



Designation: D3452 – 06 (Reapproved 2021)

## Standard Practice for Rubber—Identification by Pyrolysis-Gas Chromatography<sup>1</sup>

This standard is issued under the fixed designation D3452; 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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

*This standard has been approved for use by agencies of the U.S. Department of Defense.*

### PART 1. IDENTIFICATION OF SINGLE POLYMERS

#### 1. Scope

1.1 This practice covers the identification of polymers in raw rubbers, and cured and uncured compounds, based on a single polymer, by the gas chromatographic patterns of their pyrolysis products (pyrograms). Implementation of this guide presupposes a working knowledge of the principles and techniques of gas chromatography, sufficient to carry out this practice and to interpret the results correctly.<sup>2</sup>

1.2 This practice will identify the following polymers:

1.2.1 Polyisoprene of natural or synthetic origin,

1.2.2 Butadiene-styrene copolymers,

1.2.3 Polybutadiene,

1.2.4 Polychloroprene,

1.2.5 Butadiene-acrylonitrile copolymers,

1.2.6 Ethylene-propylene copolymers and related terpolymers, and

1.2.7 Isobutene-isoprene copolymers.

1.3 This practice will not differentiate the following polymers:

1.3.1 Natural polyisoprene from synthetic polyisoprene.

1.3.2 Butadiene-styrene copolymers produced by solution and emulsion polymerization. It is sometimes possible to distinguish butadiene-styrene copolymers containing different amounts of styrene as well as random polymers from block polymers.

1.3.3 Polybutadiene with different microstructures.

1.3.4 Different types of polychloroprenes.

1.3.5 Butadiene-acrylonitrile copolymers with different monomer ratios.

<sup>1</sup> This practice is under the jurisdiction of ASTM Committee D11 on Rubber and Rubber-like Materials and is the direct responsibility of Subcommittee D11.11 on Chemical Analysis.

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<sup>2</sup> Definitions of terms and general directions for the use of gas chromatography may be found in Practices E355 and E260.

1.3.6 Ethylene-propylene copolymers with different monomer ratios, as well as the copolymers from the related terpolymers.

1.3.7 Isobutene-isoprene copolymers (butyl rubbers) from halogenated butyl rubbers.

1.3.8 Polyisoprene containing different amounts of *cis-trans* isomers.

1.3.9 The practice does not identify ebonite or hard rubbers.

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

1.5 *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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.6 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

#### 2. Referenced Documents

2.1 *ASTM Standards*:<sup>3</sup>

D297 Test Methods for Rubber Products—Chemical Analysis

E260 Practice for Packed Column Gas Chromatography

E355 Practice for Gas Chromatography Terms and Relationships

#### 3. Significance and Use

3.1 For research, development, and quality control purposes, it is advantageous to determine the composition of rubbers in cured, compounded products.

<sup>3</sup> For referenced ASTM standards, visit the ASTM website, [www.astm.org](http://www.astm.org), or contact ASTM Customer Service at [service@astm.org](mailto:service@astm.org). For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

3.2 This practice provides such composition analysis, utilizing a gas chromatograph and pyrolysis products from rubber decomposition.

#### 4. Principle of the Practice

4.1 This practice is based upon comparison of the gas chromatographic pattern of the pyrolysis products of a known rubber with an unknown rubber. The results of this separation will hereafter be referred to as the pyrogram.

4.2 The pyrogram of the known rubber is filed for future reference. The pyrogram of the unknown rubber is compared to this for identification.

4.3 The success of the method depends upon examining the known and unknown rubbers under exactly the same experimental conditions.

4.4 The qualitative composition of the pyrolysis products depend upon the type of polymer being studied.

4.5 The quantitative composition of the pyrolysis products may be affected by the degree of cure, and recipe used, etc., but the most important factor is the type of pyrolysis device.

#### 5. Apparatus

5.1 *Pyrolysis Devices*—The applicability of this practice has been checked on the following types:

5.1.1 *Quartz Tubes*, electrically heated at a prefixed temperature. The volatile products enter the chromatograph through heated tubing.

5.1.2 *Platinum Filaments*, electrically heated. Pyrolysis is carried out within the chromatograph inlet and immediately swept into the column by the carrier gas.

