



# Standard Test Method for Purity of Monomeric Plasticizers by Gas Chromatography<sup>1</sup>

This standard is issued under the fixed designation D 3465; 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 approval. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

## 1. Scope \*

1.1 This gas chromatographic test method covers a procedure for extending the range of purity determination of monomeric plasticizers beyond that now determined by other methods. Due to the need to volatilize the plasticizer, only monomeric plasticizers having definitive boiling points and a molecular weight less than 1000 Daltons, such as dioctyl phthalate, are applicable to this test method.

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

1.3 The text of this test method references notes and footnotes that provide explanatory material. These notes and footnotes (excluding those in tables and figures) are not to be considered as requirements of this test method.

1.4 *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.* Specific precautionary statements are given in Section 9

NOTE 1—There is no ISO equivalent for this test method.

## 2. Referenced Documents

### 2.1 ASTM Standards:

D 883 Terminology Relating to Plastics<sup>2</sup>

D 1600 Terminology for Abbreviated Terms Relating to Plastics<sup>2</sup>

D 2124 Test Method for Analysis of Components in Poly-(Vinyl Chloride) Compounds Using an Infrared Spectrophotometric Technique<sup>2</sup>

E 177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods<sup>3</sup>

E 260 Practice for Packed Column Gas Chromatography<sup>3</sup>

E 355 Practice for Gas Chromatography Terms and Relationships<sup>3</sup>

E 594 Standard Practice for Testing Flame Ionization Detectors in Gas or Supercritical Fluid Chromatography<sup>3</sup>

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee D20 on Plastics and is the direct responsibility of Subcommittee D20.70 on Analytical Methods (Section D20.70.03).

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<sup>2</sup> *Annual Book of ASTM Standards*, Vol 08.01.

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 14.02.

E 1510 Practice for Installing Fused Silica Open Tubular Capillary Columns in Gas Chromatographs<sup>3</sup>  
IEEE/ASTM SI-10 Practice for Use of the International System of Units (SI), the Modernized Metric System<sup>4</sup>

## 3. Terminology

### 3.1 Definitions:

3.1.1 *General*—Definitions are in accordance with Terminology D 883 and Terminology D 1600 unless otherwise indicated.

3.1.2 All gas chromatography terms and relationships used in this test method are consistent with, or refer to, Practice E 355.

## 4. Summary of Test Method

4.1 A test portion of the plasticizer to be analyzed is injected onto a gas chromatographic column and separated into its components, which are sensed by the detector and quantified by an electronic data acquisition system (computer) or an integrator. The purity is based on the total area response of the principal peak(s). All other components are impurities.

## 5. Significance and Use

5.1 Infrared techniques frequently cannot detect low-level materials. Gas chromatographic methods possess higher sensitivity, and are used to extend (FL) limits of detection.

5.2 It is expected that this test method will be suitable for specifications, manufacturing control, and research and development. An area percent method of determining concentration of the components shall be used if the area percent of the plasticizer is 99.0 % or higher. However, if the area percent of the plasticizer is less than 99.0 % or should any question arise about the data, an internal standard shall be used.

5.3 Impurities that may be found in monomeric plasticizers include alcohols, dibasic acids, and monoesters.

## 6. Interferences

6.1 Gas chromatography (GC) retention times are dependent on several variables, and it is possible to have two or more components with identical retention times. The GC operator should take the necessary steps to insure that adequate separation of the plasticizer components is achieved. Analysis by

<sup>4</sup> *Annual Book of ASTM Standards*, Vol 14.04.

\*A Summary of Changes section appears at the end of this standard.

gas chromatography/mass spectrometry may identify the presence of overlapping components.

## 7. Apparatus

7.1 *Gas Chromatograph*, equipped with a flame ionization or thermal conductivity detector and capable of operating in the range from 250 to 350°C.

7.1.1 *Capillary or Packed Gas Chromatographic Column*, capable of operating in the range from 250 to 350°C that provides adequate separation and definition of components. Examples are as follows:

7.1.2 *Packed Columns*, stainless steel, 1.83 m (6 ft) long, with an outside diameter of 6.4 mm (¼ in.) and filled with Chromosorb W or WAW,<sup>5</sup> 60 to 80 mesh, as the solid support.

7.1.2.1 *Liquid Phase*—The liquid phase sensitivity changes the utility in detecting various impurities. Examples of detectability of alcohol impurities are illustrated as follows:

7.1.2.2 A coating of 5 to 15 % of SE-30<sup>6</sup> silicone gumstock results in reasonably symmetrical peaks and accurate quantitative measurements between 0.1 and 1 % alcoholic impurities.

7.1.2.3 A coating of 15 % Igepal CO-990<sup>7</sup> results in separations of similar types of esters such as diisooctyl phthalate and di (2-ethylhexyl) phthalate at the 1 % level.

