THE ISOTHERMAL AND ADIABATIC COMPRESSIBILITIES OF OIL.

By A. Cameron, Ph.D.

Summary.

The work published on both the isothermal and adiabatic compressibilities of oils is considered and average curves are given for both compressibilities over a range of temperatures.   The ratio isothermal/adiabatic compressibility equals gamma the ratio of the specific heats, which is shown to be 1·135 for mineral oils.

Introduction.

The compressibility of oils is a subject that is becoming of increasing interest to industry as working pressures become higher and higher. High-pressure oil hydraulic systems and direct-injection heavy oil engines are the two main types of equipment where a knowledge of it is necessary.

In the first case the compressibility is mainly isothermal, and in the other it is adiabatic.   It does not appear to be generally appreciated that the values of these two quantities are different though they are related by γ, the ratio of the specific heats.

It was thought profitable to collect all the data published on this subject, as these are rather scattered.   It is hoped that the references which have been found and are given here are substantially complete.

Published Data.

(i) *Isothermal Compressibility.*

Almost all the work which is published on the compressibility of oils is concerned with the isothermal compressibility, and generally deals with pressures up to 1500 atmospheres.

All the high-pressure isothermal compressibilities have been correlated in a paper by Dow and Fink,[1] to which reference should be made.   These authors have shown that, within the experimental error and the experimental pressure range, all the results can be fitted on to a single curve. This curve can be approximately represented by an equation of the type

$$\rho = \rho_0(1 + \alpha p - \beta p^2)_t,$$

where ρ = density of the oil at pressure p and temperature t,

ρ_0 = density of the oil at atmospheric pressure and temperature t,

α and β are constants for the given temperature t.

The compressibility can be obtained from this equation by means of the relation $\dfrac{d(\rho/\rho_0)}{dp} \times \left(\dfrac{\rho}{\rho_0}\right)^2$, whence it can be seen that at atmospheric pressure the compressibility equals α.   The quadratic equation for ρ/ρ_0 is satisfactory in the medium and high-pressure range, but, as Dow and Fink indicate, at low pressures the equation is only approximate, and so the

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first differential is somewhat uncertain. The atmospheric compressibility, therefore, when derived from the equation, is not very accurate.

Very accurate work was carried out by Jessup [2] of the American Bureau of Standards, using a glass apparatus and working at pressures up to 50 kg./sq. cm. and temperatures to 300° C. He studied three classes of oil, four gas oils, two spindle oils, and four machine oils. The viscosities
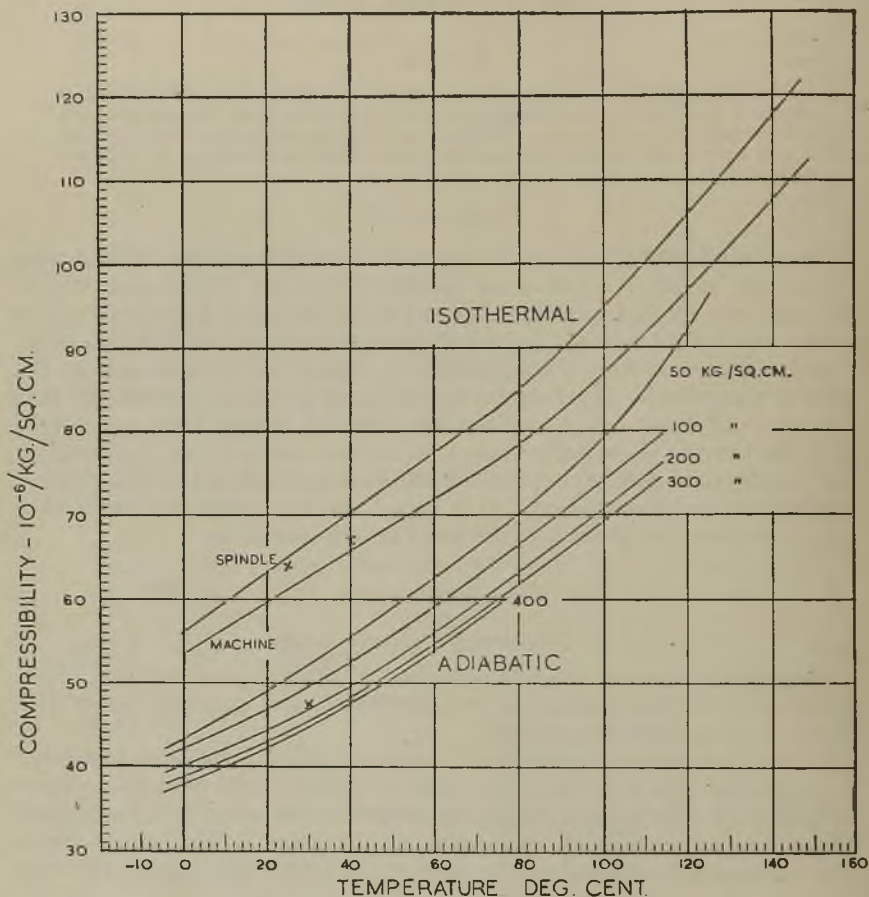

Fig. 1.

of the gas oils were about 5 centistokes, the two spindle oils had the same viscosity, 31·7 cs., and the machine oils averaged 75 cs. These were all taken at 100° F.

Each group was found to have about the same compressibility, which increased with increasing temperature. The thicker oils were found to have slightly smaller compressibilities than the thinner ones, but the differences were not very large. He found the compressibility of the two heavier oils was sensibly constant over the pressure range 0–50 kg./sq. cm. up to 100° C.

The mean values of the compressibilities of the spindle and machine oils at various temperatures up to 150° C. are plotted in Fig. 1 and are marked " Isothermal." The two crosses, at 25° and 40° C., are mean values worked out from the results of Dow [3] and Dow and Fenske [4] for the range 0–50 kg./sq. cm. From the isothermal curves in Fig. 1 it is possible to read off the compressibility at any temperature up to 150° C. For higher temperatures Jessup's original work must be consulted.

(ii) *Adiabatic Compressibility.*

Parsons and Cook [5] studied both the adiabatic and isothermal compressibilities of a number of liquids, and among them was a cylinder oil. The apparatus used was a large direct plunger machine, and the authors give a rather elegant method for finding the change in volume of the steel container with pressure. The interpretation of their results is not at all certain. They used a large volume of liquid—2000 c.c.—and apparently added a dead volume correction of 36·6 c.c. on to the mean volume–pressure curve (curve 2 minus the mean of curve 1 on p. 336 gives a constant difference of 36·6 c.c.). Using this dead volume correction the volume pressure curve for a " Cylinder Oil " can be constructed from their curve 4. The value of the compressibility is, however, very much lower than that found by any other investigator. Parsons and Cook give a very interesting calculation for the change of temperature on adiabatic compression or expansion, and this will be discussed later in the theoretical section.

In 1927 D. H. Alexander [6] constructed a simple direct plunger apparatus for measuring the compressibility of a fuel oil on which he was then working. The change in volume of the vessel was calculated theoretically, and he obtained a value of $3\cdot30 \times 10^{-6}$/lb./sq. in. at 5018 lb./sq. in. This corresponds to an adiabatic compressibility of $47\cdot0 \times 10^{-6}$/kg./sq. cm. at 350 kg./sq. cm. The temperature was not stated, but a value of 60–70° F. will probably not be far out. No account was taken of leakage, which was, therefore, presumably considered to have been small.

In 1933 G. Hamabe and F. Nagao [7] published an extended investigation on nine fuel oils, up to 500 kg./sq. cm., and at temperatures from $-4°$ to 100° C. and in one case up to 137° C. The apparatus used was modified from the design given by Alexander. Various refinements were added, such as two thermocouples inserted in the oil and means for removing the air. The text is in Japanese, so it is probably best to give a fairly extended description of it in order that the original can be followed if necessary.

The volume of oil used was 503 c.c., and Parsons and Cook's method for estimating ΔR, the change in volume of the container under pressure, was employed. In this case steel balls were used instead of a steel cylinder, and the curve of ΔR against pressure is plotted in Fig. 3 of the paper. The change in volume of the cylinder with pressure corresponded to about 10 per cent. of the volume change, due to the compression of the oil at any pressure.

They accounted for the leakage L, which was stated to be very small, by assuming that if the plunger descended a distance h_1 on loading and

came back a smaller distance h_2 on unloading, the true distance h would be $(h_1 + h_2)/2$, it being assumed the time of loading equalled the time of unloading. The change in volume Δv of the steel balls, under pressure, was calculated from their atmospheric volume v by the equation

$$\Delta v = 3 \frac{m-2}{m} \frac{P}{E}$$

where
$$
\begin{aligned}
m &= 1/\text{Poisson's ratio}, \\
P &= \text{pressure}, \\
E &= \text{Young's modulus}.
\end{aligned}
$$

They also list the names and characteristics of the nine oils used (Table I of their paper). Only three can be identified, and these are Borneo and Sarawak fuel oils. The densities are given at 18° C. and are rather high, varying from 0·893 to 0·940. The Engler viscosities listed at 20° C. are normal for fuel oils—i.e., between $1\frac{1}{2}°$ and 10°. Finally, the carbon, hydrogen and sulphur analyses are tabulated.

Their results are plotted in graphical form, compressibility against pressure at about six different temperatures for each oil which were apparently arbitrarily chosen. As the compressibilities do not materially change with the various oils, they have been re-plotted here in the form of average compressibility–temperature curves at different pressures for all nine oils (Fig. 1) and are marked " Adiabatic." The pressures (in kg./sq. cm.) at which the compressibilities were measured are noted on each curve. Alexander's result is given as a cross. Hamabe and Nagao state that for one of the oils investigated by them (Miri fuel oil) the isothermal compressibility is 15 per cent. greater than the adiabatic, at 30° C. They do not definitely state if this was a calculated or measured result, but it is probably measured, as they do not give any theoretical discussion at all. Now, the ratio isothermal/adiabatic compressibility equals γ, the ratio of the specific heats, and this can be determined. A specimen calculation gives γ equal to 1·135, so that theoretically the isothermal should be 13·5 per cent. greater than the adiabatic. The curves in Fig. 1 show that the ratio is 1·20—1·28 at 20° C. and 1·15—1·23 at 60° C., which is somewhat larger than theory. As the results are from quite different workers and with different oils, the difference is perhaps no greater than would be expected. Hamabe and Nagao's own result for Miri fuel oil fits in well.

