Designation: D 3303 – 74

AMERICAN SOCIETY FOR TESTING AND MATERIALS
1916 Race St., Philadelphia, Pa., 19103
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Standard Method for

RAPID GAS CHROMATOGRAPHIC ESTIMATION OF HIGHER BOILING HOMOLOGUES OF CHLORINATED BIPHENYLS FOR CAPACITOR ASKARELS[1]

This Standard is issued under the fixed designation D 3303; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval.

1. Scope

1.1 This method covers a rapid empirical determination of the level of higher boiling homologues in Specification D 2233, Types D and A. Higher boiling homologues are defined in 3.2. This procedure is not intended for the precise analysis of polychlorinated biphenyl products or mixtures.

2. Applicable Documents

2.1 *ASTM Standards:*

D 2233 Specification for Chlorinated Aromatic Hydrocarbons (Askarels) for Transformers[2]

E 260 Recommended Practice for General Gas Chromatography Procedures[2]

E 355 Recommended Practice for Gas Chromatography Terms and Relationships[2]

3. Summary of Method

3.1 *The sample is injected into a support-coated* open tubular gas chromatography column. The components are separated as they pass through the column with helium carrier gas and their presence in the effluent is measured by a flame ionization detector and recorded on a chromatogram. The method is made quantitative by internal normalization comparing the area of the higher boiling homologue peaks to the total area of all the peaks in the chromatogram.

NOTE 1—Reference should be made to Recommended Practices E 260 and E 355.

3.2 This method arbitrarily splits up the chromatogram into two regions. The major region represents mostly mono, di-, tri-, and tetra-chlorobiphenyls. The lesser region represents the higher boiling homologues and is mostly penta- and hexa-chlorobiphenyls. However, there is some overlap of the tetra- and penta-chlorobiphenyls between the two regions. Some of the important peaks in the major region contain both tetra- and penta-chlorobiphenyls.

3.3 The only way to obtain a closer approximation to true composition of these samples is to use a longer column with a gas chromatography-mass spectrometry (GS/MS) combination to correct for the composition of these overlap peaks. Area correction factors must also be used. However, GC/MS instrumentation is not available in many laboratories and is too cumbersome and costly for routine analysis. Therefore, this empirical short method has been adopted. This method yields values that are about 40 % of the true value when the true value is in the range of 1 %.

4. Significance

4.1 Present knowledge indicates that higher boiling homologues of chlorinated biphenyls are less degradable than the lower

[1] This method is under the jurisdiction of ASTM Committee D-27 on Electrical Insulating Liquids and Gases.

Current edition approved Feb. 27, 1974. Published April 1974.

[2] *1974 Annual Book of ASTM Standards*, Part 40.

[3] *1973 Annual Book of ASTM Standards*, Part 30.

MONS 079384

boiling homologues, if present in the environment.

4.2 Because of the disposal method of certain types of capacitors containing these askarels, it is important to limit the higher boiling homologue content.

4.3 This method is used as a process control and acceptance test for Specification D 2233, Type D.

5. Apparatus

5.1 *Chromatograph*—Any gas chromatograph with flame ionization detector and capillary column inlet splitter system.

5.2 *Recorder*, 0 to 1 or 10-mV range with full-scale response time of 1 s and chart speed of approximately ½ in./min.

5.3 *Column*, 50 ft by 0.02 in. inside diameter support-coated open tubular capillary coated with FFAP.[4]

5.4 *Integrator*—Disk chart integrator or electronic digital integrator to measure the peak areas. If an electronic integrator is used, it should be checked initially against a disk chart integrator to determine that the electronic integrator operating parameters have been set properly for correctly measuring the late eluting small peaks.

6. Calibration

6.1 The method of calculation is peak area normalization. The lack of pure knowns prevents the accurate determination of response factors (area correction factors) for the individual components. Therefore, the results are reported as area percent of higher boiling homologues.

