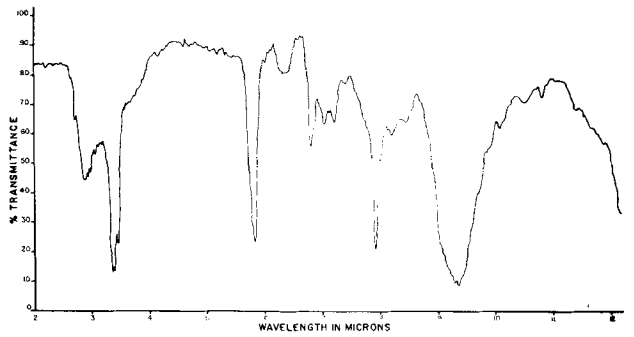

FIG. 6. Infrared spectrum of Fraction A as measured in cavity cell with carbon tetrachloride as solvent.

important to note that this buttery fraction is developed during the initial stage of reversion. When the soybean oil is highly reverted, this small buttery fraction tends to be overshadowed by the relatively large amounts of other flavor compounds.

Well-defined infrared spectra of the remaining four fractions were obtained. But their identifications are not complete.

Fraction VIII may be impure. Its infrared spectra indicates two carbonyl groups, one ester and the other aldehyde. Fraction IX is a ketone, probably a homologue of 2-heptanone. Fraction X (Figure 4) is an alcohol. Fraction XVI (Figure 5) is an ester.

An additional peak A was obtained from a repeat run of the reversion flavor. The infrared spectrum of this fraction (Figure 6) has a strong band at 5.8 μ and is therefore a carbonyl compound. It also has bands at 7.9 and 9.3 μ which are difficult to interpret. In the reference spectra only dimethyl formamide has an arrangement similar to those of these peaks.

The possibility of the presence of nitrogen compounds in reversion flavor is enhanced by ultimate analyses. The reversion flavor isolated from soybean oil which has been refined with acetic anhydride contains 0.67% of nitrogen. One of the possible precursors of nitrogen compounds is phosphatide. Soybean phosphatides were purified by precipitation from acetone and prepared in granular form. Flavor compounds isolated from the soybean phosphatides at room temperature contain 2.72% nitrogen. Therefore if phosphatides are not completely removed from the oil during refining, they may serve as one of the precursors of nitrogen compounds.

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[Received May 26, 1961]

Correlation of the Mean-Molecular Weights of Commercial Alkylbenzenes with Gas-Liquid Chromatographic Data

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Gas-liquid chromatography has been used to estimate the mean-molecular weights of commercial alkylbenzenes of the polypropylene type. Results obtained chromatographically on samples from several sources correlate well with mean-molecular weight data determined chemically via the sulfonic acids produced from them.

The chromatograms are obtained with a 200-ft. capillary column coated with Apiezon L grease. Partial resolution of the multicomponent mixtures to yield eighty to one hundred peaks, each possibly representing several components, is achieved. A plot of the logarithms of the relative retention times at the median areas of the chromatograms of narrow-cut distillation fractions of alkylbenzene vs. their known mean-molecular weights provides a linear calibrating relationship with a discontinuity at a mean-molecular weight of ca. 260. This discontinuity distinguishes "dodecylbenzenes" from the higher molecular weight "tetradecylbenzenes."

MIXTURES OF phenyl-n-dodecanes and didodecylbenzenes have been analyzed by gas-liquid chromatography using capillary columns in conjunction with an argon ionization detector (1). This separation technique has also been applied to the characterization of commercial alkylbenzenes of the polypropylene type (2). As an extension of the latter application, the work presented in this paper describes a method for evaluating the partially resolved chromatograms of commercial alkylbenzenes in terms of their mean-molecular weights.

