



Designation: D3452 – 06 (Reapproved 2017)

## 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.

Current edition approved May 1, 2017. Published May 2017. Originally approved in 1975. Last previous edition approved in 2012 as D3452 – 06 (2012). DOI: 10.1520/D3452-06R17.

<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 and health 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.

10 % high vacuum grease on a 150 to 180- $\mu\text{m}$  diatomaceous silica support. Carrier gas flow of 0.12 to 0.83  $\text{cm}^3/\text{s}$ . Inlet temperature of 170 to 200°C. Oven temperature at 50°C isothermal for 3 min or until isoprene is eluted, then raise the temperature to 130 to 150°C at 4 to 6°C/min. Maintain at the higher temperature until the dipentene is eluted.

## 8. Rubber Identification (Interpretation of the Pyrogram)

8.1 Each rubber type shows a distinctive pyrogram, under the same pyrolysis and gas chromatographic conditions.

8.2 Identification is achieved by comparing the pyrogram of the sample rubber (unknown) to the pyrogram of the known rubber, under exactly the same operating conditions.

8.3 Some rubbers produce very characteristic hydrocarbons and their identification is relatively easy. Examples of this type are:

8.3.1 Polyisoprene rubbers, which yield mainly isoprene and dipentene.

8.3.2 Butadiene-styrene copolymers, which yield mainly butadiene, vinyl cyclohexene, and styrene.

8.3.3 Polybutadiene rubbers, which yield mainly butadiene and vinyl cyclohexene.

8.3.4 Isobutene-isoprene copolymers, which yield mainly isobutylene.

8.4 Some rubbers do not yield very characteristic hydrocarbons. Careful inspection of the pyrogram is required. Supplementary tests, such as those for halogen and nitrogen may be an aid to more definite identification.

8.5 It is recommended that, in addition to maintaining a library of pyrograms, the analyst compare the unknown sample with a known, which appears most like his unknown, at the time of analysis. In this manner, slight variations in operating parameters, which might influence the pyrogram, might be avoided.

## 9. Precision and Bias

9.1 No statement is made about either precision or bias for Practice D3452 since this practice is intended primarily for the identification of polymers and their relative ratios and not the absolute levels of the polymers in the compounds being studied.

## PART 2. IDENTIFICATION OF BLENDS OF POLYMERS

### 10. Scope

10.1 This practice is a guide to the identification of blends of rubbers in the raw, vulcanized, and unvulcanized state by the gas chromatographic patterns of pyrolysis products (pyrograms). Implementation of this guide presupposes a working knowledge of the principles and techniques of gas chromatography, sufficient to carry out the practice, as written, and to interpret the results correctly.

10.2 Two methods are described, depending upon the nature of the blend.

10.2.1 *Method A*—This method is used when styrene-butadiene copolymers are absent. The absence of the styrene peak, in a preliminary pyrogram, indicates this type of blend. Method A will identify blends of the following:

10.2.1.1 Polyisoprene of natural or synthetic origin,

10.2.1.2 Butadiene,

10.2.1.3 Isobutene-isoprene copolymers, and

10.2.1.4 Halogenated isobutene-isoprene rubbers.

10.2.2 *Method B*—This method is used when butadiene-styrene copolymers are present. The presence of the styrene peak, in a preliminary pyrogram, indicates this type of blend. The method fails if other styrene polymers or copolymers or unextractable styrene-containing resins are present. Method B is particularly suitable for the identification of polybutadiene in blends with styrene-butadiene copolymers. If the presence of polybutadiene in the unknown rubber can be excluded, use Method A. Method B will identify butadiene-styrene copolymers with blends of the following:

10.2.2.1 Polyisoprene of natural or synthetic origin,

10.2.2.2 Butadiene, and

10.2.2.3 Isobutene-isoprene copolymers and halogenated isobutene-isoprene rubbers.

10.3 Methods A and B will not differentiate the following in blends:

10.3.1 Natural polyisoprene from synthetic polyisoprene,

10.3.2 Polybutadiene containing different microstructures,

10.3.3 Isobutene-isoprene copolymers and their related halogenated rubbers, and

10.3.4 Styrene-butadiene copolymers with different monomer ratios or different microstructures.

## 11. Referenced Document

11.1 See Section 2.

## 12. Significance and Use

12.1 See Section 3.

## 13. Principle of the Practice

13.1 See Section 4 in addition to the following:

13.1.1 *Method A*—This method is based upon the identification of the characteristic hydrocarbon in the pyrogram of the unknown rubber. The identification of the characteristic hydrocarbon is achieved by comparison of retention times under the same chromatographic conditions for a known rubber as for an unknown rubber. These retention times can be obtained from pyrograms of known rubbers or by direct injection of the pure hydrocarbon into the chromatograph.

