

BOILING POINTS OF C₁₀-C₁₅ STRAIGHT CHAIN ALKYL BENZENE ISOMERS FROM GAS CHROMATOGRAPHIC RETENTION DATAFREDERICK BAUMANN, ALAN E. STRAUS AND JULIAN F. JOHNSON
California Research Corporation, Richmond, Calif. (U.S.A.)

(Received February 26th, 1965)

INTRODUCTION

Although the American Petroleum Institute (API) boiling point data are available for the primary C₁₀-C₁₅ straight chain alkylbenzenes, accurate data are not available for the other positional straight chain isomers. This is because the many C₁₀-C₁₅ straight chain alkylbenzene isomers are difficult to synthesize and isolate with the necessary purity for conventional boiling point determinations. However, mixtures of these isomers can be synthesized easily and separated on an analytical scale by gas chromatography using capillary columns¹⁻⁴. For these reasons, gas chromatographic retention data were used to estimate the boiling points of these isomers.

PRINCIPLE

The correlation of boiling points of homologous series to the logarithm of the retention volume is often used in gas chromatographic practice⁵. These correlations normally hold only for a single homologous series due to some selectivity of even the most nonpolar liquid phases. The selectivity is measured by the activity coefficient of the solute in the stationary phase⁶. The stationary phase is completely unselective when the activity coefficient is equal to unity. Linear correlations of boiling point and logarithm of the retention volume are often observed in instances where the activity coefficient changes with carbon number for members of a homologous series. This is due to the fact that the activity coefficient as well as the volatility are regular functions of the carbon number⁷.

The approach used in this study is based on a boiling point-log retention time correlation of the primary isomers for which accurate API boiling points are known. The accuracy of the method is dependent on the selectivity of the liquid phase to the other homologous series distinguished by the position of attachment of the phenyl group to the normal alkyl group. Any changes in activity coefficient as a function of carbon number are cancelled by the use of the corresponding primary alkylbenzenes as reference compounds.

The nonpolar stationary phases, Apiezon L and General Electric SF-96 silicone fluid, were chosen in order to reduce selective interactions with the polarizable phenyl groups. Initially, two factors pointed to little selectivity of these liquid phases for the isomers. Firstly, the relatively high carbon number of the alkyl group tends to reduce the effect of the phenyl group. Secondly, PIEROTTI *et al.* in a study of solvent effects

in gas-liquid chromatography showed that primary alkylbenzenes in paraffinic solvents exhibit activity coefficients of near unity⁷. This means that the interactions between the stationary phase and the phenyl group are small and positional differences should cause small changes also. Actually, slight interactions of the positional isomers with the stationary phase were observed as the following study shows. These interactions amounted to errors in boiling points of 0.7-4.1° depending on the positional isomer. A method of correcting for these activity effects was developed which necessitated obtaining the boiling point of at least one additional isomer other than a primary isomer.

EXPERIMENTAL

Columns

A 200-ft. by 0.02-in. I.D. column made of No. 1 temper Type 347 stainless steel capillary tubing (Handy and Harman Tube Company, Inc., P.O. Box 549, Norristown, Pa.) was used. The column was coated by slowly passing 2 ml of a solution containing 10% General Electric SF-96 silicone fluid in methylene chloride through the column. The solvent was evaporated by flushing with nitrogen overnight at ambient temperatures. The column was operated at 190° using helium carrier gas at an inlet pressure of 15 p.s.i.g. Methane was eluted at 2.43 min under these conditions.

A 200-ft. by 0.01-in. I.D. stainless steel capillary column coated with Apiezon L was used as purchased (Barber-Colman Company, Rockford, Ill.). The column was operated at two conditions: 210° at 50 p.s.i.g. inlet pressure and 240° at 40 p.s.i.g. inlet pressure. Retention time of methane under these conditions was 4.31 min and 5.63 min, respectively.

