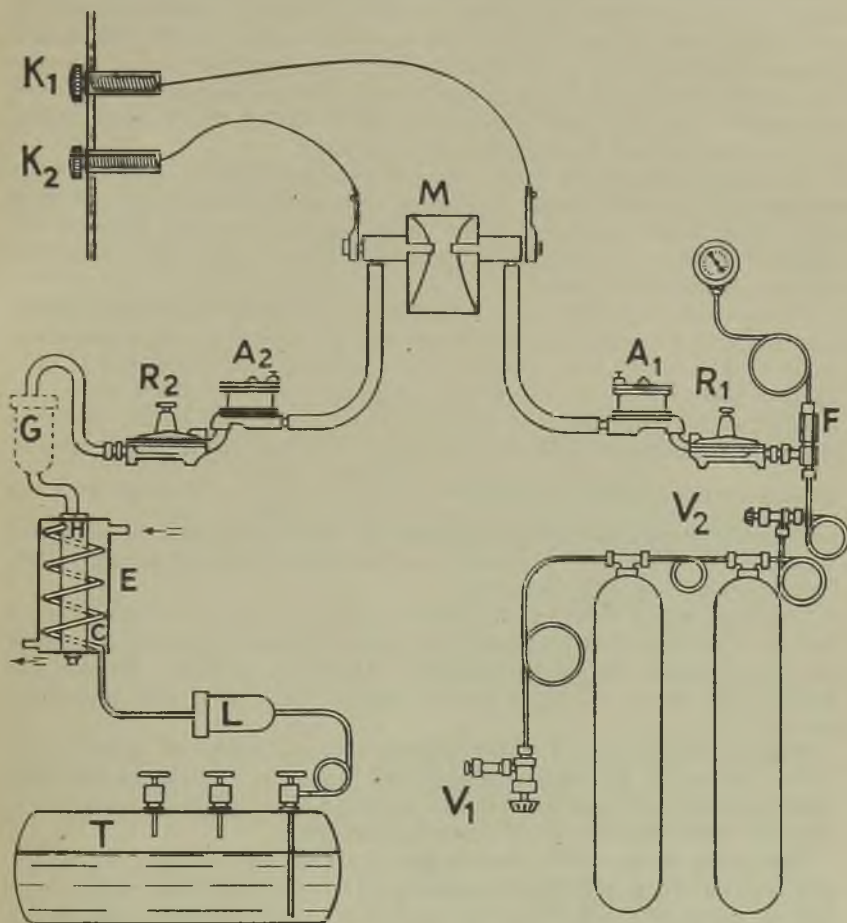


FIG. 2.

FLOW SHEET OF GAZAMO EQUIPMENT.

is the filler valve, *V1*, fitted with a special connector for coupling with the high-pressure filling hose or tubing, and on the other side the shut-off valve, *V2*.

The compressed gas passes from the cylinders through the filter, *F*, into the pressure regulator, *R1*, where the pressure is reduced to 1–2 lb./sq. in. An atmospheric or “zero” regulator, *A1*, acts as a very sensitive shut-off valve to stop the flow of the gas while the motor is at a standstill.

The slightest pull on the right side of *A* opens a balanced valve inside the regulator, and the gas flows freely into the mixer-proportionator, *M*.

The mixer, made of steel or aluminium (no copper or copper alloys may be used), replaces the standard carburetor used on liquid-fuel motor vehicles. A Venturi tube of suitable size is fitted, at a place slightly below its neck towards the motor, with two injectors, which are part of two angle cock valves with flexible controls leading to the dashboard. Through one injector a controlled quantity of coal gas is led into the mixer while the other injector supplies the required amount of vaporized ammonia. The air enters through the open end of the Venturi, which may be fitted with a dashboard-controlled choke.

The liquid ammonia is drawn from the storage tank *T*, which is fixed permanently on the vehicle. In other cases mobile containers are used and, when empty, replaced. The liquid ammonia passes through the strainer *L* before entering the vaporizer *E* heated with water from the cylinder jacket of the engine.

There is a marked difference in regard to the heat of vaporization necessary for vehicles using liquefied petroleum gas and those using ammonia as fuel. The L.P.G. have a high B.T.U. content (about 21,500 B.T.U./lb.), against 8500 B.T.U./lb. in case of ammonia. On the other hand, the latent heat of vaporization of L.P.G. is but 170–190 B.T.U./lb., while the figure for ammonia is 342 B.T.U./lb. at 32° F. Thus for the same amount

of heat energy supplied to the motor $\frac{21,500}{8500} \times \frac{342}{180} = 4.8$ times as much heat must be supplied to the vaporizer in case of ammonia as compared with L.P.G. This must be borne in mind when trying to adapt L.P.G. equipment for use with ammonia.

Liquid ammonia enters at the bottom of coil *C*, and after being heated and to a great extent vaporized, it passes through chimney *H*, where the vaporization becomes complete. Another (optional) strainer, *G*, removes the last particles of foreign matter which may have previously escaped.

Regulators *R2* and *A2* work similarly to those described above. The inlet pressure in *R2* rarely exceeds 300 lb./sq. in. While special steel seats and balls are used for the manufactured gas regulators, composition discs are more suitable for the ammonia regulators.

The driver of the vehicle has the two control knobs *K1* and *K2* handy, and thus has the possibility of regulating at will the proportion of hydrogen and ammonia as well as the total "richness" of the mixture. By closing *K2*, the engine may be started on manufactured gas alone, which also allows a certain warming up of the jacket-water. By gradually opening *K2* and closing *K1* the proper mixture can be easily obtained.

A wide range of gas-ammonia mixtures may be used. Depending on whether gas or ammonia are in any particular case harder to supply, the driver will use a mixture containing more or less of one of the components.

TANKS OR CONTAINERS.

As mentioned above, it has been found more convenient in some cases to replace the permanently fixed tanks by mobile containers. This was the

case with the six buses which started from Namur, since for various reasons a filling station could not be erected there at that time.

Standard ammonia containers (cylinders), which hold approximately 125 lb. each, were used on the Namur buses, two being fixed on each vehicle as shown in Fig. 3. This photograph was taken after the inaugural trip in May 1943. The container valve points downwards, and is connected through a steel "pigtail" with the equipment. It is important that only one container should be used at a time, owing to the possibility of one container emptying into another, and consequent grave danger from overfilling.