When the chromatograms of narrow-cut distillation fractions of alkylbenzene of the polypropylene type are examined, it is found that the relative retention time at the median area of each chromatogram is shifted exponentially to higher values with a linear

increase in the mean-molecular weights of the respective fractions. A semi-log plot of these data provides a useful calibration curve for determining the mean-molecular weights of commercial alkylbenzenes from their chromatograms. Where the molecular weights of the narrow-cut fractions exceed ca. 260, a discontinuity appears in the relationship. The lower portion of the curve correlates with the molecular weights of commercial dodecylbenzenes while the upper portion seems appropriate for the newer tetradecylbenzenes. The accuracy of this chromatographic method has been checked against molecular weight determinations made chemically via the sulfonic acids produced from commercial alkylbenzenes.

Experimental Procedures

The narrow-cut distillation fractions of alkylbenzenes (polypropylene type) were obtained from the California Research Corporation which also provided the mass spectrometric analyses.

Capillary Gas Chromatography. The use of capillary columns and ionization detectors in gas chromatography has been described elsewhere (3, 4, 5). In this investigation a Barber-Colman, Model 10, Gas Chromatograph was used in conjunction with a 200-ft. capillary column made of 0.010 in. (I.D.) stainless steel tubing and coated with Apiezon L grease. The column was also obtained from the Barber-Colman Company, Rockford, Ill. Strontium-90 was the source of radiation in the argon detector. The following instrumental parameters were found appropriate for obtaining suitable chromatograms:

Temperatures:	
Column	165°C.
Cell	210°C.
Flash heater	275°C.
Carrier Gas (Argon):	
Inlet pressure	20 psig.
Column flow	2.0 ml./min.
Scavenger flow	60 ml./min.
Sensitivity:	
Detector voltage	1250 v.
Relative gain	30
Recorder range	5 mv.
Chart speed	6 in./hr.
Sample Size:	
Injected	0.75 μl.
Split	1:25
On column	0.03 μl.

Chemical Method. The mean-molecular weights of the commercial alkylbenzenes were determined indirectly via the sulfonic acids produced from them by the usual sulfonation processes.

In this method, ca. 1.0 g. of sulfonic acids is dissolved in 50 ml. of 1:1 ethanol-water mixture. After neutralization with NaOH, the solution is freed of unsulfonated matter (ca. 1% of the acid sample) using 5 extractions, each with 30 ml. of petroleum ether. The aqueous phase is then evaporated to near dryness to volatilize all of the alcohol. The salts are taken up in 100 ml. of 3-M. HCl, and the sulfonic acids extracted with ethyl ether as originally suggested by House and Darragh (6). The pure sulfonic acids are recovered by volatilization of the ether and HCl on a steam bath at a temperature slightly below 100°C. The reddish brown sulfonic acids are dissolved in neutralized 3A alcohol and titrated to the phenolphthalein end point with a standardized 0.2-*N* solution of NaOH. The number of milliequivalents of caustic consumed is noted for subsequent calculations.

The precisely neutralized solution of sulfonic acids is then transferred to a 125-ml. glass-stoppered Erlenmeyer flask and evaporated to dryness. The flask is placed in an oven at 105°C. until essentially constant weight is achieved. The weight of the dried salts thus obtained, after correction for residual moisture by Karl Fischer titration, divided by the number of milliequivalents of caustic consumed above provides the mean-molecular weight of the sulfonic acids as their sodium salts.

No interference from chloride or sulfate has been found on using this method. The results can be calculated in terms of the mean-molecular weight of alkylbenzene by subtracting 102 from the value obtained. A coefficient of variation well within ±1% has been found for this procedure.

Results

Evaluation of a Chromatogram. A typical chromatogram of a commercial dodecylbenzene is shown in Fig. 1. The highest peak in the chromatogram, indicated by an arrow in the figure, has a corrected retention time of 98 min. This peak, which is usually found in commercial dodecylbenzene, is used as an internal reference for calculating relative retention times. Retention time data are measured from the solvent peak (not shown in the figure). The solvent peak results from an intentional contamination of the syringe used for injecting the sample on the column with a trace of acetone.

When the reference peak is absent in a particular chromatogram (*vide infra*), a sample known to contain the reference peak must be run either immediately before or after the sample of interest in order to correlate retention time data between chromatograms under identical chromatographic conditions. In this way the position of the missing reference peak can be estimated quite accurately from its corrected retention time in the chromatogram of the known sample.