Gas chromatography

All data were obtained on a Perkin-Elmer Model 800 gas chromatograph (Perkin-Elmer Corporation, Norwalk, Conn.) equipped with a capillary column attachment. The injection temperature was 275°. A sample size of 3 μ l was injected; the split ratio was determined by a 27-gage needle placed in the outlet of the injector splitter. All data were obtained on the most sensitive attenuation using a Leeds and Northrup Model G 1-mV recorder. Small sample sizes and high sensitivity of the detecting system were chosen to avoid errors due to asymmetrical peaks. Retention times were obtained by measurement of distance on the chromatogram.

RESULTS AND DISCUSSION

Retention data

Adjusted retention time data are shown in Table I. These retention times are measured from the methane peak and are not corrected for gas compressibility. Duplicate chromatograms gave identical results, and the data from a single chromatogram are shown in Table I.

The two columns exhibit considerable differences in spite of the fact that they were picked for minimum selectivity. The Apiezon L column separates isomers considerably better than the SF-96 column but gives overlap between successive carbon numbers. The Apiezon L column very closely duplicates the Apiezon L column

described by CARNES¹, while the SF-96 column is nearly identical to the DC 550 column described by CARNES and the SE-30 column described by SWISHER^{3,4}.

Linear plots of carbon number *versus* logarithm of the adjusted retention time are obtained in the range C₁₁-C₁₄ for both SF-96 and Apiezon L. Such a plot is shown in Fig. 1 with the experimental points encircled. The linearity of the lines justified the extrapolation of the data to obtain the retention data for the C₁₀ and C₁₅ isomers.

TABLE I

EXPERIMENTAL RETENTION TIME DATA FOR C₁₀-C₁₄ STRAIGHT CHAIN ALKYL BENZENES

Alkylbenzene	Retention time (min)		
	SF-96, 190°	Apiezon L	
		210°	240°
5-Phenyldecane	2.78	—	—
4-Phenyldecane	2.88	—	—
3-Phenyldecane	3.13	—	—
2-Phenyldecane	3.60	—	—
6-Phenylundecane	4.08	14.81	8.24
5-Phenylundecane	4.08	15.17	8.41
4-Phenylundecane	4.27	16.20	8.84
3-Phenylundecane	4.65	18.10	9.92
1-Phenyldecane	4.76	20.73	11.21
2-Phenylundecane	5.35	21.81	11.74
6-Phenyl dodecane	5.92	21.81	11.47
5-Phenyl dodecane	6.02	22.36	11.74
4-Phenyl dodecane	6.32	24.06	12.58
3-Phenyl dodecane	6.88	26.94	13.99
1-Phenylundecane	7.08	—	—
2-Phenyl dodecane	7.95	32.60	16.56
7-Phenyltridecane	8.65	31.90	15.96
6-Phenyltridecane	8.65	31.90	15.96
5-Phenyltridecane	8.88	33.11	16.56
4-Phenyltridecane	9.33	35.69	17.71
3-Phenyltridecane	10.22	40.06	19.73
1-Phenyl dodecane	10.58	46.19	22.20
2-Phenyltridecane	11.82	48.65	23.37
7-Phenyltetradecane	12.62	46.77	22.47
6-Phenyltetradecane	12.71	47.30	22.47
5-Phenyltetradecane	13.10	49.15	23.37
4-Phenyltetradecane	13.82	53.00	29.94
3-Phenyltetradecane	15.13	59.48	27.80
2-Phenyltetradecane	17.48	71.96	32.91
1-Phenyltetradecane	23.33	102.19	44.78

Boiling point estimation

Boiling points of the C₁₀-C₁₅ secondary isomers were estimated from gas chromatographic retention time data from Fig. 1 and API Project 44 boiling point data for the primary isomers (1-isomers)⁸. Correlation of the log of the retention times *versus* boiling points of the 1-phenyl isomers is shown in Fig. 2 for the SF-96 column and for the Apiezon L column at 210°. Experimental points are indicated by circles, and interpolated points from retention times in Fig. 1 are indicated by crosses. The lines are not straight, and the extra data from Fig. 1 were helpful in drawing a smooth curve through the points. Uncorrected boiling points of the secondary isomers ob-