Incidentally, the only serious accident which occurred during the two years of utilization of ammonia as motor fuel (though not on the motor buses, which have an accident-free record, but on a private motor-car) was caused by careless overfilling of an ammonia tank. The subsequent heating up and liquid expansion of its contents blew up the tank, causing some material damage, but no casualties.

FILLING STATION.

Most of the ammonia-fuelled motor vehicles, and more particularly the buses starting from Brussels, were equipped with one or two tanks for ammonia which had to be refuelled at a special filling station. For nearly a year this station has been in continuous operation, and since it was probably the first of its kind, a short description of it may be of interest.

This station, designed and built by Etablissements Emeric Kroch in Brussels, is shown schematically on Fig. 4.

The storage tank *I*, fitted with the necessary valves and other appliances, holds the liquid ammonia under pressure. As shown on the flow sheet, the tank itself can be filled from a tank-car or truck *C*.

The amount of ammonia delivered to the customer's tank is measured by volume in the vertical container, *J*, fitted with a gauge glass and a suitable scale. *J* itself is filled from tank *I* by increasing the pressure above the liquid level in *I* by compressed air from the compressor *K*. Similarly, liquid ammonia from *J* flows to the customer's car tank through valve 2 and the hose connection 5, which is clamped on the corresponding car valve.

Venting hose connection 6 and valve 7 lead to tank *W* partly filled with water. With valves 5, 3, and 3¹ closed, the opening of valve 7 and *T* of the corresponding car valve allows for venting off. Due to the very high latent heat value of ammonia, very little venting is required to decrease the temperature in the car tank. A maximum of 1 per cent. of ammonia is lost through venting, but usually the loss is considerably less.

OPERATING RESULTS.

The results obtained during the last eight months of 1943 by the six Namur buses are given in Table II.

The first impression gathered from these figures is the wide discrepancy in the specific consumptions, which vary not only from car to car, but in the case of the same car from month to month.

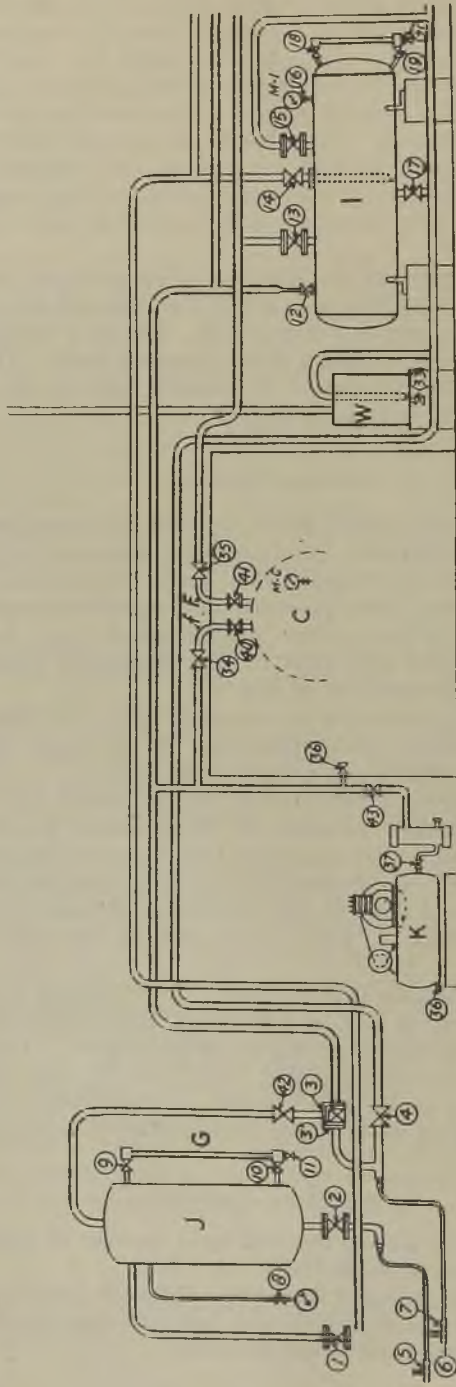


FIG. 4.
FLOW SHEET OF FILLING STATION FOR ANHYDROUS LIQUID AMMONIA.

TABLE II.
Consumption of Gas and Ammonia by Six Buses.

Bus No.	1943. Month of—	Total Run, km.	Gas Consumption, cu. m./100 km.	Ammonia Consumption, kg./100 km.
AB-233	May	471	70,480	36,888
	June	1385	78,639	30,352
	July	1633	66,400	34,900
	August	2642	57,002	42,430
	September	2119	89,098	42,095
	October	2477	77,392	29,229
	November	1677	95,825	29,397
	December	1618	98,269	20,395
AB-235	May	3141	56,980	27,666
	June	2386	65,266	30,490
	July	3580	59,300	29,600
	August	3070	57,329	39,055
	September	3034	65,293	36,025
	October	2186	69,579	40,713
	November	3362	67,102	41,671
	December	2942	75,560	49,048
AB-236	May	739	55,900	46,980
	June	1823	73,560	38,672
	July	1813	63,500	51,000
	August	2681	74,263	26,669
	September	2038	74,288	37,536
	October	1276	69,514	34,952
	November	1331	84,072	27,798
	December	1606	73,038	48,443
AB-240	May	1954	63,050	26,680
	June	1995	64,561	41,127
	July	2442	59,000	37,800
	August	4276	53,840	36,520
	September	1426	68,653	50,881
	October	3166	68,888	40,745
	November	2846	66,936	42,269
	December	1346	74,517	44,948
AB-246	May	1810	71,320	47,924
	June	2192	57,527	33,667
	July	2293	58,400	36,700
	August	3080	65,097	33,019
	September	3573	62,244	27,511
	October	2069	80,521	43,160
	November	2885	70,849	37,227
	December	2545	81,611	45,225
AB-252	May	1635	67,550	31,900
	June	3467	55,494	38,967
	July	2429	53,300	40,300
	August	2339	68,704	46,344
	September	2158	85,403	53,336
	October	2889	66,355	38,311
	November	3147	69,558	34,159
	December	3370	66,646	32,789

There is, of course, one obvious variation—*viz.* the *relative* consumption of gas and of ammonia. As explained in a previous paragraph, the driver of the bus can regulate within a wide margin the gas/ammonia ratio.