With this point on the time axis defined as 1.00, the abscissa of the chromatogram is subdivided into relative retention time units, and the area under the curve within equal time intervals is measured with a planimeter. These area data are converted into relative values in the usual way and then tabulated as illustrated in Table I for the chromatogram in Fig. 1.

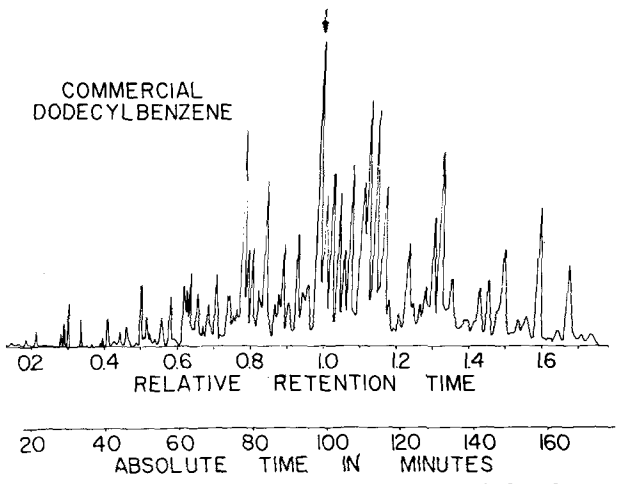

FIG. 1. Chromatogram of typical commercial dodecylbenzene.

TABLE I

Arithmetic Evaluation of Chromatogram of Dodecylbenzene

Relative retention time interval[a]	Relative area per cent	Cumulative relative area per cent
0.0–0.1	....	....
0.1–0.2	....	....
0.2–0.3	0.1	0.1
0.3–0.4	0.5	0.6
0.4–0.5	1.0	1.6
0.5–0.6	2.3	3.9
0.6–0.7	4.2	8.1
0.7–0.8	6.2	14.3
0.8–0.9	8.9	23.2
0.9–1.0	10.0	33.2
1.0–1.1	15.3	48.5
1.1–1.2[b]	17.2	65.7[b]
1.2–1.3	6.6	72.3
1.3–1.4	9.5	81.8
1.4–1.5	5.3	87.1
1.5–1.6	5.6	92.7
1.6–1.7	4.6	97.3
1.7–1.8	1.7	99.0
1.8–1.9	1.0	100.0

[a] Relative to defined reference peak in the chromatogram (see Fig. 1).
[b] Relative retention time at the median area is 1.11; obtained by interpolation.

The relative retention time at the median area of the chromatogram is obtained by interpolation within the time interval in which the 50%-cumulative area falls.

Narrow-Cut Distillation Fractions. The dependence of the relative retention time at median area upon the mean-molecular weight of the alkylbenzene is evident from the chromatograms shown in Fig. 2. These curves are chromatograms of three narrow-cut distillation fractions of alkylbenzene with mean-molecular weights of 231, 246, and 258, respectively. In the chromatogram of the 246-fraction, the peak defined above as the internal reference for calculating relative retention times is particularly prominent; it is just barely evident in the 231-fraction; and missing entirely in the 258-fraction. In cases such as the latter, the relative retention time scale must be estimated indirectly as described above.

In Fig. 3, a fraction with a mean-molecular weight of 272 is compared with that of the 258-fraction (see Fig. 2). Although these samples emerge over approximately the same time interval, the 272-fraction obviously contains a preponderance of higher molecular weight components.

Similarly, Fig. 4 provides a comparison between the chromatogram of the 272-fraction with one having a mean-molecular weight of 296. In this case the times of emergence of the samples just overlap; the

