



Standard Practice for Rubber—Chromatographic Analysis of Antidegradants (Antioxidants, Antiozonants and Stabilizers)¹

This standard is issued under the fixed designation D 3156; 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 practice covers the detection and identification by thin-layer chromatography of antidegradants (antioxidants, antiozonants, and stabilizers), that may be present in raw rubber or rubber products. Analysis for other types of antidegradants is possible as long as the requirements of the practice are met.

1.2 The values stated in SI units are to be regarded as the standard.

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 Document

2.1 ASTM Standards:

D 297 Test Methods for Rubber Products—Chemical Analysis²

3. Summary of Practice

3.1 A simplified procedure (Method A, Section 13.1) based on a single-solvent system is presented, which provides for the identification of known materials. This may be used to check the presence or absence in a rubber vulcanizate or raw rubber, of an antidegradant which should be present. However, since the chromatograms obtained may not be absolutely specific for any given antidegradant, a more detailed scheme is given in 13.2.

3.2 Method B, Section 13.2, using additional solvents and sprays is included, which enables a greater degree of separation of the spots to be made and therefore may enable detection and identification of an unknown antidegradant.

3.3 Other techniques, for example: gas chromatographic (with or without treatment to obtain derivatives), spectroscopic (ultraviolet and infrared), more sophisticated thin-layer variations (two dimensional techniques), may be applied to identification of spots for improved detection and identification of an unknown antidegradant.

3.4 It is possible that the chromatographic pattern of one antidegradant may overlap that of another antidegradant; therefore each laboratory must prepare its own reference standards, based on the technique chosen from this practice.

4. Significance and Use

4.1 This practice is useful for the examination of rubber compounds or products for the presence of chemicals that prevent or greatly reduce degradation due to oxygen, ozone, or other agents.

4.2 This practice is suitable for quality assurance, factory control, and research and development applications.

5. Interferences

5.1 In the absence of extender oils, antidegradants are extracted from the rubber by a solvent and the evaporated extract is applied directly to a thin-layer chromatographic plate.

5.2 In the presence of extender oils, the oils are removed by either a pre-treatment of the plate, with light petroleum ether or by a column chromatographic technique.

5.3 Identification of the antidegradant is made by the standard technique of thin-layer chromatography, herein described.

6. Apparatus

6.1 *Spreading Device*, for making thin layer chromatographic plates with a coating 250 to 300 μm thick.

6.2 *Glass Plates*, 200 by 200-mm, or suitable for the selected tank. As an alternative to preparing plates, the use of precoated plates with a coating of 250 to 300 μm is permitted. Precoated film-backed plates are not recommended.

6.3 *Drying Oven*, 105°C minimum.

6.4 *Desiccator*, or drying box for storing plates at fixed humidity.

6.5 *Micro-pipets*, 5 and 10-mm³ (μL).

6.6 *Chromatographic Developing Tank*, of a size suitable to hold plates, approximately 250 by 250 by 70 mm to 330 by 240 by 110 mm. Small “sandwich-type” tanks are not recommended. Add about 200 cm³ of developing solvent (7.4) to the tank, swirl, cover, and allow to stand 15 min before using. Tank may be reused by repeating the swirling and standing step, as long as the solvent ratio remains constant.

6.7 *Extraction Apparatus*, in accordance with Section 18 or 25 of Test Methods D 297.

¹ This practice is under the jurisdiction of ASTM Committee D-11 on Rubber and is the direct responsibility of Subcommittee D11.11 on Chemical Analysis.

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

6.8 *Chromatographic Columns*, short, liquid-solid. Those found satisfactory are as follows:

6.8.1 *Hypodermic Syringe Barrel*, 5-cm³, fitted with a needle about 35 mm in length and 1.27 mm outside diameter (No. 18 BWG).

6.8.2 *Glass Tubes*, 120 mm in length and 10 to 12 mm in diameter, holding about 5 cm³ of silica gel.

7. Reagents

7.1 *Plate Adsorbent*—Silica gel containing calcium sulfate.³ Silica gel containing a fluorescent indicator may be useful in some cases to allow visualization of spots (before spraying) with ultraviolet light.

7.2 *Column Adsorbent*—Silica gel 200 to 600 µm (30 to 70-mesh),⁴ activated by drying at 110°C for at least 2 h, if dry in that period, or overnight (±16 h) for convenience.

7.3 *Solvents*—Use of fume hoods with volatile and toxic solvents is *mandatory*. Approved health and safety precautions should be observed for the use of any solvent or chemical mentioned in this procedure. ACS grade or equivalent should be used.

7.3.1 *Methanol*.

7.3.2 *Acetone*.

7.3.3 *Isopropanol*.

7.3.4 *Light Petroleum Ether*.

7.3.5 *Chloroform*.

7.3.6 *Toluene*.

7.3.7 *Ethyl Acetate*.

7.3.8 *n-Hexane*.

7.3.9 *n-Heptane*.

7.3.10 *Cyclohexane*.

7.3.11 *Diethylamine*.

7.3.12 *Ammonium Hydroxide* (NH₄OH, 28–30 % ammonia NH₃).