7.1.2.4 A coating of 20 % Ozonite<sup>8</sup> is also effective for alcohols in the 0.1 to 1 % concentration level.

7.1.3 *Capillary Columns*, fused silica high-temperature capillary column with a 100 % poly(dimethylsiloxane) stationary phase; length: 15 to 30 m; inside diameter: 0.25 to 0.5 mm; film thickness: 0.1 to 0.25 µm.

7.2 *Integrator or Electronic Data Acquisition System*.

7.3 *Gas Chromatographic Syringe or Autosampler*, 0.1 to 10.0 µL capacity.

7.4 *Pressure Regulators*, for all required gas cylinders.

7.5 *Flowmeter*, or other means of measuring gas flow rates.

## 8. Reagents and Materials

8.1 *Helium*, chromatographic grade.

8.2 *Hydrogen*, chromatographic grade.

8.3 *Nitrogen*, chromatographic grade.

8.4 *Purified Air*.

## 9. Hazards

9.1 Hydrogen is flammable. Ensure that all leaks are eliminated.

## 10. Preparation of the Gas Chromatograph

10.1 *Temperature Settings*—This test method requires injection port and detector temperatures of 260 to 350°C. For a plasticizer with a nominal boiling point of 410°C, the following conditions are suggested:

Injection port	260 to 350°C
Detector	300 to 350°C

10.2 Program the temperature of the column suitable to best separate the components (see 7.1 for columns). Typical settings are as follows:

10°C/min from 60 to 280°C and hold.
10°C/min from 100 to 300°C and hold for 10 min.

10.3 *Sample Size*—Select a sample size that provides an adequate chromatographic efficiency (that is, do not overload the column). Typical quantity is 1 µL.

10.4 *Carrier Gas*—Helium, flow rate 30 to 60 cm<sup>3</sup>/min.

## 11. Procedure

11.1 The method of injecting the sample onto the column and analyzing for the components is given in detail in Practice E 260, (specifically, Sections 10 and 14).

11.2 The method for analyzing the components shall be consistent with Fig. 1 of Practice E 355.

## 12. Report

12.1 Report the following information:

12.1.1 Proportion of the total area related to the principal component(s) as the purity of the plasticizer, percent,

12.1.2 Retention times of impurities, relating them to corresponding retention times of known substances,

12.1.3 Proportion of total area related to the impurities in percent,

12.1.4 Column description,

12.1.5 Gas chromatograph conditions, and

12.1.6 Internal standard when used for calibration.

## 13. Precision and Bias

13.1 *Precision*—A round robin is in progress. Table 1 is based on a single laboratory test using two different capillary columns on one gas chromatograph.

13.1.1 *Sr* is the within-laboratory standard deviation of the average;  $r = 2.8 SR$  (see 13.1.3 for application of *r*.)

13.1.2 *SR* is the between-laboratory standard deviation of the average;  $R = 2.8 SR$  (see 13.1.4 for application of *R*.)

13.1.3 *Repeatability*—In comparing two test results for the same material, obtained by the same operator using the same equipment on the same day, those test results should be judged not equivalent if they differ by more than the *r* value for the material and condition.

13.1.4 *Reproducibility*—By comparing two test results for the same material, obtained by different equipment on different days, those test results should be judged not equivalent if they differ by more than the *R* value for the material and condition. (This applies between different laboratories or between different equipment within the same laboratory.)

13.1.5 Any judgment in accordance with 13.1.2 and 13.1.3 will have an approximate 95 % (0.95) probability of being correct.

**TABLE 1 Precision and Bias Data**

Average purity, %	Material: Diundecyl Phthalate			
	<i>Sr</i>	<i>SR</i>	<i>r</i>	<i>R</i>
99.79	0.01	0.07	0.03	0.19

<sup>5</sup> Trademark of Johns-Manville Products Corp.

<sup>6</sup> Trademark of General Electric Co., Schenectady, NY.

<sup>7</sup> Trademark of General Aniline & Film Corp.

<sup>8</sup> Trademark of Applied Science Laboratories, Inc., P.O. Box 440, State College, PA 16801.

13.2 *Bias*—There are no recognized standards on which to base an estimate of bias for this test method.

#### 14. Keywords

14.1 gas chromatography; plasticizers; poly(vinyl chloride); PVC

### SUMMARY OF CHANGES

This section identifies the location of selected changes to this test method. For the convenience of the user, Committee D20 has highlighted those changes that may impact the use of this test method. This section may also include descriptions of the changes or reasons for the changes, or both.

*D 3465-00:*

(1) Added flame ionization detector.

(2) Added broader selection of packed columns and temperature ranges.

(3) Added capillary columns.

(4) Eliminated the precision and bias statement for thermal conductivity detectors (FL).

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