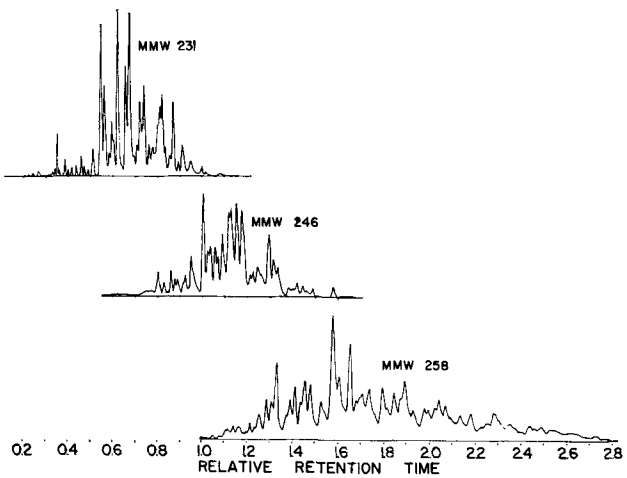

FIG. 2. Chromatograms of narrow-cut distillation fractions of alkylbenzenes (polypropylene type).

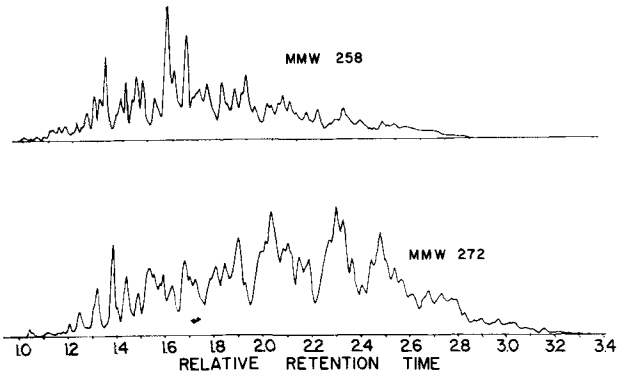

FIG. 3. Chromatograms of narrow-cut distillation fractions of alkylbenzenes (polypropylene type).

296-fraction requires almost eleven hours to be fully recorded.

Calibration Curve. Fig. 5 is a semi-log plot of the relative retention times at median areas taken from the chromatograms of each of the five narrow-cut fractions vs. their respective mean-molecular weights. The latter values were determined independently by mass spectrometry. Over the range covered by the first three fractions (mean-molecular weights of 231, 246, and 258), the plot is linear. The points for the higher molecular weight fractions (mean-molecular weights of 272 and 296), however, are displaced. A relationship paralleling the lower curve has been assumed for these two values; a discontinuity in the calibration curve results.

Commercial Samples. The mean-molecular weights of five samples of dodecylbenzene obtained from independent suppliers were determined chromatographically using the calibration curve presented in Fig. 5. Table II summarizes these results and provides a comparison of the values found with those obtained by the chemical method. Included in the table are the results obtained for two commercial alkylbenzenes of the tetradecyl type where the upper portion of the calibration curve beyond the discontinuity was used to estimate their mean-molecular weights.

Repetitive analyses of two of the samples reported in Table II indicate the precision of a single determination of mean-molecular weight to be well within one molecular weight unit. Since the calibration curve in Fig. 5 was established against independently

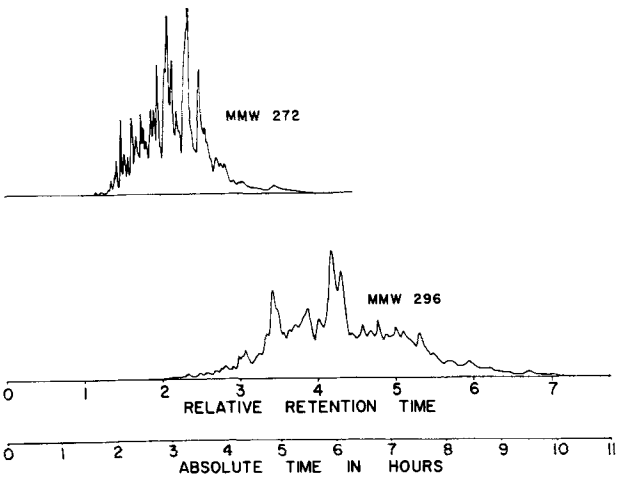

FIG. 4. Chromatograms of narrow-cut distillation fractions of alkylbenzenes (polypropylene type).

