Designation: D 5310 – 00

Standard Test Method for Tar Acid Composition by Capillary Gas Chromatography[1]

This standard is issued under the fixed designation D 5310; 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. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method covers the quantitative determination of phenol and certain homologues of phenol in tar acid and cresylic acid mixtures using capillary gas chromatography. It is a normalization test method that determines homolog distribution but is not an absolute assay since it does not account for water or other compounds not detected by a flame ionization detector.

1.2 The following applies to all specified limits in this standard: for purposes of determining conformance with this standard, an observed value or a calculated value shall be rounded off "to the nearest unit" in the last right-hand digit used in expressing the specification limit, in accordance with the rounding-off method of Practice E 29.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* For specific hazard statements, see Section 8.

2. Referenced Documents

2.1 *ASTM Standards:*

D 3852 Practice for Sampling and Handling Phenol and Cresylic Acid[2]

D 4790 Terminology of Aromatic Hydrocarbons and Related Chemicals[2]

E 29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications[3]

2.2 *Other Documents:*

OSHA Regulations, 29 CFR, paragraphs 1910.1000, and 1910.1200[4]

3. Terminology

3.1 For definition of terms used in this test method see Terminology D 4790.

4. Summary of Test Method

4.1 The sample composition is determined by capillary gas chromatography. The weight percent composition is calculated from the ratio of the individual peak areas to the total area of all peaks using appropriate response factors determined for each component by means of a calibration sample.

5. Significance and Use

5.1 This test method is suitable for the general quantitative analysis of commercial tar acid mixtures. It may be used as a tool for quality control and specification purposes by producers and users.

6. Apparatus

6.1 *Chromatograph*—A gas chromatograph compatible with capillary columns, equipped with inlet splitter and high temperature flame ionization detector. Typical Operating Conditions are given in Table 1.

6.2 *Peak Integrator*—Electronic integration is recommended.

6.3 *Recorder*, with full scale response time of 1 s or less.

6.4 *Microsyringe*, capacity of 1 μL.

6.5 *Capillary Column*—Any column capable of resolving all components of interest. Prepared columns are commercially available from chromatography supply houses. Chromatograms from three columns are presented in Fig. 1, Fig. 2, and Fig. 3. Peak identification is given in Table 2.

7. Reagents and Materials

7.1 *Calibration Standards*—Samples of known composition representative of samples to be analyzed.

8. Hazards

8.1 Consult current OSHA regulations and suppliers' material safety data sheets, and local regulations for all materials used in this test method.

9. Sampling

9.1 Sample the material in accordance with Practice D 3852.

10. Calibration

10.1 Prepare a sample of known composition to contain each component in the approximate concentration expected in

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[1] This test method is under the jurisdiction of ASTM Committee D16 on Aromatic Hydrocarbons and Related Chemicals and is the direct responsibility of Subcommittee D16.02 on Oxygenated Aromatics.

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[2] *Annual Book of ASTM Standards*, Vol 06.04.

[3] *Annual Book of ASTM Standards*, Vol 14.02.

[4] Available from Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20402.

TABLE 1 Typical Chromatographic Operating Conditions

Column Liquid Phase	Diisodecyl Phthalate	Cyanopropyl 25 %, Phenyl 25 %, Methylpolysiloxane 50 %, Bonded Phase	Dimethyl 95 %, Diphenylpolysiloxane 5 %, Bonded Phase
Column	Fused Silica	Fused Silica	Fused Silica
Column length, m	30	25	30
Column ID, mm	0.25	0.22	0.25
Film thickness,µ m	0.2	0.2	0.25
Column temperature,° C	100	100	105
Detector temperature,° C	200–275	200–275	200–275
Injection block temperature, °C	200–275	200–275	200–275
Carrier gas	H_2 or He	H_2 or He	H_2 or He
Carrier flow, linear velocity, cm/s	40–80	40–80	40–80
Hydrogen flow to flame, mL/min	30–40 (optimize)	30–40 (optimize)	30–40 (optimize)
Air flow to flame	~10·H_2 flow (optimize)	~10·H_2 flow (optimize)	~10·H_2 flow (optimize)
Make up gas[A]	N_2 or He	N_2 or He	N_2 or He
Sample size, µL	0.05–0.1	0.05–0.1	0.05–0.1
Split ratio	100:1 to 250:1	100:1 to 250:1	100:1 to 250:1

[A] Inert gas added to hydrogen fuel gas as coolant to prevent overheating and thermal emissions for optimal detector operations; each instrument should be optimized according to manufacturer's recommendations.