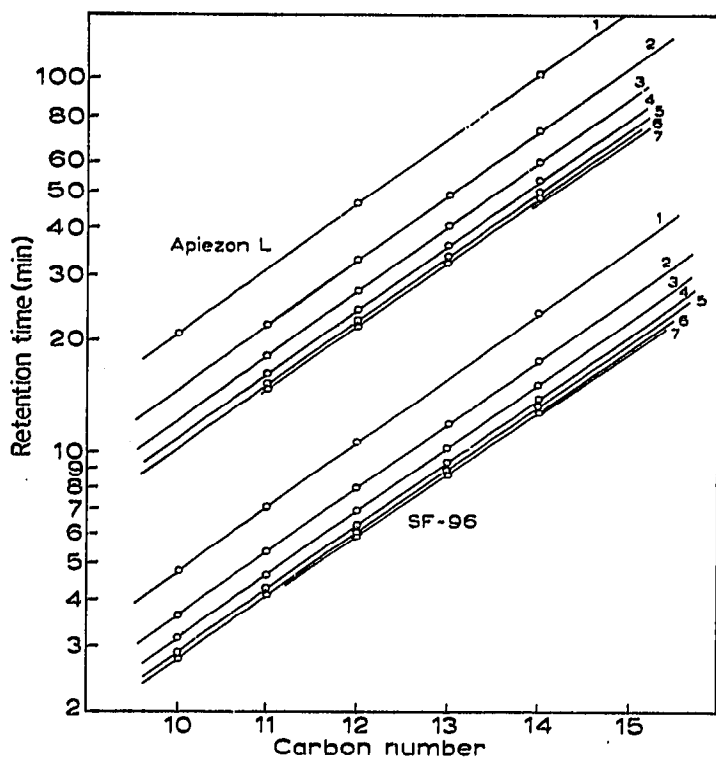


Fig. 1. Retention time *versus* carbon number of C_{10} - C_{14} alkylbenzene isomers. Numbers refer to positional isomers.

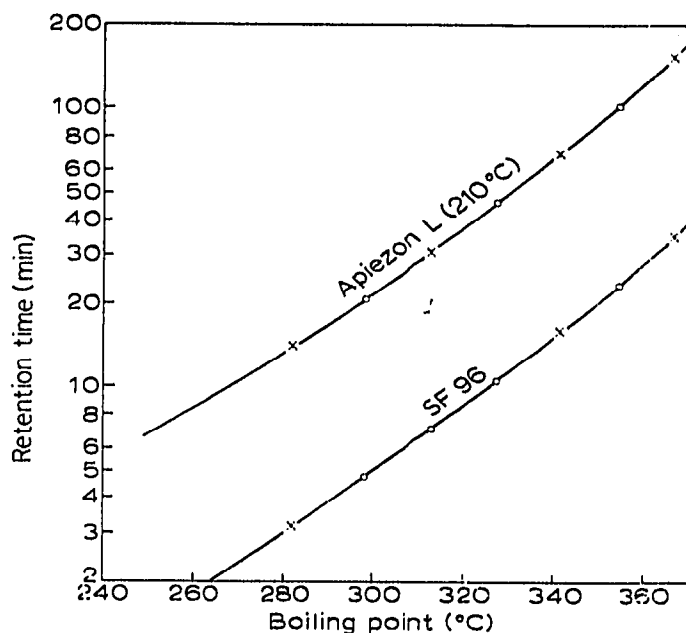


Fig. 2. Boiling point *versus* retention time for C_{10} - C_{15} 1-phenylalkanes.

tained directly from Fig. 2 are listed in Table II. The differences in boiling points obtained with the two columns increase as the phenyl group moves toward the center of the chain. This reflects the difference in behavior of the two columns noted above.