13.1.2 *Method B*—This method is based upon the identification of the peaks of vinylcyclohexene and styrene and their retention times, as in Method A. Identification of the butadiene peaks is useful but not strictly necessary.

13.2 The success of Method A or B depends upon examining the unknown rubber under exactly the same gas chromatographic conditions as were used for preparation of the calibration tables of Section 16.

## 14. Apparatus

14.1 See Section 5 in addition to the following:

14.1.1 All the devices in accordance with 5.1 may be used in Part 2, but the Curie point device is especially recommended when Method B is used.

14.2 See 5.2. Dual-column operation and temperature programming is strongly recommended, especially when Method B is used. Some means of integration is strongly recommended but not mandatory.

14.3 See 5.4. Nitrogen is the preferred carrier gas when the Curie point device is used. It should not be used with a thermal conductivity detector.

## 15. Procedure

15.1 Sections 6 and 7 apply whether Method A or B is used.

## 16. Calibration

16.1 *Method A*—Since the successful application of this guide to the analysis of rubber blends, using either Method A or B, depends upon a knowledge of the retention times of styrene, butadiene, vinylcyclohexene, isoprene, dipentene, and isobutene, the retention times of these hydrocarbons must be known. Retention times of the hydrocarbon can be found from injection of each individual hydrocarbon into the chromatograph or by pyrolysis of rubbers which will yield these hydrocarbons. This information must be obtained using the same equipment and operating conditions as will be used for analysis of unknown rubbers. Tabulate this data for ready reference.

### 16.2 *Method B*:

16.2.1 Record a pyrogram of a reference vulcanizate prepared with a suitable styrene-butadiene copolymer and three or more reference vulcanizates based on known blends of the same butadiene-styrene copolymer and polybutadiene in the range of 80 butadiene-styrene to 20 butadiene and 20 butadiene-styrene to 80 butadiene.

NOTE 1—Since the amount of free styrene produced by pyrolysis depends upon the microstructure of the styrene-butadiene rubber and its content of bound styrene, the calibration table must be prepared using the proper copolymer.

16.2.2 Measure the areas of the vinylcyclohexene and styrene peaks.

16.2.3 Calculate a ratio,  $A$ , as follows:

$$A = \frac{S}{S+3K} \quad (1)$$

where:

$A$  = ratio of styrene to vinylcyclohexene,  
 $S$  = area of the styrene peak,  
 $K$  = area of the vinylcyclohexene peak, and  
 $3$  = empirical factor.

16.2.4 Plot the ratio,  $A$ , against the known blend composition.

## 17. Identification

### 17.1 *Method A*:

17.1.1 Pyrolyze the test portion in accordance with Section 7 and measure the retention times of the characteristic hydrocarbon peaks.

17.1.2 Compare the retention times as obtained in 17.1.1 with the retention times of the known hydrocarbons tabulated in accordance with Section 16, and identify the unknown rubber.

### 17.2 *Method B*:

17.2.1 Pyrolyze the test portion in accordance with Section 7 and measure the retention times of the vinylcyclohexene and styrene peaks.

17.2.2 Obtain the area of the peaks of 17.2.1.

17.2.3 Calculate the ratio of these peaks as in 16.2.3.

17.2.4 Determine the ratio of polybutadiene-styrene to butadiene copolymer from the calibration curve of 16.2.4.


NOTE 2—If the polybutadiene content is less than 20 % in the blend, as read from the calibration curve of 16.2.4, polybutadiene may be present but its presence is questionable. If polybutadiene content is more than 20 %, as read from the calibration curve of 16.2.4, polybutadiene is definitely present. Quantities of styrene-butadiene less than 20 % are easily identified as long as the styrene peak can be found in the pyrogram.

## 18. Precision and Bias

18.1 No statement is made about either precision or bias for Practice D3452 since this practice is intended primarily for the identification of polymers and their relative ratios and not the absolute levels of the polymers in the compounds being studied.

## 19. Keywords

19.1 GC; gas chromatography; pyrogram; pyrolysis; rubber composition; rubber identification

 **D3452 – 06 (2017)**

*ASTM International takes no position respecting the validity of any patent rights asserted in connection with any item mentioned in this standard. Users of this standard are expressly advised that determination of the validity of any such patent rights, and the risk of infringement of such rights, are entirely their own responsibility.*

*This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, at the address shown below.*

*This standard is copyrighted by ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959, United States. Individual reprints (single or multiple copies) of this standard may be obtained by contacting ASTM at the above address or at 610-832-9585 (phone), 610-832-9555 (fax), or [service@astm.org](mailto:service@astm.org) (e-mail); or through the ASTM website ([www.astm.org](http://www.astm.org)). Permission rights to photocopy the standard may also be secured from the Copyright Clearance Center, 222 Rosewood Drive, Danvers, MA 01923, Tel: (978) 646-2600; <http://www.copyright.com/>*