However, one would expect that on an *absolute* basis—*i.e.* the total amount of B.T.U. supplied by both the gas and the ammonia—there would be less difference.

There are several reasons to account for this. First of all, the heating value of the coal gas used has been somewhat irregular throughout the period during which the buses have been operated. By contract with the municipality, the gas company had to furnish a gas with approximately 500 B.T.U. heating value. Actually the average figure was between 340 and 380 B.T.U., which in itself is a rather large margin. The reason for these very low figures was the large proportion of blue water gas which was added to the gas produced during the whole duration of the war.

Another factor which can only be mentioned is the lack of accuracy in measuring the amount of coal gas supplied. The figures in column 4 of Table II are taken from the monthly statements of the Gas Company. It should be borne in mind that when retailing compressed gas the quantities sold are computed on the basis of the formula :

$$V = v (P - p),$$

where V represents the amount of the gas delivered,

v the total water capacity of the cylinders fitted on the vehicle,

P the final pressure (in Belgium generally 200 kg./cm.² or about 3000 lb./sq. in.,

and

p the initial or remaining pressure in the cylinders before loading.

The formula does not take into account the gas temperature nor the fact that the Boyle-Mariotte law does not apply to high pressures.

Bearing the above in mind, it may be stated that the following figures can be considered as average actual consumptions per mile :

Coal gas (heating value 360 B.T.U./cu. ft.)	3.4 cu. ft.	= 12.250 B.T.U.
Ammonia (heating value 8060 B.T.U./lb.)	1.0 lb.	= 8.060 B.T.U.

Total = 20.310 B.T.U.

When operated on gas-oil with diesel engines before the change-over the buses averaged 8.4 miles per Imp. gal., or 7.0 miles per U.S. gal. Taking the heating value of gas-oil as of 150,000 B.T.U. per Imp. gal., or 125,000 B.T.U. per U.S. gal., the specific consumption was then 17.900 B.T.U. mile.

The comparison of the two figures shows an increase of 13.5 per cent. in case of gas + ammonia as fuel compared with gas-oil operation. However, it should be borne in mind that the buses were then overloaded by at least 25 per cent., not to mention the additional weight of the gas and ammonia equipment. There is no reason to doubt that on equal terms fairly equivalent results in thermal input could be obtained in case of the two fuels.

After a service of more than 10,000 miles one of the engines has been taken down and carefully examined. No abnormal wear or any trace of corrosion was discovered which could be attributed to the use of ammonia. The lubricating oil consumption remained unchanged.

SUMMARY.

The use of anhydrous ammonia in combination with coal gas as fuel for internal-combustion engines has been tried out on a fairly large scale during one year. When properly installed and when adequate care is taken this motor fuel gives excellent results which compare favourably with those previously obtained with gas-oil. There was no loss of power, no corrosion, and no increase of the lubricating-oil consumption.

Coal gas as the ignition promoter for ammonia may be replaced by other gases (or liquids), and particularly by hydrogen. By doing so the fuel combination ammonia + hydrogen becomes entirely independent of coal. Hydrogen can be obtained from electrolytic cells and nitrogen from air. The necessary energy can be obtained from water turbines.

No comparison of costs has been attempted, as the operations have taken place during a period of price control and all kinds of restrictions, which would not give a true picture of the possibilities of this fuel in normal circumstances.

BULK OIL MEASUREMENT.

By E. STOKOE (Member).

GENERAL DESCRIPTION OF "GAUGING" SYSTEM.

ALTHOUGH meters and other devices are sometimes used for measuring oil in bulk, "gauging" is the usual method when large quantities are being measured. Fundamentally, the tanks used for storing the oil are carefully measured before they are put into service, calibration tables are prepared from these measurements giving the volume or capacity corresponding to various oil heights, and the oil height in the container is measured by suitable instruments. The temperature and specific gravity of the oil are determined, and the measured volume is converted to volume at standard temperature, or to weight by the use of suitable factors. This comparatively simple system enables one to determine the stock in any tank, and quantities received or delivered are measured as differences between stocks before and after the operation.

Difficulties are sometimes encountered when small deliveries are measured by gauging large tanks. Similarly, failure to allow for tank-bottom irregularities, tank-bottom movement, or quantities of oil in pipelines may lead to discrepancy, but the system works well in the majority of cases.

TANK CALIBRATION.

Vertical Cylinders.

Considering first the normal type of vertical cylindrical tank, it is evident that if one has a tank 118 feet in diameter and 35 feet high, application of the usual mensuration formula will show that it has a total capacity of approximately 2,384,000 Imperial gallons, equivalent to about 5676 Imperial gallons per inch. In practice, however, the problem is not quite so simple. Owing to variations in the dimensions of the different tiers of plates, the gallons per inch vary at different heights in the tank, and various internal fittings may affect the gallons per inch over the heights at which they occur. The precautions to be taken and the difficulties involved increase according to the degree of accuracy desired in the completed tank table.

Vertical cylindrical tanks are commonly calibrated by "strapping," which consists in measuring the external circumference by passing a graduated tape around the tank. The process is usually repeated at one or more positions on each tier of plates, so that due allowance may be made between inner and outer tiers. When the circumference of the tank exceeds the length of the calibrating tape, vertical lines are scribed on the tier to be measured and the tier is "strapped" in sections, the sum of the distances between scribed lines on any one tier giving the total tier circumference. The vertical height of each tier is measured, and other measurements are taken which enable allowances to be made for plate thickness,

vertical overlaps, butt straps, and so on, and any other obstructions which may raise the tape from the tank surface. Dimensions are taken of any fittings (such as internal ladders, heating coils, and external manholes), which reduce or increase the tank capacity, together with the vertical heights at which they occur. From these measurements the gross gallons per inch are calculated separately for each tier, and the tank table is built up, usually inch by inch, allowances being made for "dead-wood" and "additions" at the vertical heights over which they occur in the tank. The finished table thus gives directly the net capacity corresponding to each inch of height.

