Designation: D5310 – 10 (Reapproved 2014)

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

This standard is issued under the fixed designation D5310; 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 In determining the conformance of the test results using this method to applicable specifications, results shall be rounded off in accordance with the rounding-off method of Practice E29.

1.3 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.4 *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:*[2]

D3852 Practice for Sampling and Handling Phenol, Cresols, and Cresylic Acid

D4790 Terminology of Aromatic Hydrocarbons and Related Chemicals

D6809 Guide for Quality Control and Quality Assurance Procedures for Aromatic Hydrocarbons and Related Materials

E29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications

2.2 *Other Documents:*

OSHA Regulations, 29 CFR paragraphs 1910.1000, and 1910.1200[3]

3. Terminology

3.1 For definition of terms used in this test method see Terminology D4790.

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.

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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] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[3] Available from U.S. Government Printing Office Superintendent of Documents, 732 N. Capitol St., NW, Mail Stop: SDE, Washington, DC 20401, http://www.access.gpo.gov.

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.

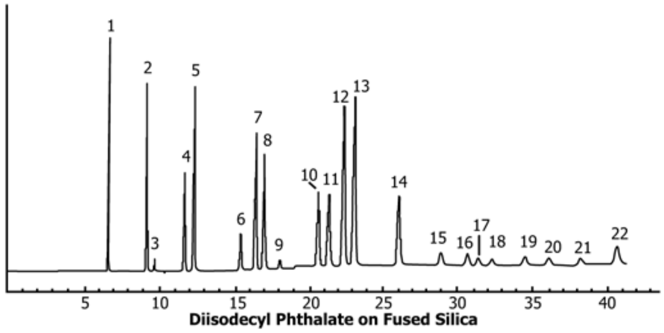

FIG. 1 Typical Chromatogram of Cresylic Acid on Column of Diisodecyl Phthalate on Fused Silica

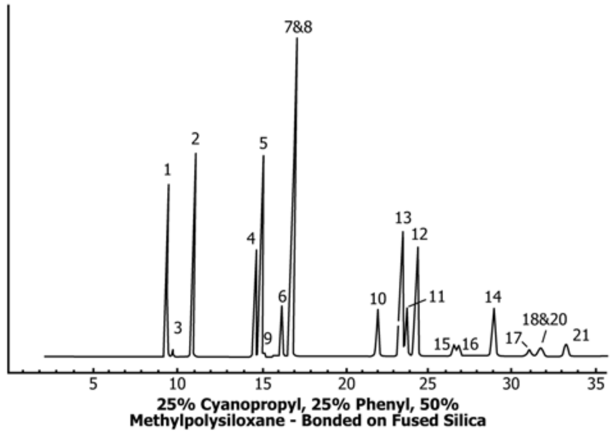

FIG. 2 Typical Chromatogram of Cresylic Acid on Column of 25 % Cyanopropyl, 25 % Phenyl, 50 % Methylpolysiloxane—Bonded on Fused Silica

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 D3852.

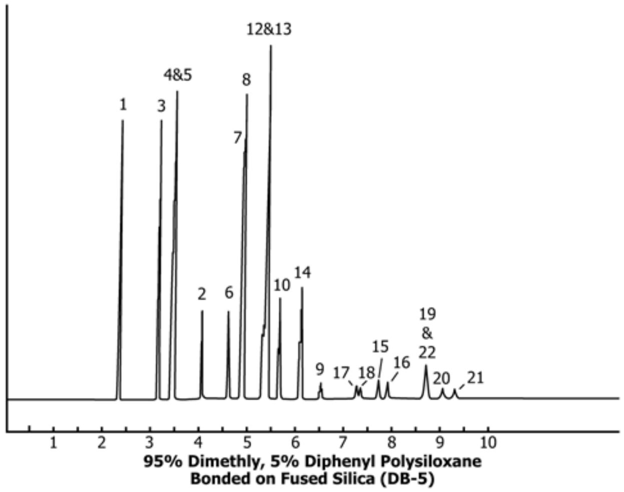

FIG. 3 Typical Chromatogram of Cresylic Acid on Column of 95 % Dimethyl, 5 % Diphenyl Polysiloxane Bonded on Fused Silica

10. Calibration

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

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

$$RF_{\mathrm{i}} = \frac{(C_{\mathrm{i}})(A_{\mathrm{r}})}{(A_{\mathrm{i}})(C_{\mathrm{r}})}$$

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.

$$C_{\mathrm{i}} = \frac{(RF_{\mathrm{i}})(A_{\mathrm{i}})}{\sum_{i=1}^{n}(RF_{\mathrm{i}})(A_{\mathrm{i}})} \times 100$$

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
$\sum_{i=1}^{n}(RF_{\mathrm{i}})(A_{\mathrm{i}})$ = 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 %.

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. Precision and Bias[4]

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.

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. Quality Guidelines

15.1 Laboratories shall have a quality control system in place.

15.1.1 Confirm the performance of the test instrument or test method by analyzing a quality control sample following the guidelines of standard statistical quality control practices.

15.1.2 A quality control sample is a stable material isolated from the production process and representative of the sample being analyzed.

15.1.3 When QA/QC protocols are already established in the testing facility, these protocols are acceptable when they confirm the validity of test results.

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[4] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D16-1013. Contact ASTM Customer Service at service@astm.org.

15.1.4 When there are no QA/QC protocols established in the testing facility, use the guidelines described in Guide D6809 or similar statistical quality control practices.

16. Keywords

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

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