These authors give data for the adiabatic heating of oil on compression. Their results, plotted in Fig. 2 of their paper, show a constant rate of heating of 1·0° C. for every 100 kg./sq. cm. up to 450 kg./sq. cm. It will be shown in the theoretical section below that this figure is very close to the theoretical value. The method of working out the compressibilities of oils at high pressures used by Hamabe and Nagao may be criticized. They calculate the compressibility at a pressure P from the relation

$$-\frac{1}{V_1} \left(\frac{V_1 - V}{P} \right)_t$$

where
$$
\begin{aligned}
V_1 &= \text{volume of oil at pressure} = 0, \\
V &= \quad ,, \qquad ,, \qquad\quad ,, \quad = P,
\end{aligned}
$$

whereas the compressibility K at constant temperature is defined as the decrease of unit volume per unit increase of pressure—*i.e.*,

$$-\frac{1}{V_1}\left(\frac{\partial V}{\partial P}\right)_t.$$

At low pressures this does not make any appreciable difference.

The adiabatic compressibility can also be measured from the speed of sound in the medium. This was done by Suge [8] using sound of a very high frequency, 4940 kilocycles/sec. The values he obtained were higher than the other adiabatic figures. Also, he found that in general fatty oils had a compressibility 10 per cent. less than mineral oils. The figures he gives are $(65 \cdot 5 \pm 2) \times 16^{-6}$/kg./sq. cm. for mineral oils and $(60 \cdot 5 \pm 1) \times 10^{-6}$/kg./sq. cm. for fatty oils. It is also possible to calculate the ratio of the specific heats of an oil from the isothermal compressibility or the velocity of sound, knowing the density and thermal expansion. Suge gives data for the speed of sound in the paper already mentioned, and the density of his oils are noted in a previous paper.[9]

We see, then, that from the data given in Fig. 1 it is possible to read off the isothermal or adiabatic compressibility over a range of temperatures. For the isothermal compressibility only the low pressure figures are given—*i.e.*, up to 50 kg./sq. cm. (or 711 lb./sq. in.), as the high-pressure compressibilities are given by Dow and Fink.[1] The experimental range considered by these authors is : up to 1500 kg./sq. cm. at 25° C., to 1000 kg./sq. cm. at 40° C., and to 4000 kg./sq. cm. at 75° C.

<div align="center">THEORETICAL.</div>

(1) *Adiabatic Heating.*

Parsons and Cook have worked out a relation for $\left(\dfrac{\partial T}{\partial p}\right)_\phi$, the adiabatic heating of a liquid with increase of pressure, in terms of the coefficient of thermal expansion and the specific heat at constant pressure.

This relation is given as :—

$$\left(\frac{\partial T}{\partial p}\right)_\phi = \frac{TVA}{JC_p}$$

where T = absolute temperature,
  V = volume per unit mass,
  A = coeff. of thermal expansion at constant pressure,
  C_p = specific heat at constant pressure,
  J = mechanical equivalent of heat.

A and C_p are known for oils at atmospheric pressures only, and so this relation is somewhat restricted in its use.

Parsons and Cook tested this relation for water and obtained satisfactory agreement. Using Hamabe and Nagao's results it is possible to test it with oil. Their experimental result for $\left(\dfrac{\partial T}{\partial p}\right)_\phi$ was 0·010° C./kg./sq. cm. at 28° C.

Now, taking T as 301° abs.,

$$A = 0.0007/° \text{ C.},$$
$$C_p = 0.45 \text{ for mineral oils,}$$
$$\rho_0 = 0.9, \text{ whence } V = 1.11 \times \text{ unit mass.}$$

$\left(\dfrac{\partial T}{\partial p}\right)_\phi = 0.012°$ C./kg./sq. cm., which agrees satisfactorily with the experimental result.

Hyde [10] found that A was the same for fatty and mineral oils, but C_p was 10 per cent. larger for fatty oils, and so for these oils the value of $\left(\dfrac{\partial T}{\partial p}\right)_\phi$ will be 10 per cent. smaller than for mineral oils.

(2) *Ratio of Specific Heats.*

Now it is possible to find γ the ratio of the specific heats from the isothermal compressibility or the velocity of sound in oil, and C_p, ρ_0 and A.

A relation for $C_p - C_v$ the difference of the specific heats is given by Birtwistle,[11] p. 73 :—

$$C_p - C_v = \frac{TVA^2}{KJ}$$

whence
$$1 - \gamma = \frac{TVA^2}{KJC_p} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(i)}$$

where C_p and C_v = specific heats at constant pressure and volume respectively,

K = isothermal compressibility.

Now U, the velocity of sound in a medium, is given by

$$U^2 = \frac{\gamma}{K\rho_0}$$

As we are considering unit mass $V\rho_0 = 1$, and thus

$$\gamma(\gamma - 1) = \frac{TA^2U^2}{C_p J} \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(ii)}$$

Thus γ can be obtained from equation (i) or (ii). Considering equation (i) first, and taking K equal to $- 64.0 \times 10^{-6}$ cm.²/kg. at 25° C. (negative sign as $\dfrac{dv}{dp}$ is negative) and $A = 0.0007/°$ C.; if the density of the oil $= 0.9$, so V, the volume per unit mass, $= 1.11$ c.c. and $C_p = 0.45$ cal./gram, then :—

$$1 - \gamma = - 0.1346, \text{ and } \gamma = 1.1346.$$

Now C_p for fatty oils is 10 per cent. larger than for mineral oils, so γ will be 1.123.

This value of γ should check with the value of γ obtained from equation (ii), using the velocity of sound. Suge [8] gives a value for the velocity of sound in liquid paraffin. From his earlier paper [9] the density of liquid paraffin is 0.88 and the temperature at which his measurements

were carried out is 18° C. It is necessary to assume the results of the earlier paper can be applied to the later one for the density and temperature of the oil.

A will be taken as $0 \cdot 00070/°$ C. and C_p as $0 \cdot 45$. This gives a value of γ equal to $1 \cdot 121$. This value will not be so accurate as the other value obtained from the compressibility.

Now γ also equals the ratio of the isothermal/adiabatic compressibility (Birtwistle, p. 73), and this provides another experimental method by which it can be obtained.

ACKNOWLEDGMENTS.

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SPECTROSCOPIC ANALYSIS.

APPLICATION OF THE ULTRA-VIOLET ABSORPTION METHOD TO THE ANALYSIS OF MIXTURES CONTAINING AROMATIC HYDROCARBONS.

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SUMMARY.

The principles, apparatus, and technique involved in the quantitative analysis of 2-, 3-, and 4-component mixtures of aromatic hydrocarbons by the ultra-violet absorption method are discussed in detail. A method has been evolved which is not dependent on comparison between the unknown mixture and synthetic blends.

The mixtures dealt with are : (*a*) benzene–toluene, (*b*) the C_8 aromatics ethylbenzene, *ortho*-, *meta*-, and *para*-xylene, (*c*) *ortho*-xylene and *iso*propylbenzene.

The accuracy attainable is calculated, and is illustrated by the analysis of a number of synthetic mixtures. The dependence of the error on the composition of the mixture is graphically illustrated, and the maximum possible error in this method of analysis is discussed.

THE need of the petroleum industry for more sensitive methods of analytical control has been explained in a previous paper,† in which infrared absorption methods of analysis have been described. These methods are applicable to a wide range of problems and, indeed, are so sensitive that care is necessary to avoid over-complexity in the mixture to be analysed. At present, however, the quantitative application of the infra-red method is limited by the number of pure hydrocarbons which have been examined, mixtures of materials having boiling points not exceeding 120° C. being the present limit. Many industrially valuable hydrocarbons have higher boiling points than this, notable among these being the aromatics. A method of simplifying the analytical problem by using the ultra-violet region of the spectrum has been evolved.

The principles involved are relatively simple, and may be summarized as follows.

The aromatic hydrocarbons, unlike the paraffins and naphthenes with which they are associated in straight-run benzines, naphthas, and saturated synthetic materials, absorb ultra-violet radiation in the wave-length range 2400–2900 Å. (1 Å. = 10^{-8} cm.). The amount of radiation absorbed is not constant over the range of wave-lengths, so that a curve of radiation absorbed versus wave-length shows a series of peaks and valleys. Among the lower-boiling members of the aromatic series these curves are different for each hydrocarbon. Thus, for example, benzene gives a different curve from that of toluene, and *p*-xylene a different curve from that of *o*-xylene. These differences form the basis of the analytical method described.

One method of analysis might be based on a comparison of the absorption due to the sample with that due to mixtures of known composition. This, however, would be an extremely laborious method, particularly in the case of mixtures containing four or five aromatic hydrocarbons, and it is necessary to adopt a simpler procedure, derived thus :

Lambert and Beer's laws of the absorption of radiation state that the amount of radiation absorbed by successive layers of the absorbing material is a definite fraction of the radiation falling on each layer, and is also proportional to the number of absorbing molecules in the radiation path. This may be expressed in mathematical symbols as—

$$E = \frac{1}{Ct} \log \frac{I_0}{I} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where I_0 is the intensity of radiation incident on the absorbing material,
  I is the intensity of the radiation emerging after traversing a thickness t (cm.) of the absorbing material,
  C is the concentration of absorbing material in gm.-mol./litre,
  E is a constant for a given material at a given wave-length.

The quantity E is called the molecular extinction coefficient, while the expression $\log \frac{I_0}{I}$ is referred to as the optical density and bears the symbol " d." E is thus the optical density corresponding to an absorbing thickness of 1 cm. and a concentration of 1 gm.-mol./litre.

If, therefore, as in the instrument used for this work and described later, the value of " d " at a given wave-length is known, and the value of E at the same wave-length has been determined using the pure absorbing component, the value of C—the concentration of the absorbing substance—may be calculated.

In a mixture containing more than one absorbing compound the optical density observed at any wave-length is the sum of the optical densities due to the individual components at that wave-length. That this statement is true for hydrocarbons is borne out by the results quoted later.

Therefore in a mixture containing two aromatics, if the optical density is measured at two wave-lengths, two simultaneous equations are obtained, e.g.—

$$\left. \begin{aligned} d_1(\text{obs.}) &= t(E_1 C_1 + E_2 C_2) \\ d_2(\text{obs.}) &= t(E_1{}' C_1 + E_2{}' C_2) \end{aligned} \right\} \quad . \quad . \quad . \quad (2)$$

where d_1 and d_2 are the optical densities observed at wave-lengths λ_1 and λ_2; E_1 and E_2 are the molecular extinction coefficients of the two aromatics at λ_1, and $E_1{}'$ and $E_2{}'$ are the molecular extinction coefficients at λ_2.

These two equations may be solved to give C_1 and C_2—the concentrations of the two aromatics in gm. mols./litre. When three aromatics are present together, the determination of optical densities and molecular extinction coefficients at three wave-lengths is necessary, and in this case three simultaneous equations have to be solved and so on.

The method of analysis discussed, therefore, involves the determination of the molecular extinction coefficients of each pure aromatic at a series

of wave-lengths, and the use of these values in the examination of unknown mixtures of these substances.

<div align="center">EXPERIMENTAL.</div>

(a) *Apparatus.*

The apparatus used comprised a Hilger medium quartz spectrograph and a Spekker photometer. This is a standard apparatus for work of this nature, and is described fully in the makers' publications. A brief description of the photometer is included here.

