Designation: D 5666 – 95 (Reapproved 2000)

Standard Test Method for P-Phenylenediamine Antidegradants—Purity by High Performance Liquid Chromatography[1]

This standard is issued under the fixed designation D 5666; 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 purity of Type I, II and III *p*-phenylenediamine (PPD) antidegradants as described in Practice D 4676 by high performance liquid chromatography using ultraviolet detection and external standard calculations.

1.2 Expertise in high performance liquid chromatography (HPLC) is necessary to the successful application of this test method.

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:*

D 3853 Terminology Relating to Rubber and Rubber Latices—Abbreviations for Chemicals Used in Compounding[2]

D 4483 Practice for Determining Precision for Test Method Standards in the Rubber and Carbon Black Industries[2]

D 4676 Classification for Rubber Compounding Materials—Antidegradants[2]

2.2 *ISO Standards:*[3]

ISO 5725 Precision of Test Methods

ISO 6472 Rubber Compounding Ingredients—Abbreviations

3. Terminology

3.1 *Definitions:*

3.1.1 *external standard calculation*—a method of calculating the percent composition by measuring the area of the analyte peak, multiplying by a response factor, and dividing by the sample concentration. All components are assumed to be resolved from the component of interest.

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

3.1.3 *specimen*—the actual material used in the analysis, also known as the test portion. It must be representative of the lot sample.

3.2 *Abbreviations*—The following abbreviations are in accordance with Terminology D 3853 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 A specimen is dissolved in acetonitrile and a fixed loop volume is analyzed by isocratic HPLC using a thermostated C18 reversed phase column and an ultraviolet (UV) detector. Peak areas are determined using a chromatographic integrator or laboratory data system with the amount of analyte being determined by external calibration.

5. Significance and Use

5.1 This test method is designed to determine the purity of *p*-phenylenediamine antidegradants.

5.2 Since the results of this test method are based on an integrated peak area as determined by HPLC, it is assumed that all analytes of interest are resolved from interfering peaks.

6. Interferences

6.1 Components co-eluting with the analyte of interest will cause erroneous results; thus it is required that the system be capable of providing a minimum of 10 000 theoretical plates.

7. Apparatus

7.1 *Liquid Chromatograph*, consisting of the following:

7.1.1 Precision chromatographic pump,

7.1.2 Variable wavelength UV detector,

7.1.3 A method for thermostating the column at 35 ± 1°C, for example, a column oven or water jacket,

7.1.4 A fixed injector made of either a 20 mm^3 (µL) rheodyne loop or an automatic sampler.

7.2 *HPLC Columns*, consisting of:

7.2.1 A precolumn packed with C18 grafted silica with particle size of 35 to 40 µm (100 to 150 mm), and

7.2.2 A column of 10- to 15-cm length packed with C18

[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.

Current edition approved Feb. 15, 1995. Published April 1995.

[2] *Annual Book of ASTM Standards*, Vol 09.01.

[3] Available from American National Standards Institute, 11 W. 42nd St., 13th Floor, New York, NY 10036.

grafted silica with particle size of 3 to 5 µm.

7.3 *Integrator/Data System*, capable of determining absolute amounts of analyte of interest by means of integration of detector output versus time.

7.4 *Analytical Balance*, capable of measuring within ±0.01 mg.

7.5 *Shaking Machine*, or ultrasonic tank.

7.6 *Volumetric Flask*, 100 cm^3.

7.7 *Syringes*, with rheodyne loop, 2 cm^3.

7.8 *Clear Screw—top Vials*, with suitable septa, 125 cm^3.

8. Reagents and Materials

8.1 *Acetonitrile*, HPLC grade.

8.2 *Ethanolamine*, HPLC grade.

8.3 *Water*, HPLC grade or double distilled water or water of resistivity greater than 2 megohms/cm.

9. Calibration and Standardization

9.1 A primary standard of known purity is used to determine the response factor for each analyte.

10. Procedure

10.1 *Chromatographic Conditions*:

10.1.1 Determine the eluant phase composition and the flow rate by adjusting the chromatographic parameters for the particular column chosen. The eluant phase consists of the appropriate mixture of HPLC grade acetonitrile and HPLC grade or equivalent water, both containing 0.2 kg/m ^{3}(g/L) ethanolamine or less according to the product to be tested.

NOTE 1—Different liquid chromatography columns may exhibit different elution characteristics. See Table 1 for suggested chromatographic starting parameters for analysis.

10.2 *Detector*—Monitor the absorbance of the sample at the prescribed wavelength. The detector should be set to 1 absorbance unit full scale (AUFS).

10.3 *Integrator/Data System*—The integrator settings should be adjusted to give a full-scale response to 1 absorbance unit (AU).

10.4 *Sample Storage Before Analysis*— Samples must always be stored in a refrigerator.

10.5 *Standard Preparation*—Weigh the clear vial to the nearest 0.1 mg, introduce approximately 20 mg of the standard using a spatula and weigh the standard and vial to the nearest 0.1 mg. Using a volumetric flask, add 100 cm^3 of acetonitrile to the vial. Stopper the vial so that it is hermetically sealed immediately after adding the solvent. Dissolve the product at 23 ± 3°C in the ultrasonic bath tank or on the shaking machine. The standard must be analyzed within 4 h of being prepared.