Boiling point correction

The correction to be applied to the data in Table II was obtained by measuring the boiling points of 3-phenyldodecane and 7-phenyltridecane using a differential thermal analysis (DTA) technique in which the liquid is placed on an inert packing and slowly heated to the boiling point⁹. These isomers were picked because they are available in reasonable purity. 3-Phenyldodecane as purchased (Eastman Organic Chemicals) was 95.7% pure according to the above gas chromatographic procedure. The principal impurity is eluted after 3-phenyldodecane and gives a peak with a large tail typical of a polar compound such as an alcohol. This impurity was judged to be higher boiling than 3-phenyldodecane based on retention time. A boiling point of 310.2° was measured for 3-phenyldodecane using the DTA technique. The 7-phenyltridecane was obtained from the American Petroleum Institute Project 42, Pennsylvania State University inventory of high molecular weight hydrocarbons. Gas chromatographic analysis showed a purity of 99.1%. The boiling point as determined by DTA was 318.9°.

An attempt was made to purify the 3-phenyldodecane by preparatory gas chromatography. The separation was made at 180° on a 40-ft. by 3/8-in. O.D. aluminum column containing 20% General Electric SE-30 on 45-60 mesh hexamethyl-

TABLE II

BOILING POINT DATA FOR C₁₀-C₁₅ STRAIGHT CHAIN ALKYL BENZENES

<i>Alkylbenzene</i>	<i>Apiezon L</i>		<i>SF-96</i>		<i>Boiling point (°C) from literature</i>		
	<i>Boiling point (°C) Un-corrected</i>	<i>Boiling point (°C) Corrected</i>	<i>Boiling point (°C) Un-corrected</i>	<i>Boiling point (°C) Corrected</i>	<i>Ref. 10</i>	<i>Ref. 11</i>	<i>Ref. 12</i>
5-Phenyldecane	269.8	273.8	276.5	274.7			275
4-Phenyldecane	272.0	275.7	278.0	276.3			
3-Phenyldecane	276.2	279.3	281.4	280.0			
2-Phenyldecane	284.3	286.3	287.1	286.2	307		299
1-Phenyldecane		297.9*		297.9*			
6-Phenylundecane	284.6	288.7	292.0	290.2			285
5-Phenylundecane	286.0	289.9	292.0	290.2			
4-Phenylundecane	288.4	292.0	293.5	291.8			
3-Phenylundecane	293.0	295.0	297.0	295.6			
2-Phenylundecane	300.0	301.9	302.5	301.6	314		298
1-Phenylundecane		313.2*		313.2*			
6-Phenyldodecane	300.0	304.0	306.3	304.5	302	304	209
5-Phenyldodecane	301.0	304.8	306.9	305.1	307	304	316
4-Phenyldodecane	303.9	307.3	308.8	307.2	295	314	343
3-Phenyldodecane	308.1	310.9	312.0	310.7	310	311	318
2-Phenyldodecane	315.5	317.2	317.4	316.5	313	312	310
1-Phenyldodecane		327.6*		327.6*			
7-Phenyltridecane	314.5	318.3	320.4	318.6	313		317
6-Phenyltridecane	314.5	318.3	320.4	318.6			
5-Phenyltridecane	316.0	319.6	321.3	319.6			
4-Phenyltridecane	318.5	321.8	323.1	321.6			
3-Phenyltridecane	322.8	325.5	326.3	325.0			
2-Phenyltridecane	329.5	331.2	331.4	330.6	314		
1-Phenyltridecane		341.3*		341.3*			
7-Phenyltetradecane	328.1	331.8	333.5	331.8			
6-Phenyltetradecane	328.5	332.2	334.0	332.3			
5-Phenyltetradecane	329.8	333.3	335.0	333.4			
4-Phenyltetradecane	332.2	335.3	336.7	335.2			
3-Phenyltetradecane	336.5	339.0	339.7	338.5			
2-Phenyltetradecane	342.5	344.2	344.5	343.7	351		
1-Phenyltetradecane		354*		354*			
8-Phenylpentadecane	341.0	344.6	346.7	345.0			
7-Phenylpentadecane	341.0	344.6	346.7	345.0			
6-Phenylpentadecane	341.7	345.2	347.2	345.6			
5-Phenylpentadecane	343.0	346.3	348.2	346.7			
4-Phenylpentadecane	345.4	348.4	350.0	348.6			
3-Phenylpentadecane	349.2	351.6	352.8	351.7			
2-Phenylpentadecane	355.5	357.0	357.5	356.8			
1-Phenylpentadecane		366*		366*			