In an alternative system, commonly used in Britain, measurement of external circumference is replaced by measurement of internal diameters. For this purpose, a tape is stretched along a diameter inside the tank, the tension is adjusted to 10 lb. by a rather ingenious automatic device, and the tape reading is noted. The tape is unsupported throughout its length, and allowance for sag is made by the use of catenary tables. A large number of diameters is taken at different positions within each tier, and the gross gallons per inch are calculated from the average tier diameter so obtained. Allowance is made for "dead-wood" and so on, but no allowance is necessary for plate thickness, etc. The standard American method specifies that tanks should be "strapped" full and the increase in capacity due to elastic extension under oil head may be quite appreciable in vertical tanks of large diameter. When necessary measurements by the internal diameter method may be converted to the "full-tank basis" by applying suitable corrections.

Horizontal Cylinders.

Horizontal cylindrical tanks are usually measured by taking a large number of internal diameters and lengths. "Bumped" or hemispherical ends may be dealt with by measuring a series of offsets against a vertical rule or thread, the shape of the end then being determined graphically. The calculation of tables for horizontal cylindrical tanks is somewhat tedious, although much of the work can be reduced by using extended tables and standard curves. The work is further complicated if the tanks are slightly sloping, but slopes up to about 6 inches in 30 ft. may be allowed for in the calculations; tanks with a greater slope are usually more conveniently calibrated by water.

Calibration by Water.

The water-calibration method is also used for small tanks of irregular shape. The tanks are first filled with water, which is then drained off in a carefully calibrated standard measure, the change in height being continually measured throughout the drawing-off process. The method is tedious, great care must be exercised, and allowance must be made when necessary for changes in the temperature of the water during the operation. When calibrating larger containers by water, the measuring liquid is commonly passed into the tank through a barrel filler or from a small and carefully calibrated tank, in order to reduce the time.

Floating Roof, Spheroidal, and Spherical Tanks.

In recent years considerable attention has been devoted to the reduction of evaporation losses from tanks containing volatile products. With this object, tanks of unconventional shape have been developed, particularly in America, and various problems are involved in their calibration and measurement.

The floating-roof type of tank, in which the vapour space above the liquid is largely eliminated, comprises an open-top vertical cylindrical shell, the roof floating upon the surface of the oil with a seal between the roof and the tank sides. A tank table is prepared in the manner previously described for normal vertical tanks, allowance for deadwood which moves with the roof being usually made in the position it occupies when the roof is resting on its supports. When using the tank table, allowance for the volume displaced by the roof is made, when necessary, by other means described later.

Spheroidal tanks were developed to provide means for storing volatile liquids under pressure in order to reduce evaporation losses, the plain spheroidal type being used for small and medium tanks and the noded shape for the larger sizes. The purpose of the noded form is to avoid the excessive height and consequent high ground loading which would be necessary if the plain shape were used for the higher capacities. It should be noted that the oil level does not extend above the highest point of the outside curve of the noded variety. When it is considered that the internal gas pressure tends to inflate the tank, whereas the weight of the liquid contents tends to flatten it, it will be evident that such tanks tend to deform slightly in shape as a result of changes in the pressure and weight of contents. Such tanks were usually calibrated by means of water, but the second edition of A.P.I. Code No. 50 B, in addition to describing the water displacement method, now gives details of a "strapping" method to be used when conditions are favourable.

The spherical tanks used for storing liquids under high pressure are usually constructed so rigidly, that little difficulty is experienced with deformation in service. Methods for calibrating such containers either by water displacement or by "strapping" are given in the A.P.I. Code.

Ships' Tanks.

The calibration by measurement of the cargo tanks of ocean tankers presents various difficulties. The shape of the tanks varies according to changes in the shape of the hull of the ship, and the internal fittings are considerably more complex than those in a land tank. The same degree of accuracy in oil measurement cannot be obtained for various other reasons, and ships' calibration tables are, therefore, usually calculated from the builder's plans, average factors based on previous experience being commonly used to allow for the internal structure.

TANK GAUGING.

Dipping.

In use, the dip tape with dip weight attached is lowered carefully through the oil until the weight just touches the tank bottom. The tape is held

taut while the dip is being taken, but with viscous oils a few seconds must be allowed until the oil has risen to the correct level on the tape. The tape is then rapidly withdrawn and the length of tape which has been wetted with oil is read off. In cases of difficulty, an oil-soluble ullage paste may be smeared on the tape when measuring volatile liquids, but chalk or other porous materials should not be used as the liquid tends to creep.

The flat-bottomed type of weight is popular in Britain, but there is a tendency at the present time towards the use of a semi-pointed type of weight which is found to slip off rivets and other obstructions more easily. A good practice, often followed, is to mark the approximate total depth near to the gauge hatch, and when more than one gauge hatch is fitted to a tank to mark also some means of identification on the tank top.

Gauge Glasses.

Gauge glasses are frequently used in Continental countries for measuring light-petroleum products. They are particularly convenient for measuring volatile products in pressure storage. Unless the density of the oil in the glass is the same as that of the oil in the tank, the gauge reading will obviously not truly represent the oil level inside the tank. When used, therefore, it is important that the glasses should be flushed a sufficient number of times to ensure that the temperature, and consequently the density of the liquid in the glass, is substantially the same as that in the tank.

In cases of difficulty, gauge fittings are sometimes provided with pipes extending about 3 feet into the body of the oil, so that the oil in the glass shall be drawn from the main bulk. Similarly, a series of short glasses is to be preferred, in order to reduce errors due to any differences in the oil density at varying heights below the oil level.

Ullaging.

Ships' oil cargo-tanks contain various obstructions which may interfere with accurate dipping, and they are therefore usually measured by "ullaging," the ullage being the distance from a fixed gauge hatch on the deck down to the oil surface. For example, if a ship's tank has a total height of 38 feet to the top of the gauge hatch, an ullage of 3 feet would correspond to 35 feet depth of oil in the tank.

