Designation: D6387 – 99 (Reapproved 2014)ε1

Standard Test Methods for Composition of Turpentine and Related Terpene Products by Capillary Gas Chromatography[1]

This standard is issued under the fixed designation D6387; 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.

ε[1] NOTE—Note 6 was corrected editorially in December 2014.

1. Scope

1.1 These test methods describe the determination of the amounts of α-pinene, β-pinene, dipentene, terpene alcohols, and other terpene compounds in turpentine and related terpene products using capillary gas chromatography. The two methods for determining the amount of the individual terpene compounds are the "internal standard" method, which yields absolute values, and the "area percent" method, which yields relative values.

1.2 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this 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 the standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

NOTE 1—Overall this test method gives excellent repeatability but only moderate reproducibility. This greater than normal differential is a consequence of the variety of gas chromatography (GC) columns and other variables used by participants. These variables, coupled with the complex composition of the test products, enabled some workers to separate peaks that others reported as one peak; thus, this test method gives excellent precision within a given laboratory on a given GC. When laboratory to laboratory comparison have to be made, however, it is essential that the GC operating conditions be defined closely.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D13 Specification for Spirits of Turpentine

D801 Test Methods for Sampling and Testing Dipentene

D802 Test Methods for Sampling and Testing Pine Oils

D804 Terminology Relating to Pine Chemicals, Including Tall Oil and Related Products

D3009 Test Method for Compostition of Turpentine by Gas Chromatography (Withdrawn 1999)[3]

E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

3. Terminology

3.1 For definitions see Terminology D804.

4. Summary of Test Method

4.1 A weighed mixture of the sample and internal standard is prepared, and an aliquot is injected into a temperature programmable capillary gas chromatograph to obtain the chromatogram. The peak areas for the compounds to be determined and also for the internal standard are measured. The percentages of the compounds present are calculated from the peak area of the compounds/internal standard, weight of internal standard/sample, and the calibration factors. Alternately, the relative concentration of the compounds may be calculated using the area percent method. For hydrocarbons, the latter quantitation method usually is adequate to use since turpentine and related terpene products contain few noneluting compounds, and the individual response factors are of a similar value. A polar or nonpolar capillary column may be used for the analysis, depending on the particular compounds requiring separation and quantitation.

NOTE 2—Response factors should be employed if significant quantities of polar and nonpolar compounds are present in the sample.

5. Significance and Use

5.1 Earlier methods for characterizing turpentine and related terpene products were based on physical properties, such as those in Specification D13 and Test Methods D801 and D802, and packed column gas chromatography for the major constituents (for example, α-pinene, β-pinene) as in Test Method

[1] These test methods are under the jurisdiction of ASTM Committee D01 on Paint and Related Coatings, Materials, and Applications and are the direct responsibility of Subcommittee D01.34 on Pine Chemicals and Hydrocarbon Resins.

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[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[3] The last approved version of this historical standard is referenced on www.astm.org.

D3009. As terpene products became widely used as chemical raw material, the separation and quantitation of compounds present at lower concentrations in the product became more important. The capillary gas chromatographic technique described in these test methods is a rapid and convenient means to perform these analyses.

6. Apparatus

6.1 *Gas Chromatograph*—A temperature programmable instrument equipped with a flame ionization detector (FID) that can be operated at the conditions given in Section 8.

6.2 *Column*—Either a polar (polyethylene glycol) or nonpolar (methylsilicone) capillary column, or both, may be used depending on the polarity of the particular components needing separation and quantitation. The recommended column dimensions are 30 m in length, a 0.25-mm internal diameter, and a 0.25 μ film thickness. A column of differing dimensions may be used depending on the separations required.

NOTE 3—If the separation involves primarily polar compounds, the polyethylene glycol column should be employed. When primarily nonpolar compounds are involved, a methyl silicone column should be selected.

6.3 *Analytical Balance,* readable to 0.1 mg.

6.4 *Syringe,* 10 μL.

7. Reagents

7.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society[4], where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 α-*Pinene,* purity 99+%.

7.3 β-*Pinene,* purity 99+%

7.4 Other terpene compounds, suitable for use as reference materials.

7.5 *n-Decane,* purity 99+% (internal standard).

7.6 *Hexane*—capillary C grade or equivalent.