The Spekker photometer is a device for the quantitative measurement of the intensity of absorption of solutions. In it the radiation is split by quartz rhombs into two beams which pass, the upper through the solution being examined, the lower through a blank cell filled with solvent. These two beams are then brought to a focus on the slit of the spectrograph, the resulting photographs appearing as a pair of spectra in close juxtaposition. In the beam passing through the blank cell is placed a variable aperture operated by a drum on which is a scale giving the logarithms of the area ratios of the fixed to the variable aperture. The drum is therefore calibrated in optical densities.

When equality of photographic blackening at any wave-length is observed between the two halves of each spectrum pair, then the intensity has been cut down by the variable aperture to the same extent as it has by the solution. The amount of this reduction is known from the drum reading, and hence a quantitative measure of light absorption is obtained.

Since the intensity of absorption varies considerably and in an irregular manner with wave-length, it is necessary to make exposures over a range of drum readings in order to be certain of covering the optical densities at a series of wave-lengths.

The source of ultra-violet radiation employed is a high-tension spark operating between tungsten steel electrodes at 15,000 volts, a $0.005 \mu F.$ condenser being connected in parallel with the electrodes. The use of the hydrogen discharge lamp as an alternative source will form the subject of a subsequent paper.

To prevent interference with radio and other sensitive apparatus, due to the high-frequency spark, the photometer part of the equipment is enclosed in a double steel box, the space between the boxes being filled with glass-wool as a sound insulator. These two boxes are earthed independently, and it is advisable to keep all leads to the instrument and earth lines as short as possible. Attention should also be paid to the direction of the axis of the instrument, if it is to be operated near other sensitive apparatus. A filter in an earthed metal box is interposed between the mains supply and the transformer feeding the spark.

Ilford Zenith plates have been employed throughout the present work, and these have been developed in a maximum contrast developer for a standard development time of 1 minute.

The spectroscopic solvent employed has been a mixture of C_7 and C_8 paraffins or alkylate, which has been given two washes of $12\frac{1}{2}$ per cent. by vol. of 96 per cent. H_2SO_4. This washing is followed by a soda wash in an all-glass apparatus, and the product is distilled in a 40-plate, eyelet-

packed column at 10 to 1 reflux ratio.   The cut representing 10–80 per cent. of the charge to the still is used as solvent.

(b) Procedure.

The determination of aromatic hydrocarbon contents by the ultra-violet spectroscopic method depends largely on the interpretation of the photographic plates obtained, and in particular on determining the points at which equal blackening occurs of the two halves of each pair of spectra produced by the photometer.   This is an art which is acquired by experience, and it has been found that an unskilled operator requires about six weeks' practice before he becomes proficient.   The comparison is made using a low-power microscope (magnification about × 4) for viewing purposes.

Since the procedure followed is the basis of this and following papers, a detailed example is given of the determination of the molecular extinction coefficients of benzene.   This particular case is described because the absorption spectrum of benzene is very well defined, and the interpretation of the photographic plate is relatively simple.

TABLE I.

Physical Properties of Pure Aromatics.

Compound.	B.P. ° C.	F.P. ° C.	d_4^{20}.	n_D^{20}.	Purity. Per cent.
Benzene	80·20	5·48	0·8792	1·5012	99·98
Toluene	110·85	−94·97	0·8669	1·4968	99·83
Ethylbenzene	135·95	−95·02	0·8672	1·4961	99·6
m-Xylene	139·15	−48·05	0·8644	1·4971	99·98
p-Xylene	138·35	13·21	0·8610	1·4957	99·96
o-Xylene	144·45	−25·31	0·8803	1·5054	99·92
isoPropylbenzene	152·45	−95·89	0·8619	1·4915	99·9

A solution of benzene (for properties see Table I) in aromatic-free solvent is prepared by weighing a small quantity of the former and diluting it to a known volume with the solvent.   (In a particular case 0·7060 gm. benzene was made up to 50 ml.; 4 ml. of the resulting solution were then made up to 50 ml. with the same solvent, and finally 10 ml. of the second solution again made up to 50 ml. with solvent.   This procedure gave a diluted solution containing 0·2259 gm. benzene per litre equivalent to 0·002896 gm.-mol./litre, and avoided the use of large volumes of solvent.)

The next step is to make a series of exposures on the plate by which to measure the zero error of the instrument—*i.e.*, the difference between the amounts of radiation passing along the two optical paths.   This is done before the cells are placed in position, and a series of exposures is made on the plate corresponding to known small variations from the fully open position of the variable aperture.   Thus, in the example being discussed, which is illustrated in the photographic reproduction shown in Fig. 1, the three pairs of spectra shown immediately above the wave-length scale were made for zero correction purposes.   They correspond to variable aperture drum readings (optical densities) of 0·05, 0·10, and 0·15, respec-

TABLE II.

Details of Exposures Made in Determining the Extinction Coefficients of Benzene.

Variable aperture.	Exposure.	Position of plate on divided scale.
Drum reading.	Seconds.	(1 Division = 1 mm.)
0·30	2·0	15
0·35	3·0	18
0·40	3·0	21
0·45	4·0	24
0·50	5·0	27
0·60	4·0	30
0·70	5·0	33
0·80	6·0	36
0·90	6·0	39
1·00	7·0	42
1·10	7·0	45
1·20	8·0	48
1·25	8·0	51
1·30	8·0	54
1·35	10·0	57
1·40	10·0	60
1·50	10·0	63
1·55	12·0	66
1·60	14·0	69
1·65	14·0	72
1·70	16·0	75
1·75	16·0	78

TABLE III.

Results of Examination of Photographic Plate Exposed for Determination of Extinction Coefficients of Benzene.

Absorption cell length   = 2 cm.
Zero error of photometer = + 0·11.

Variable aperture drum reading (optical density).	Corrected optical density (= drum reading minus 0·11).	Wave-lengths * (Å.) at which the pairs of spectra have equal intensities.										Molecular extinction coefficient. E.
0·30	0·19	2422	—	2455	—	—	—	—	2630	2585	2628	32·8
0·35	0·24	2424	—	2455	—	2525	2530	—	2570	—	2628	41·4
0·40	0·29	2450	2465	2478	2515	2525	2530	2566	2598	2625	—	50·1
0·45	0·34	2427	2438	—	2479	—	2508	2538	2564	2601	2622	58·7
0·50	0·39	2428	2438	—	2480	—	2506	2539	2564	2601	2621	67·3
0·60	0·49	—	—	—	—	—	2500	2540	2562	—	2620	84·6
0·70	0·59	—	2435	—	2482	—	2497	2540	2559	—	2615	101·9
0·80	0·69	—	—	—	—	—	2495	2541	2557	2603	2611	119·1
0·90	0·79	—	—	—	—	—	2492	2541	2556	2604	2606	136·4
1·00	0·89	—	—	—	—	2484	2490	2542	2555	2605	—	153·7
1·10	0·99	—	—	—	—	—	2490	2542	2554	2605	—	170·9
1·20	1·09	—	—	—	—	2485	—	2543	2550	—	—	188·2
1·25	1·14	—	—	—	—	2487	—	—	2549	—	—	196·8
1·30	1·19	—	—	—	—	—	—	2544	2549	—	—	205·4
1·35	1·24	—	—	—	—	—	—	2544	—	—	—	214·1
1·40	1·29	—	—	—	—	—	—	—	2546	—	—	222·7
1·50	1·39	—	—	—	—	—	—	—	2548	—	—	240·0
1·55	1·44	—	—	—	—	—	—	—	—	—	—	—
1·60	1·49	—	—	—	—	—	—	—	—	—	—	—
1·65	1·54	—	—	—	—	—	—	—	—	—	—	—
1·70	1·59	—	—	—	—	—	—	—	—	—	—	—
1·75	1·64	—	—	—	—	—	—	—	—	—	—	—

* As recorded on wave-length scale in instrument.

tively, and constant exposures of 1 second. Examination of these spectra shows that at a drum reading of 0·10 the upper half is a trifle darker than the bottom half, whereas at a drum reading of 0·15 the reverse is the case, so that the true zero lies between these two figures. Interpolation by a skilled operator gives a value of 0·11.

After the zero has been determined, the absorption cells (a standard cell length of 2 cm. is used) are filled with solution and solvent respectively. They are then placed in position in the Spekker photometer, that con-

WAVELENGTH - ANGSTROM UNITS
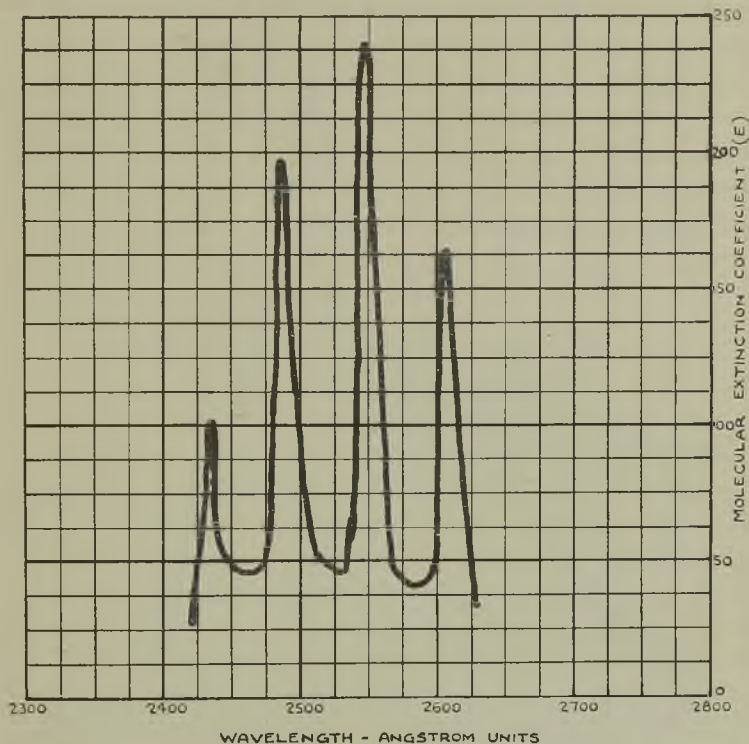
FIG. 2.

ULTRA-VIOLET ABSORPTION SPECTRUM OF BENZENE.

taining the solution being uppermost. The apparatus is now ready for the analysis.

The following cycle of operations is carried out :

1. Adjust plate to proper position as shown by the scale on the rack-and-pinion device.

2. Adjust the variable-aperture recorder drum to the required value.

3. Switch on spark for the required exposure time.

The cycle of operations is repeated for a series of drum readings covering the whole scale as shown in Table II.

It should be noted that as the aperture in the photometer is reduced the exposure time has to be increased correspondingly to give an image of reasonably constant density on the developed plate. The exposure times given in Table II apply in a general way to all mixtures, but may require to be shortened or increased, depending on the intensity of the spark line to be used in measurement.