* API boiling points.

disilizane-treated Chromosorb P. The principal impurity which originally eluted after 3-phenyldodecane apparently was decomposed to a compound which had an identical retention to 4-phenyldodecane (perhaps the unsaturated analog from dehydration of the alcohol). The purity after preparatory separation was 95.4%. This mixture could not be further purified by preparatory gas chromatography. The

boiling point of this mixture was 310.5° as determined by DTA. Since the two boiling points are within experimental error, the assumption was made that neither the original higher boiling impurity nor the final lower boiling impurity affects the boiling point significantly, and an average value of 310.4° was adopted.

Comparison of the DTA boiling points for 3-phenyldodecane and 7-phenyltridecane with the gas chromatographic uncorrected values in Table II indicates that neither column is behaving exactly as a boiling point column. Since the deviation of boiling points between the two columns increases as the phenyl group moves toward the center of the molecule, a correction was made for the secondary alkylbenzene isomers which is a linear function of the difference between the boiling point of the corresponding primary isomer and the uncorrected boiling point of the secondary isomer. This method of correction was assumed to hold for all secondary isomers in the C_{10} - C_{15} range. This assumption is reasonable in view of the good correlation in Fig. 1 and corresponds to each homologous series having slightly different activity coefficients but the same trend with carbon number. This results in each homologous series having curves parallel to the primary isomers in Fig. 2. The deviations are shown in Fig. 3. The points deviate from a straight line; the deviation amounts to 0.55° for the Apiezon L data and 0.3° for the SF-96 data. This deviation reflects scatter in the gas chromatographic data and errors in the DTA data.

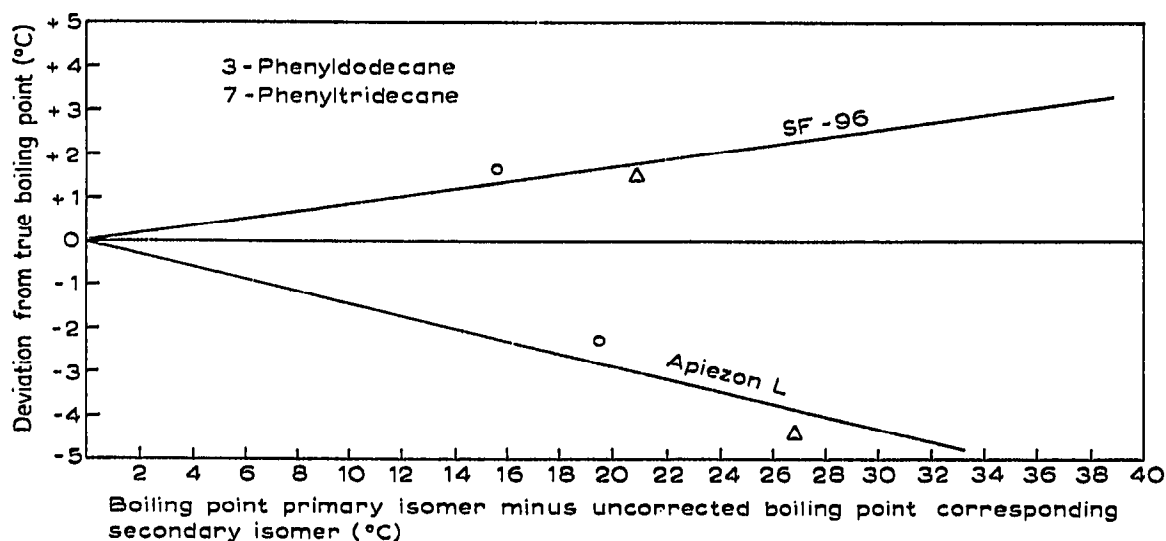


Fig. 3. Corrections to gas chromatographic boiling points.

