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Standard Test Method for *p*-Phenylenediamine Antidegradants Purity by Gas Chromatography[1]

This standard is issued under the fixed designation D4937; 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 determination of the purity of Class I, II, and III *p*-phenylenediamine (PPD) antidegradants as described in Classification D4676 by gas chromatography (GC) detection and area normalization for data reduction.

1.2 The values stated in SI units are to be regarded as the standard. The values given in parentheses are for information only.

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.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D3853 Terminology Relating to Rubber and Rubber Latices—Abbreviations for Chemicals Used in Compounding

D4483 Practice for Evaluating Precision for Test Method Standards in the Rubber and Carbon Black Manufacturing Industries

D4676 Classification for Rubber Compounding Materials—Antidegradants

E260 Practice for Packed Column Gas Chromatography

2.2 *ISO Standard:* [3]

ISO 6472 Rubber Compounding Ingredients—Abbreviations

3. Terminology

3.1 *Definitions:*

3.1.1 *area normalization*, *n*—a method of calculating the percent composition by measuring the area of each observed peak and dividing each peak area by the total area. This assumes that all peaks are eluted and that each component has the same detector response.

3.1.2 *lot sample*, *n*—a production sample representative of a standard production unit, normally referred to as the sample.

3.1.3 *specimen*, *n*—the actual material used in the analysis. It must be representative of the lot sample.

3.2 *Abbreviations*—The following abbreviations are in accordance with Terminology D3853 and ISO 6472:

3.2.1 77PD—*N,N′*bis-(1,4-dimethylpentyl)-*p*-phenylenediamine.

3.2.2 DTPD—*N,N′*-ditolyl-*p*-phenylenediamine.

3.2.3 IPPD—*N*-isopropyl-*N′*-phenyl-*p*-phenylenediamine.

3.2.4 PPD—*p*-phenylenediamine.

3.2.5 6PPD—*N*-(1,3 dimethylbutyl)-*N′*-phenyl-*p*-phenylenediamine.

4. Summary of Test Method

4.1 The analysis is performed by temperature programmed GC utilizing either a packed column (Procedure A) or a capillary column (Procedure B). Quantification is achieved by area normalization using a peak integrator or laboratory data system.

5. Significance and Use

5.1 This test method is designed to assess the relative purity of production PPDs. These additives are primarily used as antiozonants for tires and other rubber or polymeric products.

5.2 Since the results of this test method are based on area normalization, it assumes that all components are eluted from the column and each component has the same detector response. Although this is not strictly true, the errors introduced are relatively small and much the same for all samples; thus, they can be ignored since the intent of the test method is to establish relative purity.

5.3 Although trace amounts of "low boilers" are present in production samples, they are disguised by the solvent peak when using packed columns (Procedure A).

6. Interferences

6.1 Utilizing the chromatographic conditions prescribed there are no significant co-eluting peaks; however, degradation of column performance could result in interference problems.

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[1] This test method is under the jurisdiction of ASTM Committee D11 on Rubber and is the direct responsibility of Subcommittee D11.11 on Chemical Analysis.

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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 the American National Standards Institute, 25 W. 43rd St., 4th Floor, New York, NY 10036.

Thus, when using the packed column it is essential that the total system be capable of 5000 theoretical plates before being used for this analysis. The evaluation of system efficiency is described in 7.4.

7. Apparatus

7.1 *Gas Chromatograph*:

7.1.1 *Procedure A: Packed Column*—Any high-quality temperature programmed gas chromatograph equipped with a thermal conductivity detector (see Note 1) is sufficient for this analysis. Refer to Practice E260 for general gas chromatography practices.

NOTE 1—Although a thermal conductivity detector is recommended, a flame ionization detector can be used if appropriate adjustment is made for flow rate and specimen size. Since this probably would involve using a smaller diameter column, the adjustment in flow and injection volume should be proportional to the cross-sectional area of the column. A procedure for this calculation is included at the end of Section 9.

7.1.2 *Procedure B: Capillary Column*—A temperature programmable unit with flame ionization detector (FID) equipped for capillary columns. When utilizing the full capillary columns (0.25 mm), a split injection system is required; however a "cold on-column" injector is preferred for the wide bore (0.53 mm) capillaries. The FID should have sufficient sensitivity to give a minimum peak height response of 30 µV for 0.1 mass % of 6PPD when operated at the stated conditions. Background noise at these conditions is not to exceed 3 µV.