A photograph of the developed plate obtained is reproduced in Fig. 1.

Each pair of spectra is now examined under a low-power microscope to determine at what wave-lengths the intensities of the upper and lower
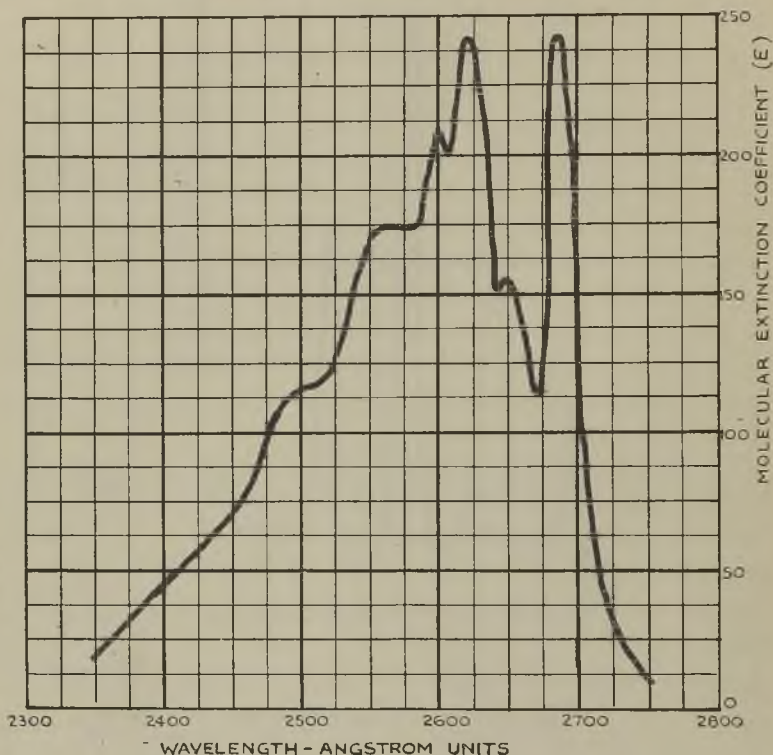

FIG. 3.

ULTRA-VIOLET ABSORPTION SPECTRUM OF TOLUENE.

spectra are equal. These points of equality of blackening are marked on Fig. 1. Thus, as shown in Fig. 1, at a drum reading of 1·00 these are equal at wave-lengths of 2485, 2490, 2542, 2554 and 2605 Å. and at no other wave-lengths. Table III gives the data obtained at all settings of the variable aperture, and the molecular extinction coefficients calculated from equation (1). The extinction coefficient/wave-length relation is shown in Fig. 2.

It should be noted that the true values of the optical densities are obtained by subtracting the zero error from all variable-aperture drum readings. In doing this, the zero error at the actual wave-length to be

Drum Reading.	Exposure (secs.).
1·75	16
1·70	16
1·65	14
1·60	14
1·55	12
1·50	10
1·40	10
1·35	10
1·30	8
1·25	8
1·20	8
1·10	7
1·00	7
0·90	6
0·80	6
0·70	5
0·60	5
0·50	4
0·45	4
0·40	3
0·35	3
0·30	2
0·15	1
0·10	1
0·05	1

Zeros.

Scale.

FIG. 1.

PLATE EXPOSED TO DETERMINE THE MOLECULAR EXTINCTION COEFFICIENTS OF BENZENE.

It should be noted that as the aperture in the photometer is reduced the exposure time has to be increased correspondingly to give an image of reasonably constant density on the developed plate. The exposure times given in Table II apply in a general way to all mixtures, but may require to be shortened or increased, depending on the intensity of the spark line to be used in measurement.

A photograph of the developed plate obtained is reproduced in Fig. 1.

Each pair of spectra is now examined under a low-power microscope to determine at what wave-lengths the intensities of the upper and lower
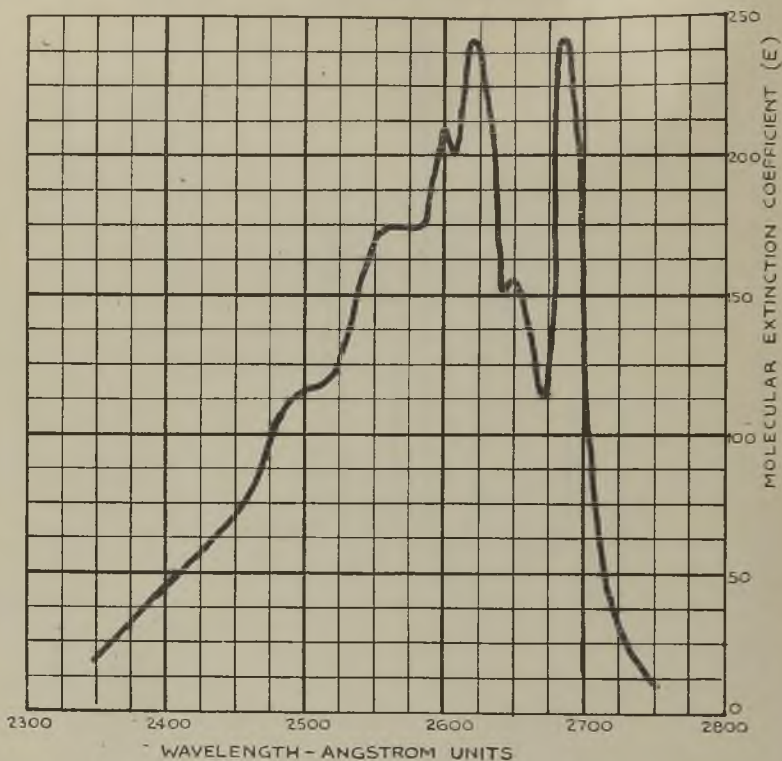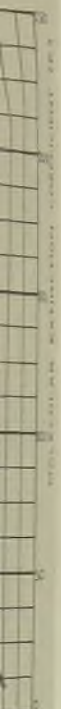

Fig. 3.

ULTRA-VIOLET ABSORPTION SPECTRUM OF TOLUENE.

spectra are equal. These points of equality of blackening are marked on Fig. 1. Thus, as shown in Fig. 1, at a drum reading of 1·00 these are equal at wave-lengths of 2485, 2490, 2542, 2554 and 2605 Å. and at no other wave-lengths. Table III gives the data obtained at all settings of the variable aperture, and the molecular extinction coefficients calculated from equation (1). The extinction coefficient/wave-length relation is shown in Fig. 2.

It should be noted that the true values of the optical densities are obtained by subtracting the zero error from all variable-aperture drum readings. In doing this, the zero error at the actual wave-length to be
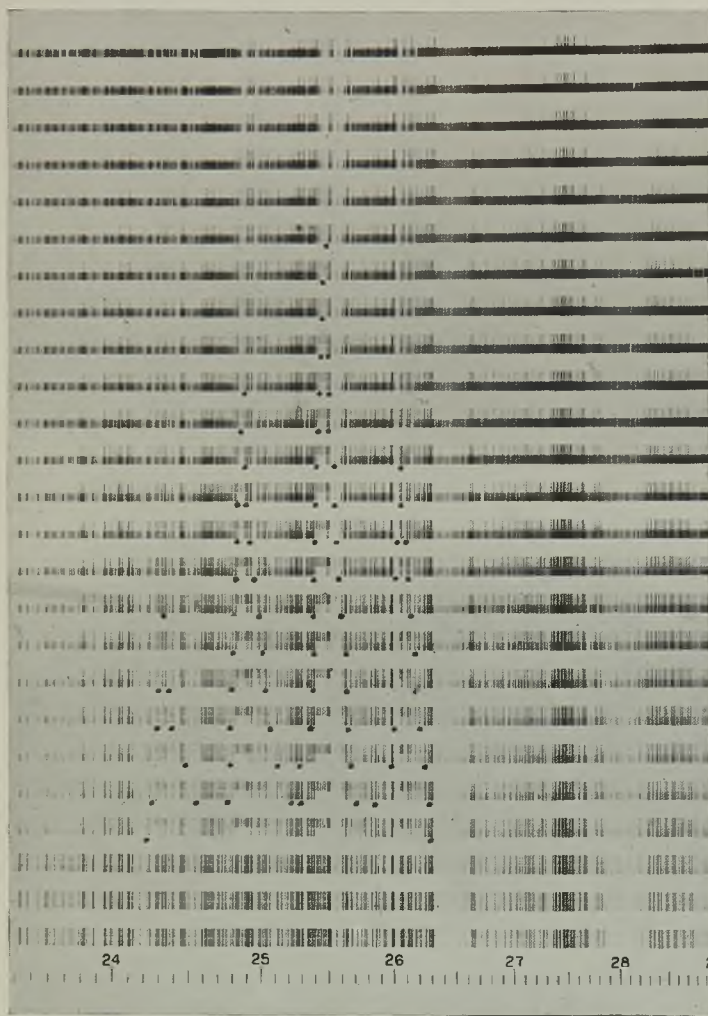
Drum Reading.	Exposure (secs.).
1·75	16
1·70	16
1·65	14
1·60	14
1·55	12
1·50	10
1·40	10
1·35	10
1·30	8
1·25	8
1·20	8
1·10	7
1·00	7
0·90	6
0·80	6
0·70	5
0·60	5
0·50	4
0·45	4
0·40	3
0·35	3
0·30	2
0·15	1
0·10	1
0·05	1

Zeros.

Scale.

FIG. 1.

PLATE EXPOSED TO DETERMINE THE MOLECULAR EXTINCTION COEFFICIENTS OF BENZENE.

examined must be used.   This zero error is usually constant over a very wide range of wave-lengths, but may be appreciably different at the two extremes of the range.   Hence the procedure followed by some workers of determining the zero error with the absorption cells already in position and relying on absence of absorption at long wave-lengths (and constancy of zero error over the full wave range) is not to be recommended.

FIG. 4.

ULTRA-VIOLET ABSORPTION SPECTRUM OF ETHYLBENZENE.

The wave-length scale provided with the instrument cannot be assumed accurate, but there is no reason to calibrate this scale for the present purpose, provided the same spectrum lines are used on every occasion. The wave-length scale may then be used as a rough indication of the spectrum lines.

(c) *Molecular Extinction Coefficients*.

Molecular extinction coefficient wave-length curves for benzene, toluene, ethylbenzene, *m*-xylene, *p*-xylene, *o*-xylene, and *iso*propylbenzene, deter-

mined in an exactly similar manner to that of benzene described above, are reproduced in Figs. 2–8.