7.3.13 *Water*—References to water shall be understood to mean distilled water or water of equal purity.

7.4 *Developing Solvents*:

7.4.1 *Test Method A*—90 parts *n*-heptane and 10 parts ethyl acetate by volume.

7.4.2 *Test Method B*, used in the following order:

7.4.2.1 *Toluene*.

7.4.2.2 95 parts toluene and 5 parts ethyl acetate by volume.

7.4.2.3 75 parts cyclohexane and 25 parts diethylamine by volume.

7.4.2.4 50 parts toluene and 50 parts *n*-heptane by volume.

7.4.3 Additional developing solvents which may prove useful for special problems:

7.4.3.1 100 parts toluene, 5 parts acetone and 0.1 part ammonium hydroxide (NH₄OH).

7.4.3.2 100 parts toluene, 5 to 10 parts acetone and 0.1 to 0.2 parts NH₄OH.

7.5 *Spray Reagents for Color Development*:

7.5.1 *Amines*:

7.5.1.1 *Diazotized Sulfanilic Acid*—0.5 g of sulfanilic acid and 0.5 g of potassium nitrite (KNO₂) dissolved in 100 cm³ of

1 *M* hydrochloric acid (HCl). Make fresh daily.

7.5.1.2 *Benzoyl Peroxide* (4 % solution in toluene).

7.5.1.3 *Tollen's Reagent* (0.5 cm³ of 5 % silver nitrate (AgNO₃) solution + 2 drops of 2 *M* sodium hydroxide (NaOH). Dissolve the precipitate in as little 2 % ammonium hydroxide (NH₄OH) as possible, and add an equal volume of 96 % alcohol.

7.5.1.4 *Bismuth Nitrate* (Bi(NO₃)₃) (7.5 g) dissolved in a mixture of 1 cm³ of concentrated nitric acid (HNO₃, density 1.42 Mg/m³) in 150 cm³ of distilled water.

7.5.1.5 *Tetracyanoethylene* (ethenetetracarbonitrile)—Saturated solution in methylene chloride.

7.5.2 *Phenols*:

7.5.2.1 *Overspray*, for use with solution 7.5.1.1 1-*M* sodium hydroxide (NaOH) solution.

7.5.2.2 *p*-Nitrophenyldiazonium Fluoroborate (1 % solution in methanol containing 0.5 % hydrochloric acid (HCl, density 1.16 Mg/m³).

7.5.2.3 2,6 *Dichloroquinonechlorimide* (0.1 % solution in methanol or toluene)—Used with 7.5.2.4.

7.5.2.4 *Buffer Spray*, for use with 7.5.2.3—Dissolve 23.4 g of sodium tetraborate (Na₂B₄O₇ · 10H₂O) and 3.3 g of sodium hydroxide (NaOH) in 1 dm³ of water.

7.6 Reagents for preliminary “screening” tests are as follows:

7.6.1 *Ferric Chloride Solution*—Mix 0.5 g of anhydrous ferric chloride (FeCl₃) with 100 cm³ of ethanol or 3A alcohol.

7.6.2 *Ferric Sulfate Solution*—Mix 1 g of ferric sulfate (FeSO₄)₃ with 100 cm³ of water.

7.6.3 *Hydroxylamine Hydrochloride Solution*—Mix 1.0 g of hydroxylamine hydrochloride with 100 cm³ of water.

7.6.4 *p*-Nitroaniline Solution—Mix 2.8 g of *p*-nitroaniline with 32 cm³ of hydrochloric acid (density 1.16 Mg/m³). Dilute to 250 cm³ with water.

7.6.5 *Sodium Nitrite Solution*—Mix 1.44 g of sodium nitrite (NaNO₂) with 250 cm³ of water.

7.6.6 *Glacial Acetic Acid* (99.7 % w/w).

7.6.7 *Titanium Tetrachloride Solution*—Mix the contents of one 5-cm³ ampoule of titanium tetrachloride (TiCl₄) with 1 dm³ of acetic acid (7.6.6).

7.6.8 *Anhydrous Alcohols*—Ethanol, 3A alcohol, or isopropanol.

8. Plate Preparation

8.1 Make a slurry of 2 parts of water to 1 part of silica gel (7.1) by mass. Immediately, spread the slurry evenly over the glass plate with the spreading device. The layer thickness should be 250 to 300 µm. Allow the plates to stand at room temperature to set the binder. Dry for 45 min at 105°C.

8.2 Plates may be spotted while warm, if it has been proven that no decomposition of the antidegradant sought, takes place. Spotting, while warm, sometimes results in more compact spots.

8.3 Plates may be stored in a desiccator over silica gel. Unused plates should be reactivated after 4 days standing.

8.4 Before using, make “lanes” on the plate, about 20 mm in width, by scoring with a knife or scribe. If this step leads to uneven development from lane to lane, eliminate.

³ Silicagel G., from E. Merck A.G., Darmstadt, Germany, or equivalent has been found satisfactory.

⁴ Silicagel #7733 from E. Merck A.G., or equivalent, has been found satisfactory.