7.2 *Gas Chromatographic Columns*:

7.2.1 *Packed Column for Procedure A*—1.828 m × 6.35 mm (6 ft × ¼ in.) outside diameter × 4 mm (0.16 in.) inside diameter glass columns packed with 10 % methyl silicone fluid (100 %) on 80/100 mesh acid washed and silanized diatomite support. The column should be conditioned with a helium flow of approximately 20 cm^3/min by programming from ambient temperature to 350°C at the rate of 2 to 3°C/min and holding at 350°C overnight with the detector disconnected.

7.2.2 *Capillary Column for Procedure B*—(*1*) 30 m × 0.25 mm ID fused silica capillary, internally coated to a film thickness of 0.25 µm (bonded) with methyl silicone; (*2*) 15 m × 0.53 mm fused silica (megabore) capillary with 3.0 µm bonded film of 5 % phenyl silicone, HP-5 or equivalent.

7.3 *Integrator/Data System*, capable of determining the relative amount of each component by means of integration of the detector output versus time. When using capillary columns (Procedure B) the device must integrate at a sufficiently fast rate so that narrow peaks (one second peak width) can be accurately measured.

7.4 When using a packed column, a minimum of 5000 theoretical plates, as measured from the 6PPD peak, with the chromatographic conditions stated in 9.1 is required for analysis. Theoretical plates (*TP*) are determined by the following formula:

$$TP = 5.5\,[X(R)/Y(0/5)]^2 \quad (1)$$

where:

$X(R)$ = retention time measured from the injection point to the apex of the 6PPD peak (adjust the attenuation to keep peak on scale), mm, and

$Y(0.5)$ = 6PPD band width at half-height, mm.

8. Calibration and Standardization

8.1 When using the conditions described for Procedure A (packed column), the detector response of 6PPD for injections of 500 to 5000 µg was found to be somewhat nonlinear (see X1.3). However, over the more limited range, 750 to 2500 µg, the response was nearly linear (see X1.4). As a result, it is suggested that the samples be prepared so that 1250 to 1500 µg injections are made.

8.2 Chromatograms from typical specimens run on the packed columns according to the prescribed procedure are given in Appendix X1.

9. Procedure

9.1 *Procedure A—Chromatographic Conditions:*

Helium flow rate	50 cm^3/min
Injection port temperature	300°C
Initial column temperature	100°C
Heating rate	8°C/min
Final Temperature	350°C
Detector temperature	350°C
Detector: TC attenuation	8

9.1.1 Integrator/data system parameters are presented in X1.2.

9.1.2 *Specimen Preparation*—To ensure specimen homogeneity, lot samples of 6PPD should be ground with a mortar and pestle prior to weighing the test unit. In the case of liquid 6PPD where partial crystallization may have occurred resulting in fractionation, the lot sample should be melted in a 50° to 60°C oven with occasional stirring, prior to weighing the test unit.

9.2 *Procedure A—Analysis*:

9.2.1 Weigh 2.5 to 3.0 g specimen (to the nearest milligram) into a 10 cm^3 volumetric flask, dilute to volume with methylene chloride, and shake well to dissolve.

9.2.2 When the instrument has equilibrated at the initial conditions described in 9.1, inject 5.0 mm^3 (µL) of sample solution and initiate the temperature program and data collection.

9.2.3 When the run is complete, inspect the chromatogram and output data for proper appearance and peak identification (see X1.1).

9.2.4 Repeat the run described in 9.2.2 on the same specimen.

NOTE 2—Specimen size and carrier gas flow rates should be adjusted in accordance with the cross-sectional area of the column utilized. For example, if a nominal ⅛ in. outside diameter column (1.87 mm inside diameter) is used rather than a ¼ in. outside column (3.54 mm inside diameter), the adjustment would be as follows: The ratio of cross-sectional areas is [3.54/1.87] squared, which equals 3.6. Thus, the sample size and helium carrier flow rate should be decreased by this factor; that is, the flow rate of 50/3.6 or 14 cm^3/min and sample size to 5/3.6 or 1.4 mm^3(µL).

9.3 *Procedure B: Chromatographic Conditions*—The suggested operating conditions for the analysis using a capillary column are given in Table 1. Column (1) is for a standard capillary and Column (2) is for a megabore capillary.