These aromatic hydrocarbons were pure specimens prepared by the Chemical Research Section of the Anglo-Iranian Oil Co., Ltd., and their physical properties are detailed in Table I.
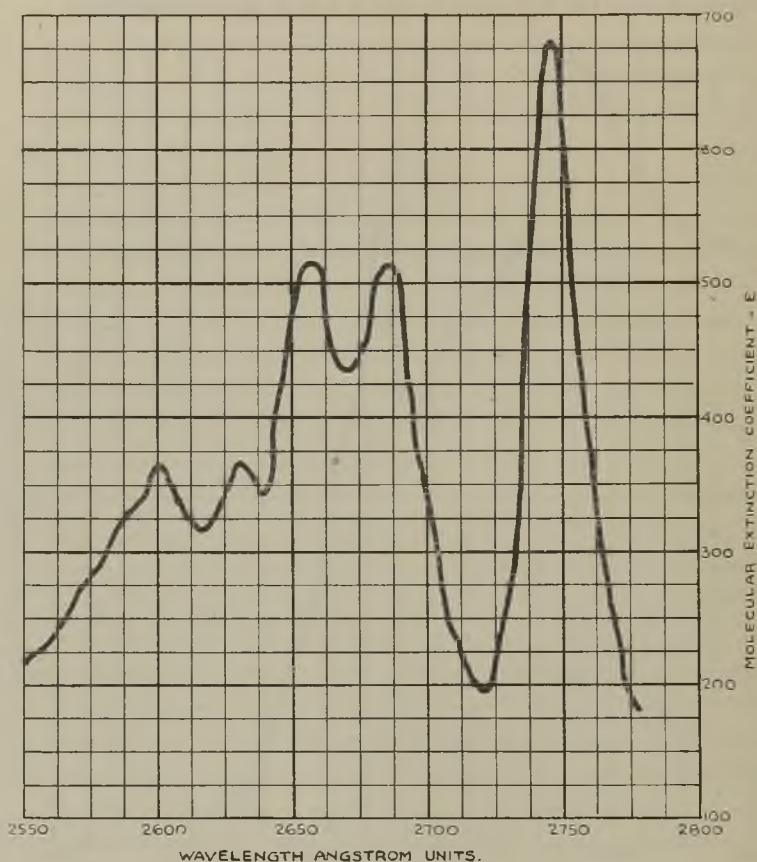

WAVELENGTH ANGSTROM UNITS.

Fig. 5.

ULTRA-VIOLET ABSORPTION SPECTRUM OF *para*-XYLENE.

ANALYTICAL METHOD.

(a) Benzene and Toluene.

The absorption spectra of benzene and toluene are shown on a single graph in Fig. 9. From this it is evident that the differences in absorption at 2548 Å. and 2686 Å. are well marked, and these two wave-lengths are therefore chosen as the " key " wave-lengths for analysis. As explained above, the optical density at a given wave-length is the sum of the optical densities due to the components, so that applying equations (2) we arrive at the following equations using the extinction coefficients shown in Table IV :—

$$240\ C_1 + 171\ C_2 = \frac{d_1}{2} \text{ at 2548 Å.}$$

$$10\ C_1 + 240\ C_2 = \frac{d_2}{2} \text{ at 2686 Å.}$$

TABLE IV.

Molecular Extinction Coefficients of Pure Aromatics at the "Key" Wave-Lengths.

Wave-length, Å.	2548.	2615.	2678.	2686.	2708.	2725.	2745.
Aromatics :							
Benzene	239	—	—	8	—	—	—
Toluene	171	—	—	240	—	—	—
Ethylbenzene	—	226	—	—	65	18	10
m-Xylene	—	202	—	—	131	275	125
p-Xylene	—	315	—	—	257	193	679
o-Xylene	—	243	—	—	215	154	51
*iso*Propylbenzene	—	—	160	—	24	—	—

where C_1 and C_2 are the concentrations of benzene and toluene respectively in gm.-mol./litre.
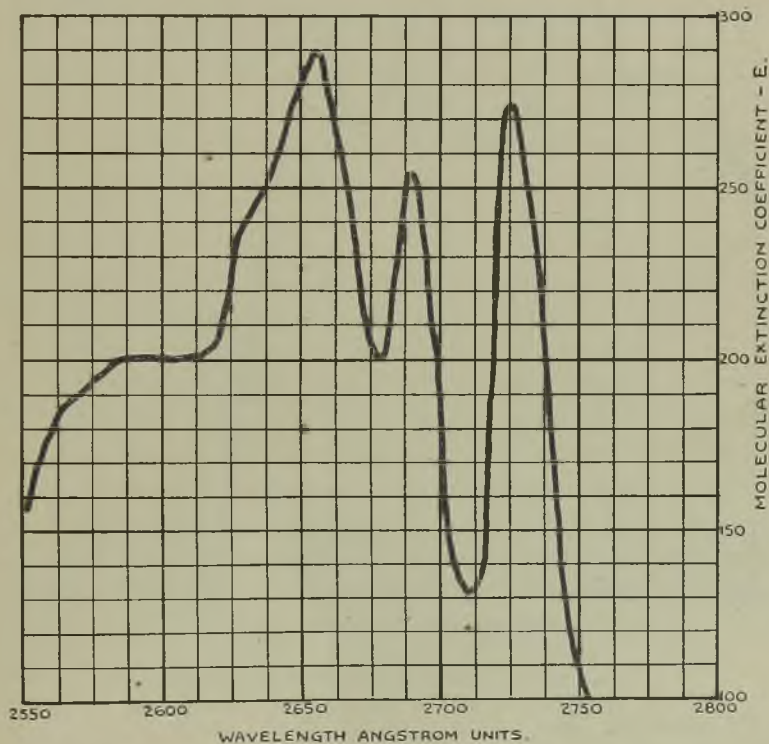

Fig. 6.

ULTRA-VIOLET ABSORPTION SPECTRUM OF *meta*-XYLENE.

K K

The factor 2 corresponds to the cell length of 2 cm.

The results of analyses of six synthetic mixtures following this procedure are given in Table V.

TABLE V.

Results of Analyses of Binary Blends of Benzene and Toluene.

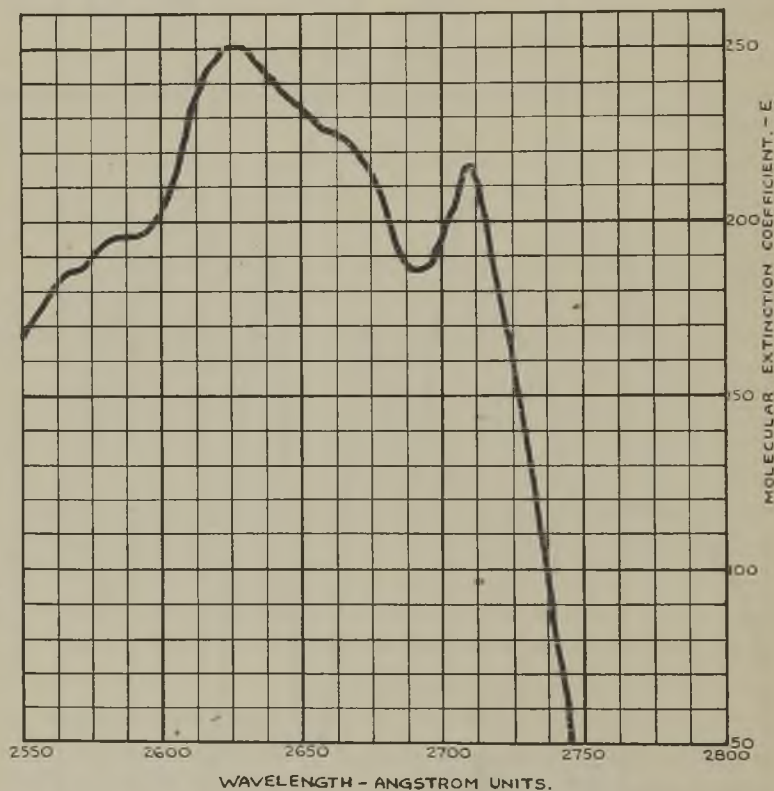| Blend No.	Benzene, wt. per cent.		Toluene, wt. per cent.	
	Actual.	Observed.	Actual.	Observed.
1	60·5	59·5 ± 1·5	39·5	38·0 ± 1·5
2	40·5	39·0 ± 1·5	59·5	59·5 ± 1·5
3	20·2	19·7 ± 1·5	79·8	79·3 ± 1·5
4	4·81	5·29 ± 1·5	95·19	93·3 ± 1·5
5	79·52	78·74 ± 1·5	20·48	22·0 ± 1·5
6	95·28	96·70 ± 1·5	4·72	5·2 ± 1·5

WAVELENGTH – ANGSTROM UNITS.

FIG. 7.

ULTRA-VIOLET ABSORPTION SPECTRUM OF *ortho*-XYLENE.

(b) C_8 *Aromatics.*

The absorption spectra of the C_8 aromatics and *iso*propylbenzene are shown on one graph in Fig. 10, from which it is evident that, while important

differences exist, they are not so well marked as we might wish, except in the case of *p*-xylene, which is outstanding. The differences are, however, such that they can be used as the basis of an analytical method. Fig. 10 shows that at a wave-length of 2745 Å. *p*-xylene has an extinction coefficient which is very much greater than that of *m*-xylene, the only other aromatic showing an appreciable absorption at this wave-length, and that at 2725 Å. and 2708 Å. the main absorption is due to *m*-xylene and *o*-xylene respectively. Due to the fact that in well-fractionated cuts *o*-xylene and ethyl-
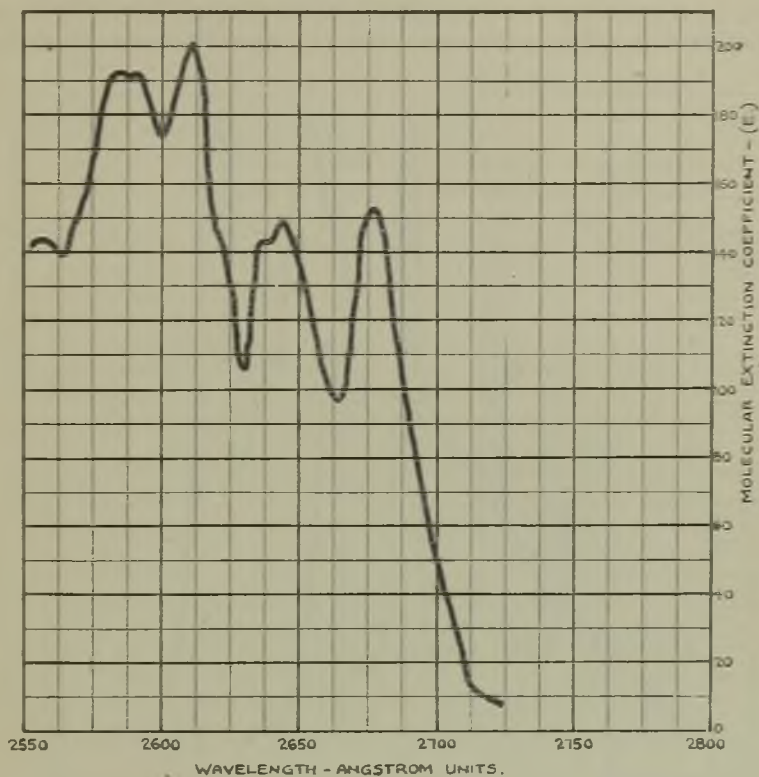

Fig. 8.