TABLE II

Comparison of Results of Mean-Molecular Weight Determinations of Commercial Alkylbenzenes

Type	Supplier	MMW by GLC	MMW by chemical method
Dodecylbenzene..	1	244	243
	2	244	244
	3	245	245
	4	247	247
	....	244	244
Tetradecylbenzene	1	270	270
	2	261	261

determined mass spectrometric data, the agreement of the results obtained chromatographically with those found chemically indicate that all three methods are providing comparably accurate mean-molecular weight data.

Discussion

Commercial alkylbenzenes are mixtures of many components of different chain lengths. The molecular weights of these components are distributed about the mean-molecular weight of the mixture. Because the number of components in a mixture is very large, the relationship between the relative retention time at median area and the mean-molecular weight of an alkylbenzene of a particular type appears to be a continuous function which is analogous to the chromatographic behavior of a homologous series of straight-chain phenylalkanes (7).

The number and type of structural isomers in the mixture having the same molecular weight are determined by the process used to polymerize the propylene prior to alkylation. Since these isomers of specific molecular weight undoubtedly have different retention times, as in the case of the phenyl-n-dodecanes (1, 7), their influence on the calibration curve shown in Fig. 5 is probably a constant factor within the limited molecular weight range of the usual commercial dodecylbenzene. Production of the tetradecyl type of alkylbenzene, however, requires a more extensive polymerization of propylene which increases the number of possible structural isomers of the same molecular weight on subsequent alkylation. Thus, the discontinuity in the calibration curve at a molecular weight of ca. 260 probably indicates the change in the number of these isomers as a result of the polymerization step. This change is evident in the chromatograms of the narrow-cut fractions with mean-molecular weights of 258 and 272, respectively, which show essentially the same times of emergence from the column (see Fig. 3). The difference in the numbers of possible structural isomers in the two samples is apparently the more significant factor in determining the character of these chromatograms than is the distribution of molecular weights of the individual species.

The correlation of chromatographic data with the mean-molecular weights of alkylbenzenes provides an additional analytical advantage for gas-liquid chromatography when this technique is used to characterize commercial alkylbenzenes. For the purpose of rapid analytical control it may be possible to shorten the time required to obtain a chromatogram at the sacrifice of the resolution of the peaks. The molecular weight correlation with relative retention time at median area may be calculatable from the profile of the peaks.

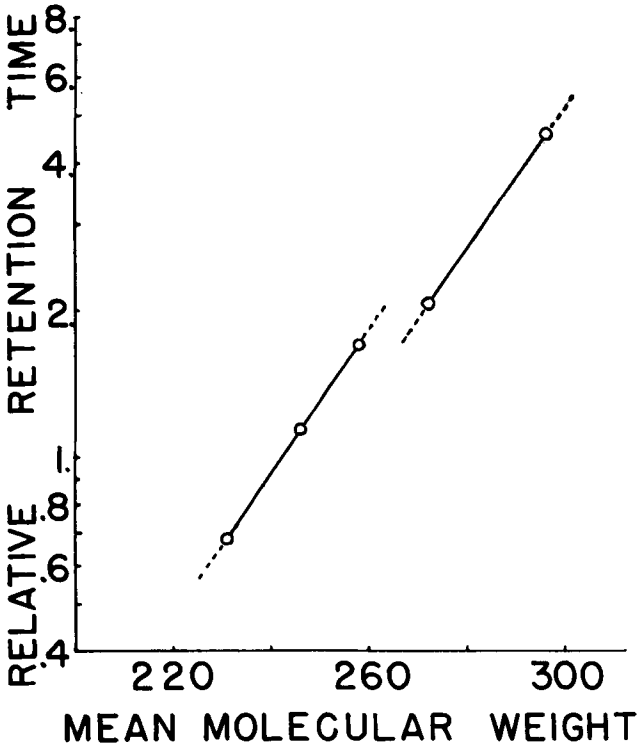

FIG. 5. Calibration curve of relative retention times at median areas *vs.* mean-molecular weights of alkylbenzenes of polypropylene type.

Acknowledgment

The authors are grateful to the California Research Corporation for the narrow-cut distillation of alkylbenzene, and their associated mass spectrometric analyses, which were used in this paper.

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[Received July 5, 1961]