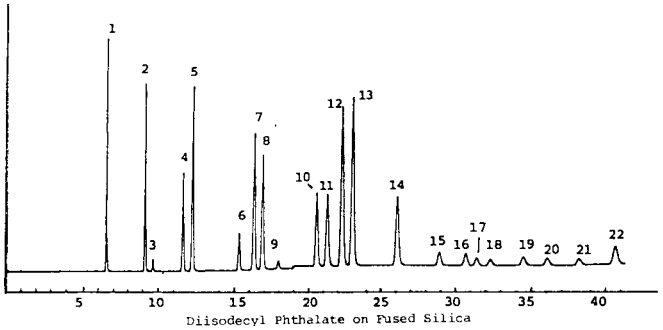

FIG. 1 Typical Chromatogram of Cresylic Acid on Column of Diisodecyl Phthalate on Fused Silica

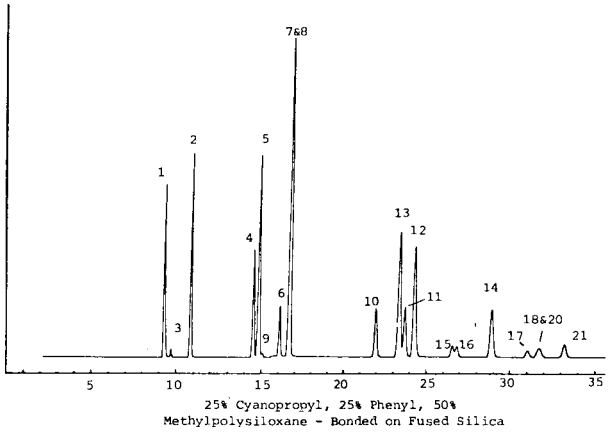

FIG. 2 Typical Chromatogram of Cresylic Acid on Column of 25 % Cyanopropyl, 25 % Phenyl, 50 % Methylpolysiloxane—Bonded on Fused Silica

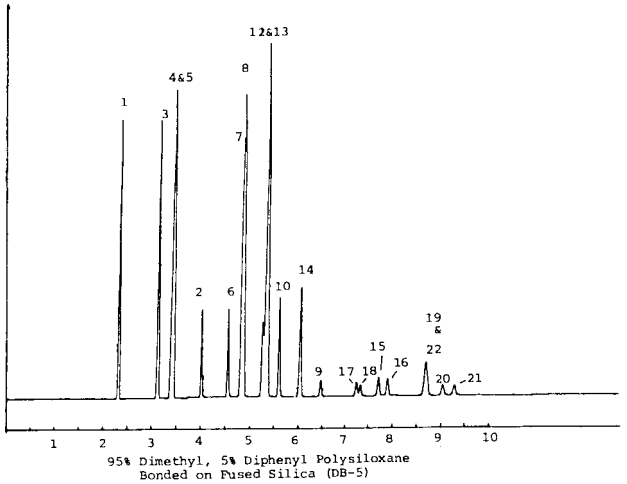

FIG. 3 Typical Chromatogram of Cresylic Acid on Column of 95 % Dimethyl, 5 % Diphenyl Polysiloxane Bonded on Fused Silica (DB-5)

the unknown sample. Make sure that each component in the preparation is of known purity. Even when purchased as reagent grade, it is prudent to verify impurities, including water.

10.2 Inject an appropriate amount of the calibration sample from 10.1 into the chromatograph and allow to run till all components clear the column. Fig. 1, Fig. 2, and Fig. 3 are chromatograms of a cresylic acid blend illustrating typical separations and retention times.