ULTRA-VIOLET ABSORPTION SPECTRUM OF *iso*PROPYLBENZENE.

benzene are rarely present together in appreciable quantities, the absorption of ethylbenzene at 2615 Å. is also important. It must be emphasized that it is not essential for each component to have an absorption band greater than all the other components at some wave-length for the analyses to be successful, since we are concerned with the sum of optical densities.

Thus we arrive at the following " key " wave-lengths :—

m-xylene	2725 Å.
p-xylene	2745 Å.
o-xylene	2708 Å.
ethylbenzene	2615 Å.

For a mixture containing all four C_3 aromatics, four simultaneous equations must be solved. The equations used are formed from the extinction coefficients listed in Table IV, and are given below :

$$226\ C_1 + 315\ C_2 + 202\ C_3 + 243\ C_4 = d_1/2 \text{ at } 2615 \text{ Å.}$$
$$65\ C_1 + 257\ C_2 + 131\ C_3 + 215\ C_4 = d_2/2 \text{ at } 2708 \text{ Å.}$$
$$18\ C_1 + 193\ C_2 + 275\ C_3 + 154\ C_4 = d_3/2 \text{ at } 2725 \text{ Å.}$$
$$10\ C_1 + 679\ C_2 + 125\ C_3 + 51\ C_4 = d_4/2 \text{ at } 2745 \text{ Å.}$$

where C_1 = concentration of ethylbenzene in gm.-mol./litre; C_2 = concentration of p-xylene in gm.-mol./litre; C_3 = concentration of m-xylene
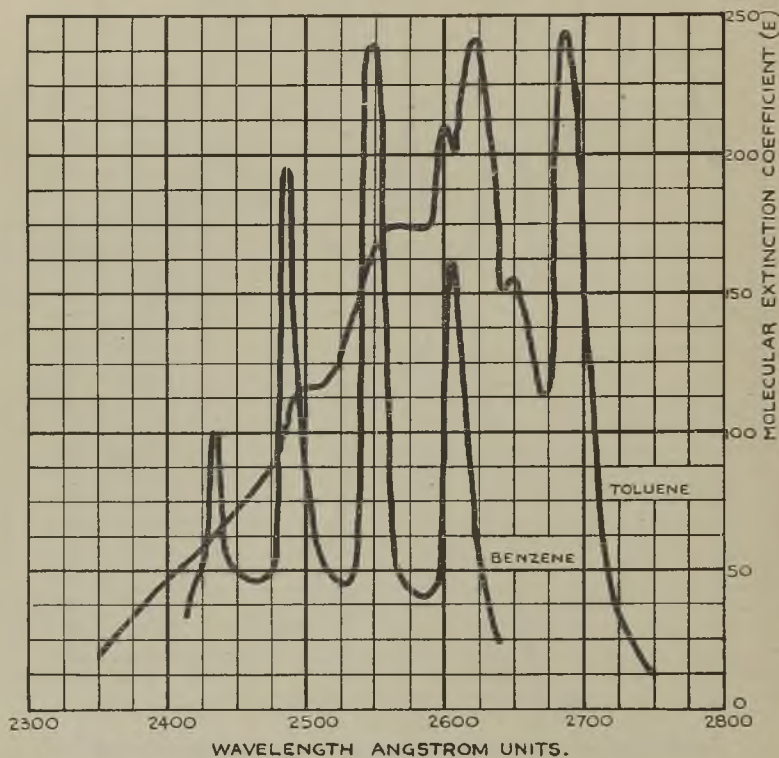

Fig. 9.

ULTRA-VIOLET ABSORPTION SPECTRA OF TOLUENE AND BENZENE.

in gm.-mol./litre; C_4 = concentration of o-xylene in gm.-mol./litre; and d_1, d_2, d_3, and d_4 are the observed optical densities at 2615, 2708, 2725, and 2745 Å., respectively.

Solution of these equations by straightforward methods is a tedious and time-consuming process when the method is used for routine analysis, and the procedure has been shortened by expressing the solution to the equations in determinant form. The solutions for various types of mixtures expressed in g/l are given below, and the results are shown in Tables VI–X :—

p-*Xylene and* m-*xylene.*

$$C_2 = - 0.0407 d_3 + 0.0896 d_4$$
$$C_3 = 0.2213 d_3 - 0.0629 d_4$$

p-*Xylene,* m-*xylene, and* o-*xylene.*

$$C_2 = 0.0116 d_2 - 0.0448 d_3 - 0.0864 d_4$$
$$C_3 = - 0.2101 d_2 + 0.2948 d_3 - 0.0042 d_4$$
$$C_4 = 0.3607 d_2 - 0.1261 d_3 - 0.1007 d_4$$

Ethylbenzene, p-*xylene, and* m-*xylene.*

$$C_1 = 0.2497 d_1 - 0.1501 d_3 - 0.0731 d_4$$
$$C_2 = - 0.0008 d_1 - 0.0403 d_3 + 0.0899 d_4$$
$$C_3 = - 0.0158 d_1 + 0.2308 d_3 - 0.0583 d_4$$

Ethylbenzene, p-*xylene,* m-*xylene, and* o-*xylene.*

$$C_1 = 0.3298 d_1 - 0.3040 d_2 - 0.0921 d_3 - 0.0118 d_4$$
$$C_2 = - 0.0050 d_1 + 0.0162 d_2 - 0.0434 d_3 + 0.0866 d_4$$
$$C_3 = 0.0522 d_1 - 0.2583 d_2 + 0.2802 d_3 - 0.0061 d_4$$
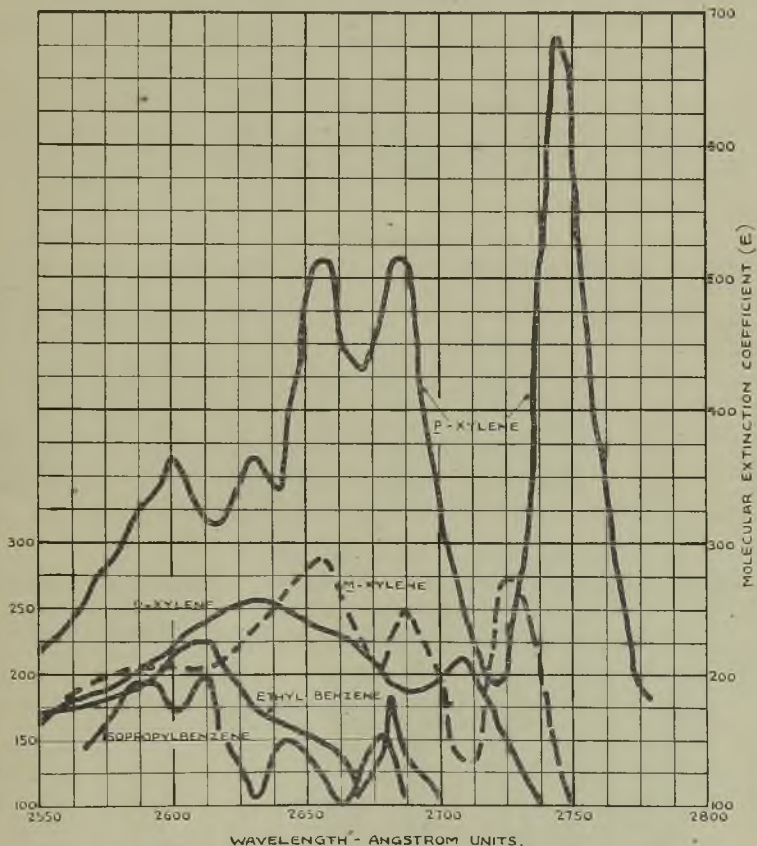$$C_4 = - 0.1255 d_1 + 0.4764 d_2 - 0.0910 d_3 - 0.0962 d_4$$

WAVELENGTH - ANGSTROM UNITS.

FIG. 10.

ULTRA-VIOLET ABSORPTION SPECTRA OF C_8 AROMATICS AND *iso*PROPYLBENZENE.

TABLE VI.

Results of Analyses of Binary Blends of m-*Xylene and* p-*Xylene.*

Blend No.	p-Xylene, wt. per cent.		m-Xylene, wt. per cent.	
	Actual.	Observed.	Actual.	Observed.
1	83·0	83·5 $\pm$ 2·5	17·0	15·6 $\pm$ 1·5
2	73·5	76·5 $\pm$ 2·5	26·5	24·3 $\pm$ 1·5
3	59·0	58·1 $\pm$ 2·5	41·0	40·0 $\pm$ 1·5
4	51·0	51·6 $\pm$ 2·0	49·0	43·8 $\pm$ 1·5
5	41·0	39·4 $\pm$ 2·0	59·0	56·3 $\pm$ 2·0
6	91·0	88·1 $\pm$ 3·0	9·0	8·5 $\pm$ 1·0
7	30·0	32·0 $\pm$ 2·0	70·0	69·6 $\pm$ 2·0
8	20·0	21·9 $\pm$ 2·0	80·0	79·2 $\pm$ 2·5
9	8·0	9·5 $\pm$ 1·5	92·0	91·3 $\pm$ 3·0

TABLE VII.

Results of Analyses of Binary Blends of m-*Xylene and* o-*Xylene.*

Blend No.	m-Xylene, wt. per cent.		o-Xylene, wt. per cent.	
	Actual.	Observed.	Actual.	Observed.
1	50·0	51·6 $\pm$ 1·5	50·0	49·1 $\pm$ 1·5
2	33·4	33·6 $\pm$ 2·0	66·6	64·2 $\pm$ 2·0
3	13·3	13·5 $\pm$ 1·5	86·7	84·9 $\pm$ 2·5

TABLE VIII.

Results of Analyses of Ternary Blends of m-*Xylene,* p-*Xylene, and* o-*Xylene.*

Blend No.	m-Xylene, wt. per cent.		p-Xylene, wt. per cent.		o-Xylene, wt. per cent.	
	Actual.	Observed.	Actual.	Observed.	Actual.	Observed.
1	71·5	73·9 $\pm$ 3·0	19·0	18·5 $\pm$ 1·0	9·5	9·0 $\pm$ 1·5
2	59·6	59·6 $\pm$ 2·5	15·7	15·7 $\pm$ 1·0	24·7	24·7 $\pm$ 1·5
3	44·2	41·7 $\pm$ 2·0	11·6	11·9 $\pm$ 1·0	44·2	44·4 $\pm$ 2·0
4	23·7	24·6 $\pm$ 1·0	6·3	6·3 $\pm$ 1·5	70·0	73·3 $\pm$ 2·5
5	75·5	77·6 $\pm$ 3·0	19·9	18·5 $\pm$ 1·0	4·6	5·3 $\pm$ 2·0

TABLE IX.