5.1.3 *Small Coils of Ferromagnetic Wire*, heated to the Curie point temperature. The volatile products enter the gas chromatograph through heated tubing.

5.2 *Gas Chromatograph*—The applicability of this practice has been checked on a wide variety of gas chromatographs, employing both flame ionization and thermal conductivity detectors. Any commercially available instrument is satisfactory. Dual-column operation and temperature programming is strongly recommended, but not mandatory.

5.3 *Gas Chromatographic Columns*—The applicability of this practice has been checked on a wide variety of column lengths, diameters, supports, and liquid phases. The only requisite is that there be sharp separation between the following: isobutene, butadiene, isoprene, vinylcyclohexene, styrene, and dipentene.

5.4 *Carrier Gas*—The applicability of this practice has been checked with both helium and nitrogen as the carrier gas. Both are satisfactory.

#### 6. Sample Size

6.1 For thermal conductivity detection and electrically heated platinum filaments, a sample size of approximately 3 mg has been found satisfactory. This could be increased or decreased depending on the composition of the sample and the capacity of the probe.

6.2 For flame ionization and either Curie point apparatus or electrically heated platinum filaments, a sample size ranging from 0.2 to 2.0 mg has been found satisfactory.

#### 7. Procedure

7.1 *Extraction*—Although not mandatory, some benefits may be obtained from extraction of the sample according to Test Methods **D297**, Sections 18 and 25. If the sample has been extracted prior to obtaining the pyrogram, the known must also be extracted.

7.2 *Pyrolysis*—The following conditions apply to the three types of pyrolysis devices in **5.1**:

7.2.1 *Quartz Tubes (5.1.1)*—Place 1 to 5 mg of sample in a small quartz or porcelain boat in the cold part of the pyrolysis tube. Stopper the tube and flush with carrier gas. Transfer the boat to the hot part of the tube, maintained at 500 to 800°C. Length of the time depends upon the pyrolysis device; however, time and temperature must be kept constant. To minimize condensation, convey the volatile pyrolysis products into the gas chromatograph through tubing heated to a known, fixed temperature, but slightly higher than the gas chromatograph inlet. Record the pyrogram.

7.2.2 *Electrically Heated Platinum Filaments (5.1.2)*—Place the required amount of sample in the pyrolysis probe. Insert it into the injection port of the gas chromatograph and allow the base line to stabilize. Energize the probe, using the procedure recommended by the manufacturer of the unit to obtain temperatures of 800 to 1200°C.

7.2.3 *Curie Point Apparatus (5.1.3)*—Place the required amount of sample in the coils of ferromagnetic wire or wrap the wire securely around the required amount of sample and pyrolyze according to the manufacturer's directions for proper use of the unit. Energize the apparatus to obtain the required temperature of 550 to 650°C (depending on the composition of the alloy used for the wire) and introduce the pyrolysis products into the gas chromatograph. Record the pyrogram.

7.3 *Separation of the Volatile Pyrolysis Components*—As stated in **5.3**, a wide variety of columns may be used. As an example, the following describes the separation of volatile pyrolysis components by means of suitable columns. Analysis of the products of polyisoprene pyrolysis are used in this example. In all cases, equivalent materials may be used.

7.3.1 *Polar Liquid Phase*—Stainless steel tubing, 4 to 6 m long, with an outside diameter of 3.2 mm (1/8 in.), packed with 10 to 20 % *di*(2-ethylhexyl)sebacate on a 150 to 180- $\mu$ m diatomaceous silica support.<sup>4</sup> Carrier gas flow of 0.2 to 0.3 cm<sup>3</sup>/s. Inlet and detector temperature at 170°C. Oven temperature 50°C isothermal until isoprene is completely eluted, then program at 20 to 40°C/min to 150°C and maintain at this temperature until the dipentene is eluted.

7.3.2 *Non-Polar Liquid Phase*—Stainless steel tubing, 3 m long, with an outside diameter of 3.2 mm (1/8 in.), packed with

<sup>4</sup> The sole source of supply of diatomaceous silica (Chromosorb P) known to the committee at this time is Johns-Manville Products Corp., Celite Div., 22 E. 40th St., NY, NY 10016. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,<sup>1</sup> which you may attend.