9.4 *Procedure B—Sample Analysis*:

TABLE 1 Procedure B—Chromatographic Conditions

Column	(1) 30 m × 0.25 mm	(2) 15 m × 0.53 mm	
Stationary Phase	bonded methyl silicone	bonded 5 % phenyl silicone	
Film thickness	0.25 µm	3.0µ m	
Carrier gas	(helium)	(helium)	
Linear velocity at 100°C	0.34 m/sec	NA	
Flow rate	1.0 cm^3/min	30.0 cm^3/min	
Head pressure	60 kPa, gauge (9 psig)	NA	
Detector	FID	FID	
Detector Temperature	300°C	300°C	
Injection Port Temperature	300°C	oven tracking	
Hydrogen Flow Rate[A]	30 cm^3/min	30 cm^3/min	
Air Flow Rate[A]	300 cm^3/min	300 cm^3/min	
Makeup Gas	Nitrogen or Helium	Nitrogen or Helium	
Makeup Flow Rate[A]	29 cm^3/min	10 cm^3/min	
Split Ratio	180:1	(no split)	
Column Temperature Program		Ramp A	Ramp B
Initial temperature	42°C	35°C	240°C
Program rate	9°C/min	15°C/min	8°C/min
Final temperature	300°C	240°C	290°C
Time at final temperature	22 min	3 min	17 min
Sample Size	0.4 mm^3(µL)	1 mm^3(µL)	
Solvent	methylene chloride	methylene chloride	
Sample Concentration	10 mg/cm^3	3 mg/cm^3	

[A]Consult the manufacturer's manual for optimum selection of flow rates on different instruments.

9.4.1 Prepare the sample as in 9.1.2 and the test specimen according to Table 1.

9.4.2 When the instrument has equilibrated at the initial conditions described in Table 1, inject the indicated amount of diluted test specimen and immediately start the recorder, integrator, and column temperature programming sequence.

9.4.3 When the run is complete, inspect the chromatogram and output data for proper appearance and peak identification. Typical chromatograms on the 0.53 mm megabore capillary is shown in Figs. X2.1-X2.4 (6PPD) respectively.

9.4.4 Repeat the run described in 9.4.2 on the same specimen.

10. Calculation

10.1 Calculate the relative area percent of 6PPD and the other identified components as follows:

$$A = (A_C/A_T) \times 100\ \% \quad (2)$$

where:

A = area of 6PPD, %,
A_C = area of component, and
A_T = total area.

11. Report

11.1 Report the following information:

11.1.1 The combined area of all unidentified peaks as percent other,

11.1.2 All results to the nearest 0.1 %, and

11.2 The final report should include proper identification of the specimen and the data from the two individual injections plus their average.

12. Precision and Bias—Procedure A

12.1 This precision and bias section has been prepared in accordance with Practice D4483. Refer to Practice D4483 for terminology and other statistical details.

12.1.1 The precision results in this precision and bias section give an estimate of the precision of this test method with the materials (antidegradants) used in the particular interlaboratory programs as described below. The precision parameters should not be used for acceptance/rejection testing of any group of materials without documentation that they are applicable to those particular materials and the specific testing protocols that include this test method.

12.2 A Type 1 (interlaboratory) precision was evaluated in 1987. Both repeatability and reproducibility are short term. A period of a few days separates replicate test results. A test result is the mean value, as specified by this test method, obtained on two determinations or measurements of the property or parameter in question.

12.3 Four different materials were used in the interlaboratory program. These were tested in four laboratories on two different days.

12.4 The results of the precision calculations for repeatability and reproducibility are given in Table 2, in ascending order of material average or level, for each of the materials evaluated.

12.5 The precision of this test method may be expressed in the format of the following statements which use an "appropriate value" or *r, R,* (*r*), or (*R*), that is, that value to be used in decisions about test results (obtained with the test method).

TABLE 2 GC Purity of PPD'S, Percent (Procedure A)

Material	Average	Within Laboratory[A]			Between Laboratory[A]		
		S_r	r	(r)	S_R	R	(R)
M1-6PPD	97.09	0.1651	0.4673	0.481	1.926	5.45	5.61
M2-IPPD	96.05	0.2792	0.7900	0.822	1.239	3.50	3.65
M3-77PD	96.05	0.1121	0.3172	0.330	1.382	3.91	4.07
M4-DTPD	94.85	0.2894	0.8191	0.864	2.080	5.88	6.20
Pooled values[B]	96.01	0.2301	0.6512	0.678	1.6588	4.6943	4.889

[A]

S_r = repeatability standard deviation.
r = repeatability = 2.83 times the square root of the repeatability variance.
(r) = repeatability (as a percent of material average).
S_R = *reproducibility standard deviation.*
R = reproducibility = 2.83 times the square root of the reproducibility variance.
(R) = reproducibility (as a percent of material average).
[B]No values omitted.