TABLE 1 Suggested Chromatographic Starting Parameters

	N,N′-dialkyl-paraphenylene-diamine 77-PPD	N-aryl-N′-alkyl-paraphenylene-diamine IPPD 6-PPD	N,N′-diaryl-paraphenylene-diamine DPPD DTPD
Eluant phase			
% acetonitrile	85	65	70
% Water	15	35	30
Ethanolamine (g/L)	0.2	0.1	0.1
Flow rate (cm^3/min)	1	1	1
Wavelength (nm)	260	290	280

NOTE 2—*Preparation of Standards*—The analytical standards are prepared by multiple recrystallizations or distillations of the paraphenylenediamines. The procedure can be repeated until the desired purity is obtained. The purity of the standard is estimated by gradient HPLC analysis of the impurities and Differential Thermal Analysis (DTA). The impurities in the standard should be reestimated every 90 days by HPLC. The standard should be stored at 5°C or lower.

10.6 *Sample Preparation*—To ensure sample homogeneity, 5 g of sample should be ground with a mortar and pestle.

10.7 *Sample Analysis*:

10.7.1 Weigh at least 20 mg to the nearest 0.1 mg of the sample in a clear vial and dissolve it in 100 cm^3 acetonitrile following the procedure in 10.5. The sample must be analyzed within 4 h of being prepared.

10.7.2 *Injection of the Solutions*:

10.7.2.1 *Manual Method*—Take approximately 100 µL of the solution using a syringe and inject a quantity greater than the volume of the rheodyne loop, that is, approximately 60 µl for a 20-µl loop. Rinse the syringe with solvent and dry.

10.7.2.2 *Automatic Method*—Put the flasks containing the sample and standard solutions in place and program the automatic sampler.

10.7.3 Chromatograph the samples using parameters as prescribed in 10.1.1.

11. Calculation

11.1 *Response Factor*—Calculate the response factor for the standard by dividing the concentration of the standard by the measured area count and multiplying this by the purity of the standard:

$$RF = (\text{concentration/area count}) \times \%\ \text{purity} \quad (1)$$

NOTE 3—Throughout the calculation the units of concentration must be consistent (that is, kg/m^3(mg/cm^3)).

11.2 *Product Purity*—To determine the purity of the product, multiply the response factor by the measured area count of the analyte and divide by the sample concentration:

$$\%\ \text{purity} = \text{RF} \times \text{area count/sample concentration} \quad (2)$$

12. Report

12.1 Report percent paraphenylenediamine to the nearest 0.1 %.

13. Precision and Bias [4]

13.1 This precision and bias section has been prepared in accordance with Practice D 4483. Refer to Practice D 4483 for terminology and other statistical details.

13.1.1 The precision results in this precision and bias section give an estimate of the precision of this test method with the materials 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

[4] Supporting data are on file at ASTM Headquarters, Request RR: D11-1063.

those particular materials and the specific testing protocols that include this test method.

13.2 This precision and bias data was obtained in an interlaboratory test organized in France in 1992. In this program one material was analyzed by 13 different laboratories. Six measurements were taken over six days by one to three operators. Statistical evaluation was carried out in accordance with ISO 5725-1986 which is equivalent to the calculation algorithms of Practice D 4483. The results from this precision and bias study are given in Table 2.

13.3 *Repeatability*—The difference between two single test results (or determinations) found on identical test material under the repeatability conditions prescribed for a particular test will exceed the repeatability (*r*), as given in Table 2, on an average of not more than once in twenty cases in the normal and correct operation of the test method.

TABLE 2 Precision (Type 1)—Paraphenylenediamine Purity

Material	Mean[A] level	Within laboratories[B]			Between laboratories[B]		
		S_r	r	(r)	S_R	R	(R)
6PPD	95.27	0.335	0.948	0.995	0.441	1.248	1.31

[A]Mean level values (in percent).
[B]Symbols are defined as follows:
S_r= within laboratory standard deviation,
r = repeatability (in measurement units),
(r) = repeatability (in percent),
S_R = *between laboratory standard deviation,*
R = reproducibility (in measurement units),
(R) = reproducibility (in percent)

13.4 *Reproducibility*—The difference between two single and independent test results found by two operators working under prescribed reproducibility (*R*) conditions in different laboratories on identical test material will exceed the reproducibility (*R*), as given in Table 2, on an average of not more than once in twenty cases in the normal and correct operation of the test method.

13.5 *Bias*—Sample impurities that are not resolved from the analyte of interest will produce a falsely high result. There may be other sources of bias that have not been determined.

14. Keywords

14.1 antidegradant; high performance liquid chromatography; N-isopropl-N′-phenyl-*p*-phenylenediamine (IPPD); N-(1;3 dimethylbutyl)-N′-phenyl-*p*-phenylenediamine (6PPD); N; N′ bis-(1;4-dimethylpentyl)-*p*-phenylenediamine (77PD); N; N′-ditolyl-*p*-phenylenediamine (DTPD);*p*-phenylenediamine (PPD)

APPENDIX

(Nonmandatory Information)

X1. RECOMMENDATIONS

X1.1 De-gas the eluents.

X1.2 Use an appropriate guard column.

X1.3 Acid-clean the glassware.

X1.4 Keep the temperature of the samples and standard the same.