6.2 Final check-out of the total chromatographic system for this analysis can best be done using the reference samples of Aroclor 1016 and Aroclor 1242[5] referred to in Section 9.

7. Procedure

7.1 Adjust the chromatograph to the following conditions:

7.2 *Temperatures:*

Column	220°C (isothermal)
Sample inlet system	320°C
Detector	300°C

7.3 *Gas Flow Rates:*

Column	8 ml/min (7 psi) helium
Inlet splitter	210 ml/min helium
Auxiliary or make-up	30 ml/min helium
Hydrogen	Note 2
Air	Note 2

NOTE 2—Adjust air-hydrogen ratio to give maximum detector sensitivity. See the instrument instruction manual.

7.4 *Sample Size*—0.005 ml split 1 to 25.

7.5 Inject 5 µl of the neat sample and allow the chromatogram to proceed at attenuation settings that will keep all the peaks on the scale if the disk chart integrator is being used.

8. Calculation

8.1 Divide the chromatogram into two regions as shown on the accompanying chromatograms.

8.2 Measure the total area of the peaks in each region of the chromatogram.

8.3 Calculate the result as follows:

$$A = (B/C) \times 100$$

where:

A = area % of higher boiling homologues,
B = area of higher boiling homologues, and
C = total area of all peaks.

9. Precision

9.1 Reference samples of Aroclor 1016 and Aroclor 1242 were analyzed in duplicate on two different instruments using both the disk chart integrator and an electronic integrator. An Infotronics Model CRS-100 integrator was used on a Perkin-Elmer Model 800 chromatograph and a Hewlett-Packard Model 3370A integrator was used on a Hewlett-Packard Model 7624A chromatograph. The same column was used in both instruments.

9.2 Results are given in Table 1.

9.3 The above two reference samples were each analyzed five times in another laboratory using a Varian-Aerograph Model 144410-00 gas chromatograph with an Infotronics Model CRS-11-HS electronic integrator. The 95 % confidence limits of the mean were calculated as follows:

[4] Available from Perkin-Elmer Corp., as Part No. 0105-0884. Specify that the column should be coated with Free Fatty Acid Phase (FFAP), trademark for the liquid phase of Varian-Aerograph, available from Varian Instruments, 611 Hansen Way, Palo Alto, Calif. 94303.

[5] Portions of these two reference samples are available from Dr. E. M. Emery, Monsanto Co., Mail Zone T3E, 800 N. Lindbergh Blvd., St. Louis, Mo. 63166.

95 % confidence limits of mean = $+/- \frac{tS}{\sqrt{5}}$

where:

t = 2.78 (for five measurements,
S = estimated standard deviation, and
= (0.43) (range of five measurements)

Results:

	Aroclor 1016	Aroclor 1242
Mean	0.35	6.80
S	0.0043	0.129
95 % confidence limits	0.0053	0.160

10. Sensitivity and Detection Limit

10.1 These values were determined in accordance with Recommended Practice E 260 for biphenyl on the Perkin-Elmer Model 800 Gas Chromatograph.

Results:

Sensitivity = S
= 2.37 × 10^4 mV min/millimole

Detection Limit = Q_L
= 2.82 × 10^{-5} millimoles/ml

TABLE 1 Area Percent Higher Boiling Homologues

Chromatograph	Method of Integration		
	Disk Chart	Infotronics CRS-100	Hewlett-Packard 3370A
Aroclor 1016:			
Perkin-Elmer 800	0.30, 0.27	0.23, 0.21	0.27, 0.28
Hewlett-Packard 7624A	0.30, 0.30	...	
Aroclor 1242:			
Perkin-Elmer 800	5.88, 5.78	6.22, 5.94	6.63, 6.50
Hewlett-Packard 7624A	6.14, 6.32	...	