Applying the correlations derived from Fig. 3 to the data in Table II yields the corrected boiling points shown in Table II. Good agreement is obtained between the two gas chromatographic columns. This is further proof that the assumption of linear correlation of the activity coefficients with the position of attachment of the benzene ring is valid. The slightly larger deviations of the phenyldecane isomers are caused by using an extrapolated section of Fig. 2. The extrapolation is greater for the Apiezon L data and, for this reason, the boiling points from the SF-96 column are considered to be more accurate. These values could be improved if retention data were available for 1-phenyloctane. The boiling point for 5-phenylundecane on the SF-96 column is high because it is not resolved from 5-phenylundecane.

To confirm the correct sequence of boiling points, particularly whether the 2-phenyl isomer boils before or after the lowest boiling isomer of the next higher homolog, gas chromatographic analyses using the above-described SF-96 column were obtained on individual cuts from distillation of a C_{11} - C_{14} alkylbenzene mixture. From the composition of the distillation cuts the distribution of each isomer throughout the distillation was calculated. Fig. 4 is a plot of these isomer distributions *versus* volume per cent overhead in the distillation. The boiling point, as well as per cent overhead, increases toward the right in this plot; thus each isomer is higher

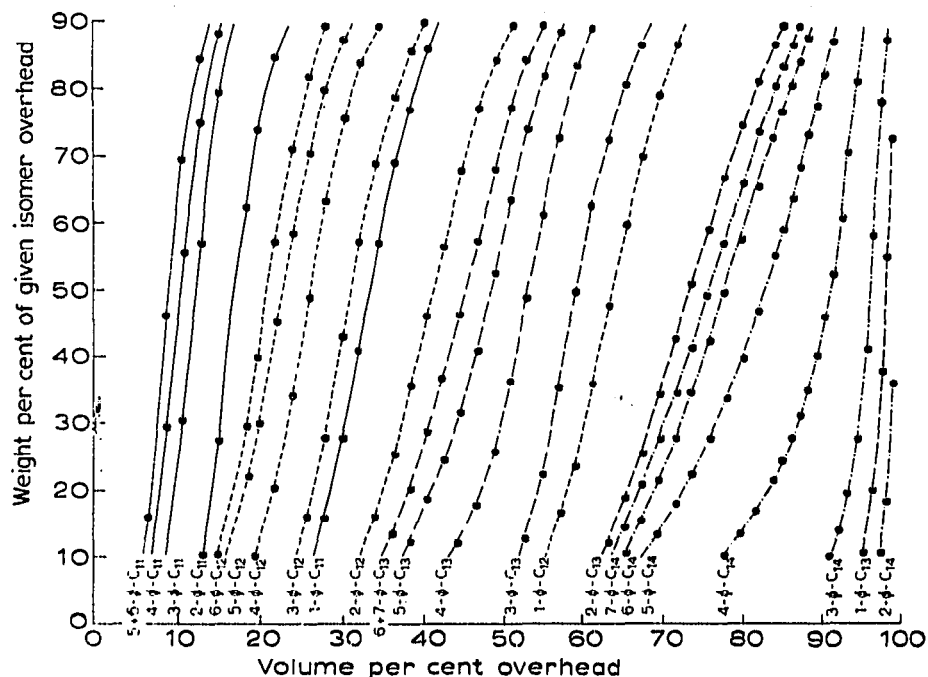


Fig. 4. Distribution of straight chain alkylbenzene isomers during distillation (4 ft. \times 1.4 in. protruded metal packed column at 50 Torr, 20:1 minimum reflux).

boiling than all isomers with curves to the left of it. The sequence of curves shows that: (1) there is no overlap between boiling points of 2-phenyl isomers and the next higher homologs; and (2) the 1-phenyl isomers boil slightly higher than the 3-phenyl isomer of the next higher homolog. These results confirm that the sequence of boiling points obtained by the technique described is correct and that an Apiezon L column gives a sequence that does not entirely correlate with boiling points. With SF-96 silicone fluid all of the straight chain alkylate components elute in the proper order, although the separation between homologs may be exaggerated. These distillation data cannot be used to obtain accurate boiling points because the overhead composition at any time is a mixture of two or more isomers.