10.3 Determine a response factor for each component. Choose one of the major components as the reference peak, and calculate response factors relative to the reference peak. The response factor for the reference peak will be 1.

$$RF_i = \frac{(C_i)(A_r)}{(A_i)(C_r)}$$

where:

RF_i = response factor for component,
A_i = area of component peak,
C_i = concentration of component peak, in weight percent,
A_r = area of reference peak, and
C_r = concentration of reference peak, in weight percent.

11. Procedure

11.1 Inject a portion of the unknown sample into the chromatograph, identical to that used for the standard sample, and obtain the chromatogram.

12. Calculation

12.1 Determine the weight percent for each component in the sample by calculating the corrected area for each component peak in the sample and dividing the corrected area by the summation of all the corrected areas and multiplying by 100.

TABLE 2 Compound Identification of Chromatographic Peaks in Figs. 1-3

NOTE 1—Compounds are listed in order of elution on diisodecyl phthalate column.

Number	Compound
1	phenol
2	o-cresol
3	2,6-xylenol
4	p-cresol
5	m-cresol
6	o-ethylphenol
7	2,4-xylenol
8	2,5-xylenol
9	2,4,6-trimethylphenol
10	2,3-xylenol
11	p-ethylphenol
12	m-ethylphenol
13	3,5-xylenol
14	3,4-xylenol
15	4-ethyl, 2-methylphenol
16	5-ethyl, 2-methylphenol
17	p-isopropylphenol
18	m-isopropylphenol
19	3-ethyl, 2-methylphenol
20	2,4,5-trimethylphenol
21	2,3,5-trimethylphenol
22	3-ethyl, 5-methylphenol

$$C_i = \frac{(RF_i)(A_i)}{\sum_{i=1}^{n} (RF_i)(A_i)} \times 100$$

where:

C_i = concentration of the component in weight percent,

RF_i = response factor for component i calculated in calibration,

A_i = area of the component, *i* peak, and

$\sum_{i=1}^{n} (RF_i)(A_i)$ = the summation of all response corrected areas in the chromatogram.

13. Report

13.1 Report each component to the nearest 0.01 % weight.

13.2 All components should total 100 %.

14. Precision and Bias [5]

14.1 The following criteria should be used to judge the acceptability (95 % probability level) of the results obtained by this test method. The criteria were derived from an interlaboratory study between six laboratories, using chromatographic columns of diisodecyl phthalate on fused silica. The data were obtained on two days by the same operator in each laboratory and three samples with components ranging in concentration from 0.04 % to 98.5 %.

14.1.1 *Intermediate Precision*—Results in the same laboratory should not be considered suspect unless they differ by more than the amount shown in Table 3.

TABLE 3 Intermediate Precision and Reproducibility

	Average Weight Percent	Intermediate Precision	Reproducibility
Phenol	0.04	0.012	0.020
	2.41	0.054	0.063
	14.82	0.171	0.189
o-cresol	0.16	0.026	0.037
	0.17	0.080	0.125
	82.94	0.133	0.164
p-cresol	0.65	0.029	0.038
	5.44	0.055	0.071
	25.27	0.262	0.262
m-cresol	9.33	0.101	0.109
	59.46	0.177	0.248
	98.53	0.093	0.176
o-ethylphenol	0.07	0.011	0.015
	0.17	0.008	0.020
	0.41	0.048	0.061

14.1.2 *Reproducibility*—Results submitted by two laboratories should not be considered suspect unless they differ by more than the amount shown in Table 3.

14.2 *Bias*—Although the interlaboratory study utilized samples prepared gravimetrically from pre-analyzed stocks of the highest available purity, the samples were not approved as accepted reference materials. Consequently, no bias is reported for this test method.

15. Keywords

15.1 cresols; cresylic acid; gas chromatography; phenol; tar acid; xylenols

[5] Supporting data are availalbe from ASTM International Headquarters. Request RR: D16-1013.