Small ullages of a few feet are sometimes measured by a wooden ullage stick fitted with a cross-piece, graduations reading downwards from a zero at the cross-piece, but for measuring larger ullages, or for more accurate work, a steel tape and ullage rule are preferred. Ships' calibration tables are usually constructed so as to show volumes present in the tank corresponding to ullages.

Although ullaging is convenient for measuring ships' tanks, conical-bottomed agitators, and so on, shore tanks should preferably be dipped when practicable because there are certain slight errors inherent in the ullaging method which make accurate measurement difficult. For example, even when the ullage reference point is rigidly mounted on the tank top, the total height of shore tanks may change appreciably in hot climates, due to upward thermal expansion of the tank shell. Furthermore, the

actual length of the graduated tape may be affected by the temperature in the tank vapour space. When dipping, the tape is at the same temperature as the oil, and when necessary due allowance can be made in the tank table.

Water Measurement.

Water at the bottom of tanks containing oil is usually measured by applying a special water-finding paste to a dip tape or to a special water-finding rule. The instrument is lowered to the bottom of the tank, and the depth of water is shown by a change in colour of the water-finding paste. When a separate rule is used for water measurement in conjunction with a dip weight, the base of the water-finding rule should preferably have substantially the same shape as that of the dip weight used for measuring the total height.

In cases of difficulty, with heavy oils, water-finding papers may sometimes give better results. The action of the paper is slower than that of the paste, and by suitably adjusting the time of immersion, it is sometimes possible to distinguish between free water and small quantities of water dispersed throughout the oil.

Temperature Measurement.

Accuracy in the measurement of temperature is at least as important as accuracy in dipping or in other parts of the measuring operation, and considerable care may be necessary to determine a reasonably accurate average temperature of oil contained in a large storage tank.

For most purposes the usual type of dip-can provided with a cork may be employed. The can is first flushed with oil so that its temperature is approximately that of the oil in the tank, the cork is inserted, and the can is lowered into the tank. When the desired depth below the oil surface is reached, the cork is sharply jerked out of the can, which then fills with oil from the level selected. The sample so obtained is withdrawn from the tank, a thermometer quickly inserted into the dip-can, the liquid stirred with the thermometer, and the temperature is noted. The number of temperatures to be taken depends on circumstances, but a common procedure is to draw top, middle and bottom samples, averaging the three temperatures so obtained. Sometimes the thermometer is lowered into the tank in the dip-can and left in the oil until the other measurements have been completed.

Sampling.

Samples for specific gravity determination are usually drawn with a dip-can in the normal way, and may conveniently be combined with the measurement of temperature.

In some circumstances, however, special methods may be required, the whole procedure for sampling petroleum products being extensively described in the Institute of Petroleum's "Standard Methods for Testing Petroleum and its Products."

Special Gauging Methods for Floating Roof and Pressure Tankage.

The development of floating-roof and pressure tankage has resulted in certain complications in gauging procedure.

Floating-roof tanks are normally provided with gauge hatches mounted on the roof, and the oil level in the hatch may be measured by dipping or ullaging in the normal manner. When it would be dangerous to descend on to the roof—as, for example, in hot climates—gauging may be carried out from the top of the tank shell, the hatch covers being operated by cords or similar means.

The roof may rise or fall slightly, due to changes in the volume of vapour under the centre deck, but this will not affect the height of the oil level above the tank bottom provided the roof is floating freely. Under these conditions the roof displaces a volume of oil corresponding to its weight, and this weight should be accurately determined before the tank is put into service. The volume or capacity shown by the tank table as corresponding to the oil height in the gauge hatch usually includes the roof displacement, and, when required, correction can be made by deducting the known weight of the roof or the equivalent oil volume from the gross weight or volume calculated from the tank table. When necessary, however, allowance must be made for the estimated weight of any snow or other foreign material which cannot be removed from the roof. If the measurements before and after an oil movement are both taken when the roof is fully floating, the roof displacement may usually be neglected. Difficulties arise if the roof is partly floating and partly resting on its supports, and this condition should therefore be avoided when accurate measurement is desired. Tank tables for floating-roof tanks should preferably show the roof weight, the oil depth at which oil first reaches the lowest part of the roof, and the oil depth when the roof just floats clear of its supports, the latter for various oil densities.

Closed vapour-tight tanks are sometimes gauged by means of a dip-pipe which is attached to the roof, and is free to move up and down in accordance with roof flexure. Dips are taken through the dip-pipe in the normal way, but since the oil in the dip-pipe is open to the atmosphere, whilst the vapour space inside the tank is closed, the oil depth in the gauging-pipe will be higher or lower than that in the tank when the pressure in the vapour space is higher or lower than that of the atmosphere. A manometer, usually filled with kerosine, is therefore mounted on the roof and connected with the vapour space. The measured dip is then corrected according to the manometer reading. A difficulty with this system is the tendency of the oil to surge in the dip-pipe.

Alternatively, vapour-tight tanks including spheroids may be gauged by means of a vapour-tight dip-hatch assembly. This comprises a vapour-tight "look-box," which is fastened to the top of the dip-hatch. A gate-valve is installed between the "look-box" and the tank, so that when the valve is shut, the apparatus may be opened without loss of vapour, and the dip-weight or other instrument may be attached to a gauge-tape mounted inside the apparatus. The "look-box" is then closed, the gate-valve is opened, and gauging is performed by operating the gauge-tape by means of an external handle. The apparatus is somewhat inconvenient, and vapour-tight tanks are frequently measured by means of gauge-glasses. For measuring spherical tanks, only gauge-glasses are recommended, owing to the high pressures frequently encountered.

METHODS OF CALCULATION.

Form of Calibration Table.

Tank tables may be compiled in various ways. In England the usual system is to give the total gallons corresponding to each inch of oil height, separate interpolation being necessary for calculating decimals or fractions of an inch. The work can be considerably reduced by providing a proportional parts table showing the average gallonage corresponding to each fraction of an inch, which is then used on any oil height in the tank. The loss in accuracy is usually well within the experimental error, and considerable savings in time should be effected. The American Petroleum Institute Code No. 25 specifies that tables should be prepared in eighths of an inch, and that dips should also be taken in the same units. An extended table of this kind, in eighths or tenths, avoids the necessity for any calculation, but will normally run into several pages. When a large number of tanks are constructed from the same drawings, a careful examination of the measurements obtained during calibration will sometimes indicate that one table can be prepared covering all tanks in a batch without departing from the desired degree of accuracy. If this is permitted by official regulations, the reduction in complication and the saving in time will be obvious.