CONCLUSIONS

The accuracy of the boiling point data is difficult to determine. Literature values shown in Table II compare rather poorly with the gas chromatographic data. Aside from the usual experimental difficulties in determining boiling points, errors

caused by extrapolating the data to atmospheric pressure are included in all the literature-derived boiling points. The data were extrapolated using nomographs prepared by FERRIS¹². These nomographs were constructed from tables of "Vapor Pressures and Boiling Points at 10-1500 mm Hg" from the API Research Project 44⁸. All of the literature data for the phenyldodecanes show inconsistencies. The data of OLSON which agree most closely with the gas chromatographic data report a higher boiling point for 4-phenyldodecane than for 3-phenyldodecane¹¹. This is also inconsistent with the above distillation data which show that 4-phenyldodecane is lower boiling. The value obtained by OLSON for 2-phenyldodecane is certainly low, based on the distillation data. The remainder of the data reported by OLSON show good agreement with the gas chromatographic data.

Ultimately the accuracy depends on the boiling points of 3-phenyldodecane and 7-phenyltridecane as determined by DTA. Based on API Project 44 reference compounds, the DTA method is accurate to $\pm 0.5^\circ$ or better. With the exception of the phenyldecane isomers, the gas chromatographic boiling points are estimated to be within 1.0° of the true value. The boiling point differences between isomers are estimated to be within 0.5° .

SUMMARY

Boiling points of the secondary C₁₀-C₁₅ straight chain alkylbenzene isomers were obtained from a correlation of gas chromatographic retention times with boiling points of the primary alkylbenzene isomers for which accurate API boiling points are available. Accurate boiling points for the secondary isomers are not available due to the difficulty of obtaining these compounds in pure form. Apiezon L and General Electric SF-96 silicone fluid capillary columns were used to reduce selective interaction of the alkylbenzenes with the liquid phase, but slight interactions necessitated a boiling point correction of $0.7-4.1^\circ$. The correction was determined by independent measurements of the boiling points of 3-phenyldodecane and 7-phenyltridecane using a differential thermal analysis technique. The gas chromatographically determined boiling points are estimated to be within 1° , while boiling point differences between isomers are estimated to be within 0.5° .

REFERENCES

- 1 W. J. CARNES, *Anal. Chem.*, 36 (1964) 1197.
- 2 R. D. SWISHER, E. F. KAEUBLE AND S. K. LIU, *J. Org. Chem.*, 26 (1961) 4066.
- 3 R. D. SWISHER, *Soap Chem. Specialties*, 39, No. 2 (1963) 58.
- 4 R. D. SWISHER, *J. Water Pollution Control Federation*, 35 (1963) 877.
- 5 H. PURNELL, *Gas Chromatography*, John Wiley and Sons, New York, 1962, p. 221.
- 6 H. PURNELL, *Gas Chromatography*, John Wiley and Sons, New York, 1962, p. 207.
- 7 G. J. PIEROTTI, C. H. DEAL, E. L. DERR AND P. E. PORTER, *J. Am. Chem. Soc.*, 78 (1956) 2989.
- 8 *American Petroleum Institute Research Project 44*, Carnegie Institute of Technology, Pittsburgh, Pa.
- 9 E. M. BARRALL, *Anal. Chem.*, 37 (1965) 1053.
- 10 A. W. FRANCIS, *Chem. Rev.*, 42 (1948) 107.
- 11 A. C. OLSON, *Ind. Eng. Chem.*, 52 (1960) 833.
- 12 S. W. FERRIS, *Handbook of Hydrocarbons*, Academic Press, New York, 1955.