Results of Analyses of Ternary Blends of m-*Xylene,* p-*Xylene, and Ethylbenzene.*

Blend No.	m-Xylene, wt. per cent.		p-Xylene, wt. per cent.		Ethylbenzene, wt. per cent.	
	Actual.	Observed.	Actual.	Observed.	Actual.	Observed.
1	28·0	30·0 $\pm$ 1·5	28·0	25·1 $\pm$ 1·5	44·0	44·9 $\pm$ 2·0
2	60·0	59·2 $\pm$ 2·0	15·0	15·6 $\pm$ 1·0	25·0	24·8 $\pm$ 2·5
3	50·5	51·8 $\pm$ 2·0	15·5	15·5 $\pm$ 1·0	34·0	37·4 $\pm$ 2·0
4	44·5	46·2 $\pm$ 1·7	11·0	11·2 $\pm$ 1·0	44·5	47·6 $\pm$ 2·0
5	72·5	76·4 $\pm$ 2·0	18·0	18·4 $\pm$ 1·0	9·5	10·2 $\pm$ 1·5
6	25·0	26·2 $\pm$ 1·5	6·0	6·3 $\pm$ 1·0	69·0	70·2 $\pm$ 2·5

TABLE X.

Results of Analyses of Blends Containing m-*Xylene,* p-*Xylene,* o-*Xylene, and Ethylbenzene.*

Blend no.	m-Xylene, wt. per cent.		p-Xylene, wt. per cent.		o-Xylene, wt. per cent.		Ethylbenzene, wt. per cent.	
	Actual.	Observed.	Actual.	Observed.	Actual.	Observed.	Actual.	Observed.
1	30·1	31·8 ± 1·5	10·3	9·4 ± 1·0	10·4	9·0 ± 2·0	30·2	31·3 ± 1·5
2	40·2	38·8 ± 1·5	6·0	5·8 ± 1·0	12·4	14·5 ± 2·0	12·4	13·4 ± 2·0
3	15·21	16·5 ± 1·5	5·06	4·6 ± 1·0	25·56	25·5 ± 2·0	5·24	4·9 ± 1·5
4	60·9	56·3 ± 1·5	16·0	17·1 ± 1·0	20·1	23·5 ± 2·0	3·0	4·5 ± 2·0
5	32·4	32·8 ± 1·5	12·1	12·2 ± 1·0	15·6	13·2 ± 2·0	39·9	44·1 ± 1·5
6	47·5	45·5 ± 1·5	10·2	10·2 ± 1·0	32·8	32·6 ± 2·0	9·5	10·2 ± 2·0
7	49·5	46·6 ± 1·5	10·5	10·5 ± 1·0	13·6	12·0 ± 2·0	26·4	28·4 ± 2·0
8	60·2	61·7 ± 2·0	15·1	13·5 ± 1·0	14·4	16·3 ± 2·0	10·3	9·9 ± 2·0
9	46·9	48·4 ± 1·5	12·4	13·1 ± 1·0	9·4	8·6 ± 2·0	31·3	33·8 ± 2·0
10	37·5	38·1 ± 1·5	12·5	11·6 ± 1·0	25·0	25·4 ± 2·0	25·0	24·3 ± 2·0
11	16·4	15·7 ± 1·5	4·3	4·2 ± 1·0	24·3	25·2 ± 2·0	4·1	3·9 ± 2·0
12	23·7	22·2 ± 1·5	4·0	4·3 ± 1·0	24·3	25·4 ± 2·0	4·0	5·1 ± 2·0
13	42·8	42·1 ± 1·5	21·8	21·4 ± 1·0	20·4	20·7 ± 2·0	15·0	15·8 ± 2·0

The compositions of blends 1, 2, 3, 11, 12, and 13 were not known to the spectrograph operators.

It is to be noted that the above equations are correct for optical densities determined using a 2-cm. absorption cell; for other lengths of cell—*e.g.*, L cm.—the coefficients of d_1, d_2, d_3, and d_4 in the above equations should be multiplied by $2/L$.

These equations should hold for other instruments of the same design by the same makers, though they may not necessarily apply to instruments made by other manufacturers and using different methods of measuring the optical densities.

(c) *Mixtures containing* iso*Propylbenzene.*

This hydrocarbon has a boiling point of 152·45° C., and is therefore likely to be present in small amounts in the higher-boiling C_8 aromatic fractions (*i.e.*, those containing o-xylene). It must accordingly be taken into account. The wave-length/extinction coefficient curve for *iso*propylbenzene is reproduced in Fig. 8, and is closely similar to that of ethylbenzene. It follows from this that *iso*propylbenzene behaves very much like ethylbenzene in analyses. Since *iso*propylbenzene is not likely to occur in well-

TABLE XI.

Results of Analyses of Binary Blends of o-*Xylene and* iso*Propylbenzene.*

Blend No.	o-Xylene, wt. per cent.		isoPropylbenzene, wt. per cent.	
	Actual.	Observed.	Actual.	Observed.
1	90·3	93·9 ± 3·0	9·7	8·4 ± 3·0
2	80·0	75·7 ± 3·0	20·0	18·3 ± 2·5
3	68·7	68·9 ± 3·0	31·3	37·3 ± 2·0
4	60·0	59·0 ± 2·5	40·0	40·0 ± 2·0
5	51·1	48·1 ± 2·5	40·9	47·3 ± 2·5
6	40·1	41·7 ± 2·0	59·9	63·1 ± 2·5
7	24·6	25·7 ± 2·0	75·4	73·1 ± 3·0
8	9·8	10·8 ± 2·5	90·2	90·8 ± 3·0
9	5·2	6·3 ± 3·0	94·8	93·9 ± 3·0

fractionated cuts in aromatics with any C_8 aromatic other than o-xylene, only this combination has been studied and the " key " wave-lengths 2678 and 2708 Å. have been selected. The results of tests on synthetic blends of these two hydrocarbons are given in Table XI.

If a sample has a wide boiling range and includes ethylbenzene as well as isopropylbenzene, it is not possible, without prior fractionation, to distinguish between these components.

QUANTITATIVE ACCURACY OF THE METHOD.

The results of all tests made with synthetic blends are given in the following tables :—

As an overall check on the accuracy of analyses to be expected on samples from distillations, a synthetic mixture (composition unknown to spectroscopic operators) was made containing the C_8 aromatics, together with other hydrocarbons. This mixture was then fractionated in a 40-plate helix-packed column at a reflux ratio of 40 to 1. When an overhead temperature of 125° C. was reached, the residue was transferred to a Stedman column, and the distillation continued at the same reflux ratio as before. The following fractions were submitted for spectroscopic analysis :—

Boiling range, ° C.	Wt. per cent. of original mixture.
125–132	4·65
132–138	10·06
138–141	8·71
141–145	4·02
145–152·8	3·72

The results obtained from the spectroscopic analysis are given in the following table, compared with the actual composition of the mixture as regards the C_8 aromatics :—

Boiling range, ° C.	Wt. per cent.				
	Ethyl-benzene.	m-Xylene.	p-Xylene.	o-Xylene.	isoPropyl-benzene.
125–132	0·423	0·237	0·074	—	—
132–138	2·193	2·525	0·664	—	—
138–141	0·671	3·937	0·714	0·732	—
141–145	—	0·679	0·101	1·608	—
145–152·8	—	—	—	0·431	0·305
Total (obs.)	3·287	7·378	1·553	2·771	0·305 *
,, (act.)	3·170	7·36	1·75	3·15	—

* Part only of the total amount of isopropylbenzene appears in this fraction.

In Tables V–XI the estimated experimental error is shown for each component, these figures being obtained by examination of the photographic plates to determine the extent to which differences in line intensities may be detected.   Having determined our present limit in this process, the experimental error may be calculated as shown below.

Taking the basic equation—

$$d = ECt$$

or

$$C = d/Et$$

and partially differentiating, we get

$$\partial C = \frac{1}{Et}\,\partial d - \frac{d}{t}\frac{\partial E}{E^2}.$$

Dividing through by C

$$\frac{\partial C}{C} = \frac{\partial d}{d} - \frac{\partial E}{E}.$$

The individual errors in determining d and E are additive, so that the fractional error in C is given by this equation.   This is illustrated below.

The average optical density is usually adjusted, by suitable choice of the concentration of the sample in the solution in the cell, to about 1·25, and we have found by experience that the error in measuring this is about $\pm$ 0·0125.

The average error in measuring E, the extinction coefficient, is ± 5 (except in the case of p-xylene, where it may be as much as ± 10), so that in the typical case of m-xylene at 2725 Å., the maximum error involved is :—

$$\frac{\partial C}{C} = \frac{0·0125}{1·25} + \frac{5}{275} = 0·028.$$

Thus the error is 2·8 per cent.

In the case of solutions containing more than one C_8 aromatic, p-xylene is usually estimated first (if the method of computation is by the solution of equations).   Since this evaluation is almost entirely dependent on the optical density at 2745 Å., and because the extinction coefficients of m- and o-xylene are small compared with that of p-xylene, the error involved in estimating the p-xylene content reduces practically to the sum of the errors in measuring d and E for this component :—

$$\frac{\partial C}{C}\,(\text{para}) = \frac{\partial d_{2745}}{d_{2745}} + \frac{\partial E}{E}.$$

For example, at an observed optical density of 1·25, taking ± 10 as the error in measuring E for p-xylene :—

$$\frac{\partial C}{C}\,(\text{para}) = \frac{0·0125}{1·25} + \frac{10}{679} = 0·01 + 0·015 = 0·025.$$

Thus the error is 2·5 per cent.

The effect of optical density on the accuracy of analysis is demonstrated by the following example :—

When $d = 0.60$

$$\frac{\partial C}{C} = \frac{0.0125}{0.6} + \frac{10}{679} = 0.036$$

and the error is 3·6 per cent.

m-Xylene is usually the next C_8 aromatic to be determined (if the equations are solved directly), and in this case, in addition to the errors involved in measuring d and E at 2725 Å., those involved in the p-xylene estimation must also be considered.

Thus

$$\text{obs. } d_{2725} = d_{2725} \text{ due to } m\text{-} + d_{2725} \text{ due to } p\text{-}$$
$$\text{obs. } d_{2745} = d_{2745} \text{ due to } m\text{-} + d_{2745} \text{ due to } p\text{-.}$$

For example, assuming the following optical densities :—

$$d_{2725} = 0.912 + 0.258$$
$$d_{2745} = 0.596 + 0.838.$$

the value of d at 2745 due to p-xylene is 0·838, and in this case the error in evaluating p- is 3 per cent. This error will now be incurred in evaluating m- because

$$d_{2725} = d_m + d_p$$

and an error of 3 per cent. in the p- content will give rise to an error of 3 per cent. in d due to p-xylene at 2725 Å.

$$\therefore \quad \frac{\partial C}{C} \text{(meta)} = \frac{\partial d_m}{d_m} + \frac{\partial d_p}{d_m} + \frac{\partial E}{E} = \frac{0.0125}{0.912} + \frac{0.008}{0.912} + \frac{5}{275} = 0.04$$

and the error = 4 per cent.