British System.

In the British system, volumes in Imperial gallons obtained from the calibration tables are usually multiplied by ten times the specific gravity of the oil at the temperature of measurement, the pounds so obtained then being converted into tons. When volume at 60° F. is required, the pounds are divided by ten times the specific gravity at 60° F., thus giving the corresponding volume. The British system is based on the principle that ten times the specific gravity 60° F./60° F. (in vacuo) gives pounds per gallon in air, and whilst this is not strictly true, the error for normal petroleum products will not exceed 4 tons in 10,000 tons. The calculated weights are slightly low for high specific gravity oils and vice versa, and are very nearly correct when the specific gravity is approximately 0.870.

American System.

In the American system the gallons or barrels at temperature of measurement are usually converted to 60° F. by means of volume conversion factors obtained from standard tables. Density is measured in an arbitrary scale of A.P.I. degrees, and other tables give pounds per American gallon or barrel corresponding to various A.P.I. gravities. Volume at 60° F. multiplied by the appropriate factor gives true pounds in air, all necessary buoyancy corrections being included in the standard factors. Care should be taken, however, to use appropriate factors when measuring benzol mixtures, waxy oils or other materials markedly different in specific gravity/thermal expansion characteristics from those on which the standard tables are based.

Metric System.

In the metric system the measured volume in litres or cubic metres is usually multiplied by the density in grammes per millilitre at temperature

of measurement, and owing to the way in which the litre is defined, this procedure gives kilograms or metric tons in vacuo. When these kilograms are converted to English tons by dividing by the usual conversion factor of 1.016, the result will be English tons in vacuo, and not English tons in air, the difference amounting to about 17 tons on a cargo of 10,000 tons of motor spirit. For accurate conversion between metric and English tons, therefore, a suitable table should be employed in order to allow for the necessary buoyancy corrections.

In general, oil calculations and conversions between different systems have been considerably facilitated by a book of standard factors produced by the I.P. some years ago. A further book is now in course of preparation, which will incorporate corrections for the various slight inaccuracies just mentioned, and which should go far to unify the various systems at present unfortunately in use.

SOME EXAMPLES OF GAUGING PROBLEMS.

Despite accuracy in tank calibration, tank gauging, and office calculations, discrepancies may still arise when measuring stocks, or when oil is moved from one tank to another, and it is convenient to have some system by which other possible causes of error may be examined in turn.

“ Layered ” Tanks.

If the quantities being compared are available in units of both weight and volume, an unusual difference between the two percentage losses would indicate some discrepancy in specific gravity measurement. Discrepancies of this kind often arise if the tank contents are not homogeneous, and it has been suggested that hydrostatic gauges might be used to eliminate errors from this source. The principle of the gauge is to balance the oil column in the tank against a column of mercury in the instrument, the corresponding weight being calculated from appropriate tank tables without reference to the specific gravity of the oil.

I believe that a special gauge of this type has been successfully employed by the Iraq Petroleum Company for measurement in vertical shore tanks. Nevertheless considerable care should be exercised in the design and use of hydrostatic gauges for oil measurement, as various complications may arise, particularly if used for tanks of varying horizontal cross-section.

Bottom Irregularity.

The bottoms of tanks containing light oils, such as gasoline, kerosine, etc., are frequently covered with water, and provided the bottom is completely covered with water no allowance need be made for bottom irregularities. Difficulties arise, however, when water bottoms are not carried. In case of need, bottom allowances may be estimated by emptying the tank completely and then running in water or oil from a calibrated tank until the bottom is completely covered, measuring the quantity so run in by dips taken in the calibrated tank. Even when bottom allowances are available, however, more accurate results will usually be obtained by conducting the operations so that the tank bottom is always completely covered with oil before and after a movement.

Bottom Movement.

When the bottom plates move under varying heads of oil, or with changes in the condition of the sub-soil, the position becomes a little more complicated. When bottom movement is suspected, it will usually be found better to take dips whenever practicable, and errors may be reduced by increasing the number of dip hatches and averaging the resulting dips. In cases of difficulty, tanks have been provided with as many as nine dip-holes, largely with the object of reducing errors due to bottom movement.

Installation Pipelines.

Quantities of oil contained in pipelines are a common source of discrepancies in measurement. Difficulties may be reduced if it is possible to provide a regular and satisfactory slope when the lines are first installed. Similarly, air-vents and drain-cocks installed at high and low points assist in verifying whether the line is full or empty. When dealing with tankers, pipelines are sometimes filled before measurement, by pumping down to the loading berth via one pipeline and returning the oil to the tank via another line, so as to displace all air and water before gauging. Similarly, after discharge the pipeline would normally be left only partly full of oil, and common practice is to arrange for the ship to pump water through the line in order to displace the oil into the shore tank.

These precautions cannot be taken with heated heavy oils, and compressed air is usually employed for line clearance, common practice being to employ some standard time and procedure in order that the quantity of oil left in a given pipeline may be as near as practicable the same before and after an operation.

Long Distance Pipelines.

Long pipelines passing over open country give rise to new problems which have not yet been completely solved. When the rate of pumping is high enough to give adequate turbulence, different grades may be separated by a plug of water. Similarly, a small quantity of dye may be put into the pipeline at the pumping end, flow being diverted from one tank to another when the dyed material arrives at the receiving end. Difficulties with long pipelines may be reduced by the use of suitably installed positive displacement meters.

When displacement meters are used for ordinary work in conditions where air may be entrained with the product being measured, an air-eliminating device should be installed on the inlet side, as, otherwise, air passing through the meter would be registered as oil. For accurate work a recording thermometer is also installed in the line close to the meter, so that the measured volume may be corrected to standard temperature. Sometimes automatic sampling devices are used to obtain an average sample, and thus the mean density of the liquid passed through the meter.

THE INSTITUTE OF PETROLEUM.

STANLOW BRANCH.

