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ANALYSIS OF CRUDE BIPHENYL

The use of infrared and ultraviolet absorption as a means for analyzing crude biphenyl mixtures for biphenyl, ortho-, meta-, and para-diphenylbenzene has been thoroughly investigated. Of these two lines of investigation, only the ultraviolet proved successful. The results of each are described below.

Infrared Absorption

The major difficulty encountered - memo of 8/6/48 - was finding a solvent in which all components would be soluble to the extent of 20-30%. Attempts to use thicker absorption cells in conjunction with CCl_4 and CS_2 as solvents proved unsuccessful; the interference of the solvent became more pronounced as the cell thickness was increased. Since there was no apparent solution to this problem, the use of infrared was abandoned.

Ultraviolet Absorption

Biphenyl, ortho-, meta-, and para-diphenylbenzenes have absorption bands in the ultraviolet with maxima at 250 mu, 230 mu, 250 mu, and 280 mu, respectively. (Fig. 1). These spectra, as well as all subsequent measurements, were measured on the Beckman Quartz Spectrophotometer. Biphenyl and meta-diphenylbenzene each have their absorption bands at 250 mu. Because of this interference an analysis was developed for only the diphenylbenzene isomers. In those cases where the suspected biphenyl concentration is greater than 2%, some means of separation, such as distillation or chromatographic separation, must be resorted to.

The method of simultaneous equations was adopted for this analysis since two or more components are present. The steps involved in the development of this method are as follows:

- (1). Determination of the optimum concentration for each component which would give an optical density (D) between 0.3 and 0.7 at each component's key absorption band. This concentration was 0.0004% for all components.
- (2). Preparation of 0.0004% $\text{C}_2\text{H}_5\text{OH}$ solutions of each component from 0.1% CCl_4 solutions. A 0.4% solution of CCl_4 in $\text{C}_2\text{H}_5\text{OH}$ serves as a blank.

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(3). Measurement of the optical densities for each component at 230, 250, and 280 mμ, using 10 mm. absorption cells. The blank is used in the reference cell.

(4). Calculation of the following extinction coefficients using the equation $D = Ex$, where E is the extinction coefficient, D the optical density, and x the concentration in milligrams/100 ml:

- E_1 , the extinction coefficient of ortho- at 230 mμ
- E_2 , the extinction coefficient of meta- at 230 mμ
- E_3 , the extinction coefficient of para- at 230 mμ
- E_4 , the extinction coefficient of ortho- at 250 mμ
- E_5 , the extinction coefficient of meta- at 250 mμ
- E_6 , the extinction coefficient of para- at 250 mμ
- E_7 , the extinction coefficient of ortho- at 280 mμ
- E_8 , the extinction coefficient of meta- at 280 mμ
- E_9 , the extinction coefficient of para- at 280 mμ

(5). In a mixture the optical density at any one wavelength is equal to the sum of the optical densities of each component at that wavelength. This statement is the basis of the method and is responsible for the following set of simultaneous equations:

$$\begin{aligned} (a) \quad D_a &= E_1 x + E_2 y + E_3 z \\ (b) \quad D_b &= E_4 x + E_5 y + E_6 z \\ (c) \quad D_c &= E_7 x + E_8 y + E_9 z \end{aligned}$$

where

D_a = optical density of mixture at 230 mμ
 D_b = optical density of mixture at 250 mμ
 D_c = optical density of mixture at 280 mμ
 x = mg./100 ml. of ortho-diphenylbenzene
 y = mg./100 ml. of meta-diphenylbenzene
 z = mg./100 ml. of para-diphenylbenzene

Substituting the E values calculated in step (4)., and solving the equations for x , y , and z ,

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$$\begin{aligned} (d) \quad x &= 1.413 D_a - 0.632 D_b - 0.051 D_c \\ (e) \quad y &= 0.397 D_a - 0.822 D_b - 0.210 D_c \\ (f) \quad z &= 0.129 D_a - 0.111 D_b - 0.815 D_c \end{aligned}$$

The analysis of a mixture involves the following steps:

- (1). Weigh a 0.1 gm. sample ($\frac{1}{2}$ 1 mg.) into a 100 ml. volumetric flask and dilute to the mark with CCl_4 .
- (2). Prepare a 0.0004% $\text{C}_2\text{H}_5\text{OH}$ solution from the 0.1% solution.
- (3). Measure the optical density at 230, 250, and 280 mu in 10 mm. quartz absorption cells using a 0.4% CCl_4 solution in $\text{C}_2\text{H}_5\text{OH}$ in the reference cell.
- (4). Substitute these values in equations (d), (e), and (f) and solve for x, y, and z.

$100 x/0.4 = \% \text{ concentration of ortho-, etc.}$

The results obtained for four synthetic mixtures are shown in the table below.

Sample	Component	% Present	% Found	% Error
#1	ortho-	25.0	24.8	-0.8
	meta-	50.0	47.3	-5.4
	para-	25.0	24.2	-3.2
#2	ortho-	25.0	26.7	+6.8
	meta-	25.0	24.3	-2.8
	para-	50.0	48.1	-3.8
#3	ortho-	50.0	51.8	+3.6
	meta-	-	-	-
	para-	50.0	49.7	-0.8
#4	ortho-	-	-	-
	meta-	25.0	24.3	-2.8
	para-	75.0	76.3	+1.7

Averaging the percent errors for each component, an expected accuracy (based on amount present) of +3.2% ortho-, -3.7% meta, and +1.8% para- is obtained.

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The ultraviolet analysis of a sample of Santowax R is compared with the distillation method below.

<u>Component</u>	<u>Ultraviolet</u>	<u>Distillation</u>
ortho-	5.0%	11.9%
*meta-	60.8	53.7
para-	21.3	23.9
biphenyl	-	1.0
**Higher boiler	<u>12.9</u>	<u>9.5</u>
Total	100.0	100.0

* Includes biphenyl

** Obtained by difference of total from 100%

A single analysis can be completed in less than 30 minutes.

Although the method is based on the assumption that the higher boilers will not interfere, it might be wise to check this point in view of the differences in the analysis of Santowax R obtained by the two methods above. If you have some of the higher boiler material available, we shall be glad to measure its ultraviolet absorption spectrum.

Your suggestions as to possible methods of separating biphenyl from meta- diphenylbenzene would be most welcome. However, if the biphenyl concentration is not to be too high, we need not worry ourselves about this problem.

We sincerely hope that this method of analysis will prove useful to you.

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Figure 1.