MONS 079385

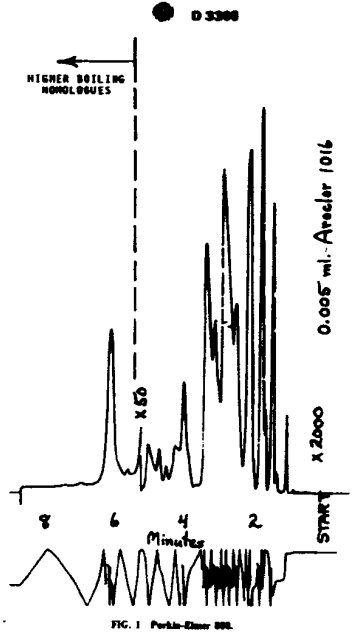

FIG. 1 Perkin-Elmer 800.

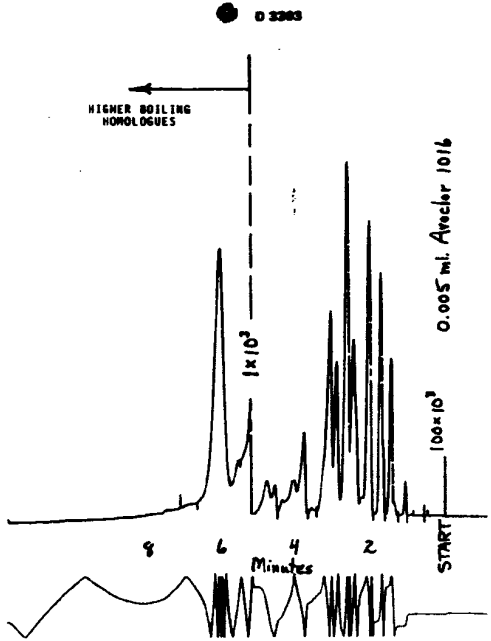

FIG. 2 Hewlett-Packard 7624A.

MONS 079386

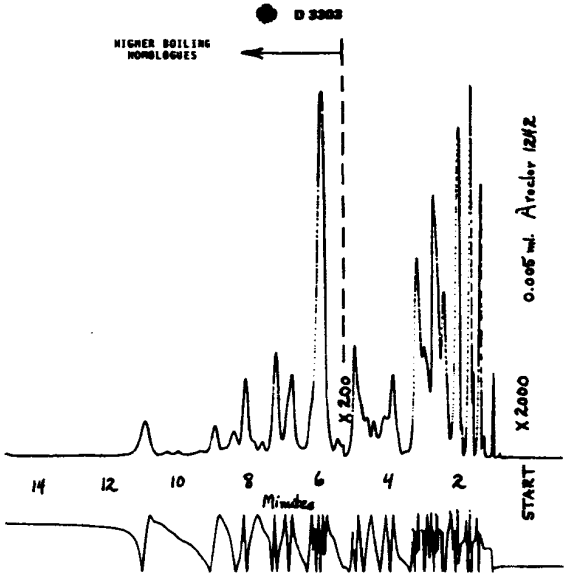

FIG. 3 Perkin-Elmer 880.

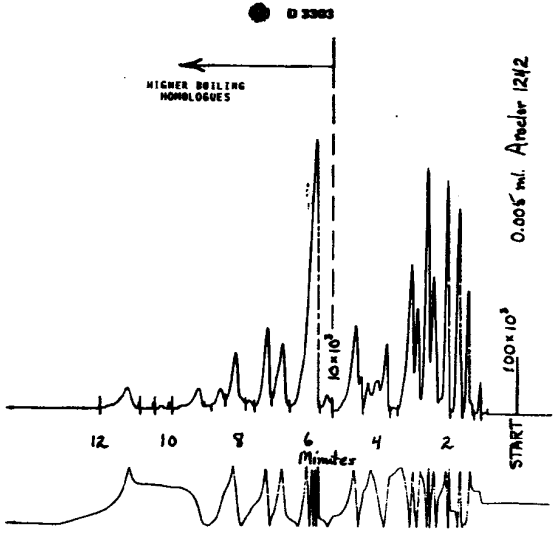

FIG. 4 Hewlett-Packard 7624A.

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MONS 079387