A MEETING of the Stanlow Branch of the Institute was held on Wednesday, 18th October, 1944, when Mr. J. S. PARKER was in the Chair.

A paper on "Bulk Oil Measurement" was presented by Mr. E. Stokoe. (See pp. 224-32.)

DISCUSSION.

The Chairman, Mr. J. S. PARKER, opening the discussion, said that Mr. Stokoe had covered the subject in an interesting and informative manner. One thing which struck him was that although process plant had been developed during the last twenty years to a major extent, the methods of calibration and measurement had remained more or less static. There were two possible explanations. Either (1) the accuracy of these original methods had been sufficient and, consequently, had provided little room for improvement or, (2) there had been little apparent profit to be derived from the capital outlay required to effect improvement. The answer was probably midway between these two explanations.

He was pleased to note the reference to the order of accuracy obtainable, as in his experience he had noted considerable accuracy abuse, mainly since the introduction of calculating machines. Quantities were often reported to four or five places of decimals, the figures after the decimal point being often meaningless from the practical angle.

In the days immediately following his scholastic training he had been dissatisfied with, for example, the rough-and-ready method in use for taking tank temperatures, and had wondered why something along the lines of a maximum/minimum thermometer had not been developed for this purpose. There was little doubt that out of the tremendous war advances in electrical recording, new fields of measurement possibilities had been opened up which might eventually revolutionize the present methods of tank measurement.

He had noted the tendency of refineries to treat calibration tables as accurate even if they had been prepared twenty or more years previously. In the interim the tanks, through poor foundations or other causes, might have assumed shapes not as originally designed. The tanks might be renovated, but seldom, in his experience, were they recalibrated.

MR. STOKOE, referring to two of the points raised by the Chairman, said that if a cylindrical tank originally vertical became tilted, the shape of the oil surface was no longer a circle, but an ellipse. In practice, however, the resulting change in area was extremely small, and before the tilt became sufficient to necessitate correction of the tank table it would usually be found desirable for other reasons to relevel the tank. As regards maximum and minimum thermometers, it was the average temperature of the tank contents which was required for measurement purposes, and this was not necessarily the mean of the maximum and minimum.

MR. PETER KERR asked if a description could be given of the procedure for calibrating a tank by water filling or emptying, with particular reference to the difficulties encountered and the method of overcoming them.

MR. STOKOE replied that one of the points to be observed carefully was the water temperature. This should be checked at intervals as the work proceeded, and, when necessary, due correction should be made. When work was suspended overnight or for a period the water level should be carefully measured and recorded. Before recommencing calibration the level should again be measured, and if necessary should be adjusted so that calibration was continued from the previous finishing datum level.

Before recalibrating a tank which had been in use, care should be taken in cleaning, so that no oil floated on top of the water during calibration. When copper standard measures were used for calibrating small tanks, they should be clean and should be carefully emptied after each measurement. Care should be taken not to dent or deform the measure by rough handling.

MR. A. CLUER stated that there could be no guarantee when the "strapping" method was used that the tank shell was the true circle on which the subsequent calculations were based. In his opinion the internal-diameter measurement method was preferable as it disclosed any deviation from the true circle.

MR. STOKOE replied that so far as he was aware the results given by the two methods were in very close agreement. He agreed that tanks might not be truly circular, but the change in area resulting from slight ellipticity was surprisingly small. The "strapping" method was very widely used, and the American system of "strapping" when the tank was full should tend to reduce errors from this source.

MR. CLUER asked whether any difficulty had been experienced with water settling on top of oils with extremely high specific gravities, and if so, how was the quantity of such water measured.

MR. STOKOE replied that although an ordinary water-finder provided with water-finding paste could be used by suspending it in the oil, it was usually difficult to obtain a clear reading. Slightly better results could sometimes be obtained by using water-finding paper and varying the time of immersion. Similar difficulties arose when measuring creosote, and he believed it was fairly common practice in such cases to draw a series of samples—for example, every 3 inches—for water content estimation.

MR. H. E. F. PRACY stated that some years previously he had made calculations to estimate the error introduced when a tank shell departed from the vertical through subsiding foundations, with the consequent alteration of the tank section from a circle to an ellipse. He found that a subsidence of 1 foot on one side of a tank about 100 feet in diameter produced an extremely small change in cross-sectional area.

With reference to the estimation of water quantities, the usual method was to sample top, middle, and bottom; but this method was not infallible, and did not always truly represent the condition of the tank contents. On occasions, "layering" had led to deliveries of material which was off-grade on water content.

MR. J. K. TURNER asked if the mechanical friction inherent in floating roofs would result in false readings being obtained.

MR. STOKOE replied that this was a possible source of error, the effect being influenced by the rate of pumping, the conditions prevailing when pumping stopped, and the construction of the tank and of the roof shoe. The error should not be very serious.

MR. TURNER said that he had seen a direct reading meter used to measure deliveries by road wagons at a filling station, and asked why such meters were not more generally used in refineries?

MR. STOKOE replied that there were various types of displacement meter in general use for the purpose indicated, and these appeared to give very satisfactory service. In refineries, however, measurement problems were more complex, and although meters were very convenient for many purposes, it appeared that the reason they were not at present used in refineries to the extent envisaged was largely a question of cost.

MR. V. BISKE asked if the capillary effect when dipping through gauging tubes in pressure tanks required correction, and if variations in capillary effect due to wetting of the tube would cause errors.

MR. STOKOE replied that the dip-pipe was usually of sufficient diameter to ensure

that the capillary effect was negligible, and that the principal difficulty in gauging these tanks appeared to arise from surging in the dip-pipe.

MR. A. N. HOLMES asked why electrical devices were not commonly used to determine oil-dips? Was it a question of cost, safety or accuracy?

MR. STOKOE stated that the question was understood to refer to float operated gauges. There was a device on the market comprising a float travelling up and down guide-wires inside the tank, the float reading being transmitted to a distance electrically. Although such a system was doubtless very convenient to use, his own preference was for the normal form of gauging, as float-gauges had been known to stick, and were usually accepted as approximate indicators only.

MR. R. MAGUINNESS asked if there was any objection to the mercury-type hydrostatic gauge of which the "Pneumercator" was a well-known example.