As an example of the method extended to a mixture containing the three xylenes and ethylbenzene, the results for blend 3 in Table VII may be quoted.

In this case the optical density at 2745 Å. due to p-xylene is 0·33 and the estimated error in measuring d is ± 0.0125.

$\therefore$ Fractional error in evaluating the p-xylene concentration is :—

$$\frac{\partial d}{d} + \frac{\partial E}{E} = \frac{0.0125}{0.33} + \frac{10}{679} = 0.055.$$

$\therefore$ error in p-xylene is 5·5 per cent.

$$d_{2725} \text{ Å. due to } p\text{-xylene} = 0.101$$
$$d_{2725} \text{ Å. due to } m\text{-xylene} = 0.474$$

$\therefore$ an error of 5·5 per cent. in p-xylene will result in an error of

$$\frac{5.5}{100} \times 0.101 \text{ in } d \text{ at } 2725 \text{ Å.} = 0.006.$$

The maximum error in m-xylene, therefore, is

$$\frac{\partial d_m}{d_m} + \frac{\partial d_p}{d_m} + \frac{\partial E}{E} = \frac{0 \cdot 0125}{0 \cdot 474} + \frac{0 \cdot 006}{0 \cdot 474} + \frac{5}{275} = 0 \cdot 026 + 0 \cdot 012 + 0 \cdot 02 = 0 \cdot 058.$$

$\therefore$ Error in m-xylene $= 5 \cdot 8 \doteqdot 6$ per cent.

The errors in the determination of p-xylene and m-xylene are inter-dependent, a negative error in the p-xylene resulting in a positive error in the m-xylene content. In the above, however, both errors have been assumed to be in the same direction, in order to evaluate the maximum error.

In evaluating the error in o-xylene two cases may be considered :—

    (a) Where the optical densities at 2725 and 2745 Å. are both read low and the optical density at 2708 Å. is read high, and

    (b) Where all three optical densities are read low or high.

Considering only the maximum possible error

$$d_{2708} \text{ Å. due to } o\text{-xylene } = 0 \cdot 575$$
$$d_{2708} \text{ Å. } \quad , \quad m\text{-xylene } = 0 \cdot 274$$
$$d_{2708} \text{ Å. } \quad , \quad p\text{-xylene } = 0 \cdot 133.$$

An error of $5 \cdot 5$ per cent. in the p-xylene content will produce an error of $0 \cdot 007$ in d at 2708 Å.

An error of $6 \cdot 0$ per cent. in the m-xylene figure will produce an error of $0 \cdot 016$ in d at 2708 Å.

Thus the maximum error in o-xylene

$$= \frac{0 \cdot 0125}{0 \cdot 575} + \frac{0 \cdot 007}{0 \cdot 575} + \frac{0 \cdot 016}{0 \cdot 575} + \frac{5}{215} = 0 \cdot 083 = 8 \cdot 3 \text{ per cent.}$$

In calculating the error involved in estimating the ethylbenzene content the assumption already made that m- and p-xylenes are low and o-xylene is high, must also be made in this case. It can be seen from equation 1 $(226\ C_1 + 315\ C_2 + 202\ C_3 + 243\ C_4 = \frac{d_1}{2}$ at 2615 Å.) that since the error in o-xylene is in one direction and those for m- and p-xylenes in the other, the resulting error due to these components is made up as follows :—

Error in o-xylene — (error in m-xylene + error in p-xylene) :—

$$d_{2615} \text{ Å. due to ethylbenzene} = 0 \cdot 124$$
$$d_{2615} \text{ Å. } \quad , \quad m\text{-xylene} \quad = 0 \cdot 374$$
$$d_{2615} \text{ Å. } \quad , \quad p\text{-xylene} \quad = 0 \cdot 150$$
$$d_{2615} \text{ Å. } \quad , \quad o\text{-xylene} \quad = 0 \cdot 682.$$

An error of $5 \cdot 5$ per cent. in p-xylene produces an error in d_{2615} Å. $= 0 \cdot 008$

,,	6·0	,,	m-xylene	,,	,,	,,	= 0·023
,,	8·3	,,	o-xylene	,,	,,	,,	= 0·056

$\therefore$ Fractional error in ethylbenzene

$$= \frac{0\cdot0125}{0\cdot124} + \frac{0\cdot056}{0\cdot124} - \left(\frac{0\cdot008}{0\cdot124} + \frac{0\cdot023}{0\cdot124}\right) + \frac{5}{275} = 0\cdot322.$$

$\therefore$ error $= 32$ per cent.

The results of a series of calculations along these lines are plotted in Fig. 11, showing the errors involved for each of the C_8 aromatics, as
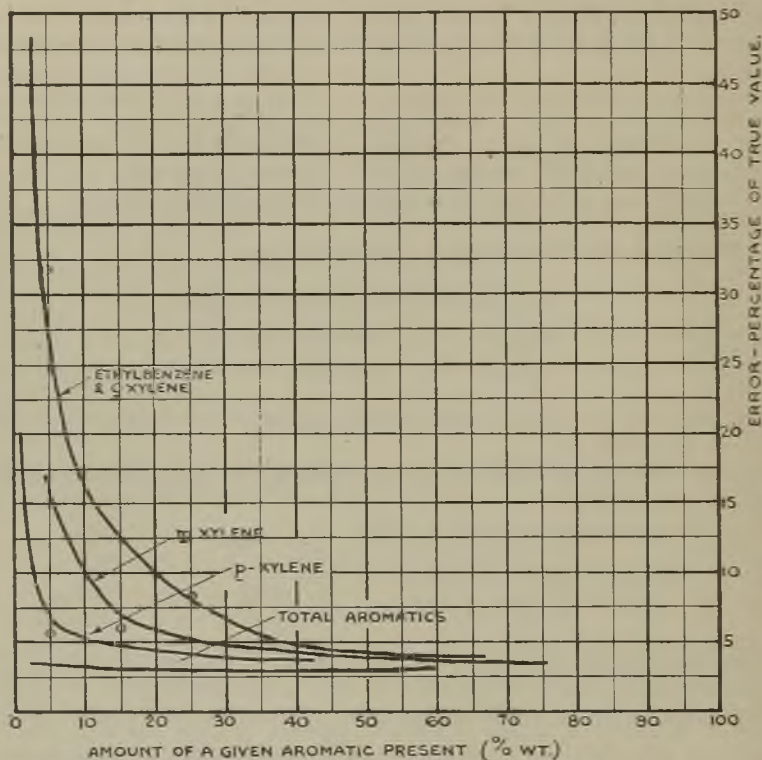

FIG. 11.

QUANTITATIVE ACCURACY OF ANALYSIS.

fractions of their actual concentrations. These results are very closely in line with the estimated errors in the tests of the synthetic blends detailed in Tables VI–XI.

The experimental errors involved when determinants are used are approximately the same as those shown in Fig. 11, the general tendency being towards lower errors.

It should be observed, however, that in actual practice if d_1 is read high (or low) and d_2, d_3, and d_4 read low (or high), the condition necessary to give the maximum error in C_1, then the errors in C_2, C_3, and C_4 will be lower than the theoretical maximum error. This can easily be seen by inspection of the determinant solutions where, for example, the coefficients

of d_2, d_3, and d_4 are negative for C_1, but may be positive in the equations for C_2, C_3, or C_4.

DISCUSSION.

The results quoted above show that the use of ultra-violet absorption methods supplies a rapid and reasonably accurate means of analysing mixtures of aromatics containing up to four components. The accuracy obtainable is governed to some extent by the composition of the mixtures to be analysed, and is at its worst when small amounts of ethylbenzene and o-xylene are present in a mixture whose main components are m-xylene and p-xylene. The main feature of the present work, however, is that even the more complicated analyses have been made by direct use of the Spekker photometer without any comparison with mixtures of known composition. The practicability of doing this has not in the past received the attention it deserves. The method has the great advantage of reducing the time required for a given analysis.

ACKNOWLEDGMENT.

FLOW TEST FOR ASPHALTIC BITUMENS.

THIS simple test has been found useful, and it is therefore being published for the information of readers.

INTRODUCTION.

1. This test is used when it is desired to compare the flowing tendencies of bitumens, asphaltic compositions, etc., at temperatures below which the determination of viscosity is difficult.

OUTLINE OF METHOD.

2. The extent to which the sample flows in a special mould when heat to a given temperature is measured.

APPARATUS.

3(a) Hollow " L "-shaped metal containers, made of brass or tinplate, with internal dimensions 2·5 cm. wide and 1·3 cm. deep, having limbs
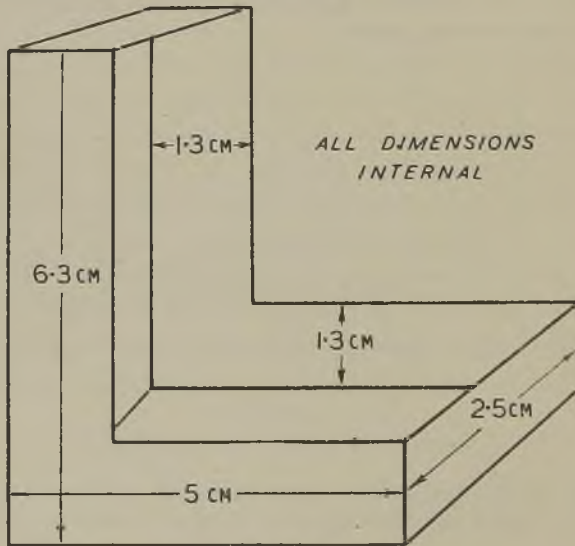

ALL DIMENSIONS INTERNAL

FIG. 1.

respectively 5 cm. and 6·3 cm. long. An illustration of a mould is given in Fig. 1.

(b) A thermostatically controlled oven.

SAMPLE.

4. 50 g. for three determinations.

PROCEDURE.

5. Heat each sample at a temperature between 75° C. and 100° C. above the approximate softening point as described for the penetration test (I.P. 49). Pour the melted sample into the shorter limb of the mould which has been placed horizontally until it is filled flush. Allow each mould and contents to cool for one hour at room temperature. Then place each side by side with the filled limb vertical on a level shelf in an oven thermostatically controlled at the desired temperature. At suitable intervals of time measure with a ruler the extent of flow in millimetres of each material along the empty limb. To do this correctly, measure the distance between the most advanced point of the flowing material and the end of the limb. Subtract the result from 50 mm.

REPORTING.

6. Tabulate the results under the heading " Relative Tendency to Flow," showing distance traversed in mm. against time in hours.