MR. STOKOE replied that in principle the system comprised the measurement of a mercury column which was arranged to balance the oil column in the tank. Owing to the high density of mercury, 1/10 inch of oil might correspond to as little as 1/200 inch on the gauge. Corrections might be required to allow for the temperature of the mercury column and for possible differences between the pressure in the tank vapour space and that of the atmosphere. Satisfactory results could be obtained, but instruments should be carefully designed, installed, and used, and all necessary corrections should be applied when calculating the oil weight or volume.

MR. MAGUINNESS then asked if it was necessary to use mercury. Could not a pressure gauge be used which would give finer readings than could be obtained with mercury?

MR. STOKOE replied that other types of hydrostatic gauge were available employing a pressure gauge as the measuring instrument in place of a mercury column. Such gauges could undoubtedly be constructed to give the finer graduations suggested, but the actual accuracy of oil measurement would depend on the accuracy obtainable under working conditions from the various types of hydrostatic gauge.

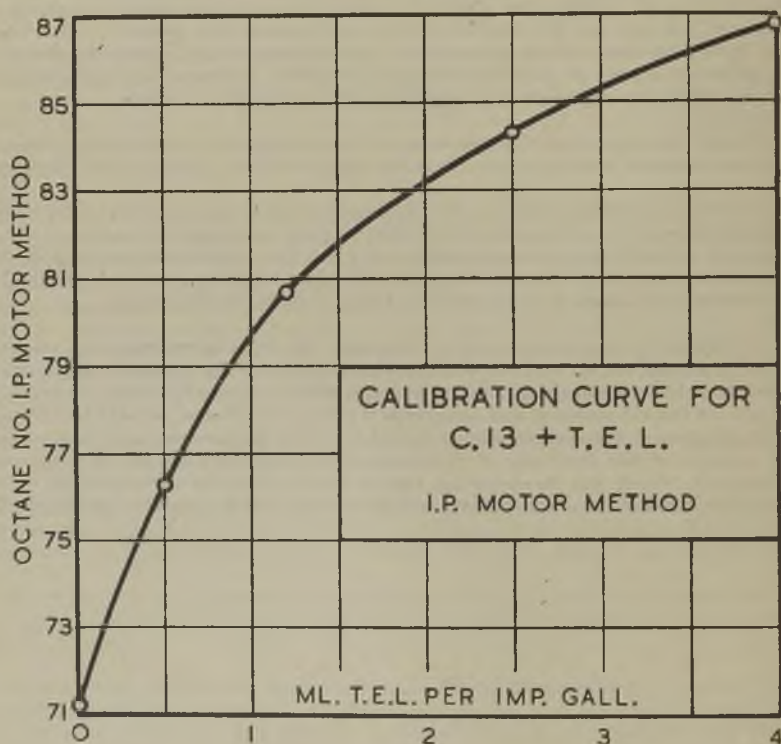
MR. H. HYAMS, in proposing a vote of thanks to Mr. Stokoe, reviewed the progress made in oil measurement, and emphasized that in spite of the apparent static state of calibration and measurement, improvements were continually being sought. It said much for the old methods and apparatus if they had remained in satisfactory use for so many years. He was pleased to record that Mr. Stokoe was a prominent and active member of the Institute of Petroleum Sub-Committee on Oil Measurement and Sampling, which was co-operating very actively with the corresponding Committee of the A.S.T.M. on standardization of oil-measurement apparatus and methods.

CALIBRATION OF C.F.R. REFERENCE FUELS

*Calibration of Secondary Reference Fuel C.13 + T.E.L. by C.F.R. Motor Method I.P. 44/45 (T).**

By SUB-COMMITTEE No. 5 (ENGINE TESTS) OF STANDARDIZATION COMMITTEE.

THE calibration of secondary reference fuel C.13 plus increments of T.E.L. has been made on fourteen engines against blends of reference fuels F.5



and C.13 clear. A curve of C.13 + T.E.L. versus Octane Number (see figure) has been obtained from this data, using the calibration of F.5 in C.13 prepared by the Motor Fuels Division of the C.F.R. Committee. The calibration is presented in the accompanying table for laboratory use.

* Paper received 11th April, 1945.

Octane Number Calibration Table for I.P. Motor Method C.13 + T.E.L.
(ml. per Imp. gal.).

T.E.L.	Oct. No.	T.E.L.	Oct. No.	T.E.L.	Oct. No.	T.E.L.	Oct. No.
0·00	71·2	0·90	79·2	1·80	82·6	2·65	84·6
0·05	71·8	0·95	79·5	1·85	82·8	2·70	84·7
0·10	72·4	1·00	79·8	1·90	82·9	2·75	84·8
0·15	72·9	1·05	80·1	1·95	83·1	2·80	84·9
0·20	73·5	1·10	80·3	2·00	83·2	2·85	85·0
0·25	74·0	1·15	80·5	2·05	83·4	2·90	85·1
0·30	74·5	1·20	80·7	2·10	83·5	3·00	85·2
0·35	75·0	1·25	80·9	2·15	83·6	3·10	85·3
0·40	75·5	1·30	81·1	2·20	83·7	3·20	85·5
0·45	75·9	1·35	81·3	2·25	83·8	3·30	85·7
0·50	76·3	1·40	81·5	2·30	83·9	3·40	85·9
0·55	76·7	1·45	81·6	2·35	84·0	3·50	86·0
0·60	77·1	1·50	81·8	2·40	84·1	3·60	86·2
0·65	77·5	1·55	81·9	2·45	84·2	3·70	86·4
0·70	77·9	1·60	82·1	2·50	84·3	3·80	86·6
0·75	78·2	1·65	82·2	2·55	84·4	3·90	86·7
0·80	78·6	1·70	82·4	2·60	84·5	4·00	86·8
0·85	78·9	1·75	82·5				

A satisfactory feature of the average data obtained is that two points supplied by the Motor Fuels Division of the C.F.R. Committee for check on engine condition—viz., 80·0 octane number = 0·87 ml. T.E.L./U.S. gal. in C.13 and 88·0 octane number = 3·8 ml. T.E.L./U.S. gal. in C.13—are almost coincident with the curve established.