INTERNAL STANDARD METHOD

8. Preparation of Calibration Standard

8.1 To a 2-dram vial, add similar milligram quantities of the compounds to be quantitated plus *n*-decane. Cap the vial and swirl to mix. Approximately 1 mL of hexane may be added to the vial to dilute the standard for easier handling and the use of lower split ratios.

NOTE 4—Other terpene compounds may be added in an identical manner to the pinenes.

9. Gas Chromatograph Operating Conditions

9.1 The following temperatures are typical operating conditions only. The individual instrument should be set to manufacturer's instructions to optimize desired separations. Adjustments in operating temperature and flow rate may be necessary to maintain optimum performance of the column due to aging.

Column Temperature (Oven Temperature)	
Initial	50°C
Hold	5 min
Ramp	4°C/min
Final	240°C
Hold	10 min
Injection port temperature	250°C
Injection port liner	Glass-split
Detector Temperature	250°C
Carrier gas	Helium
Linear gas velocity	19.5–20.5 cm/s
Split ratio	100:1 max
Detector	FID
Hydrogen	30 mL/min
Air	400 mL/min
Make up gas	30 mL/min

10. Calibration of Gas Chromatograph

10.1 Inject 0.1 to 1.0 μL of the standard prepared in 8.1. Record the retention time and the areas for each of the components. Then, calculate the individual relative response factors as follows:

$$RRF_1 = \frac{W_1}{A_1} \times \frac{A_{IS}}{W_{IS}} \quad (1)$$

where:

RRF_1 = Relative response factor of individual terpene compound;
W_1 = Weight of individual terpene compound in standard (W_1 = weight used × purity);
A_1 = Peak area of individual terpene compound;
A_{IS} = Peak area of *n*-decane internal standard; and,
W_{IS} = Weight of *n*-decane internal standard (W_{IS} = weight n-decane used × purity).

NOTE 5—For highest accuracy, the purity of this standard should be used to correct the weight terms.

11. Preparation of Test Sample

11.1 Accurately weigh ~50 mg of sample and ~15 mg of *n*-decane directly into a 2-dram vial and record the weight of each to 0.0001 g.

11.2 Approximately 1 mL of hexane may be added to the vial to make the sample easier to handle and not overload the column or detector.

[4] *Reagent Chemicals, American Chemical Society Specifications,* American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

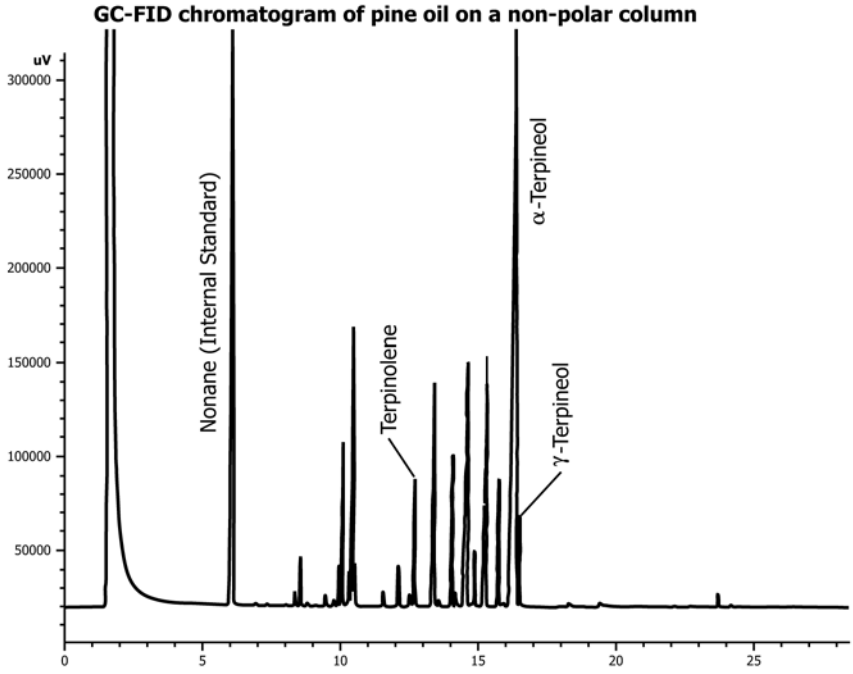

FIG. 1 (a)GC/FID Chromatograms

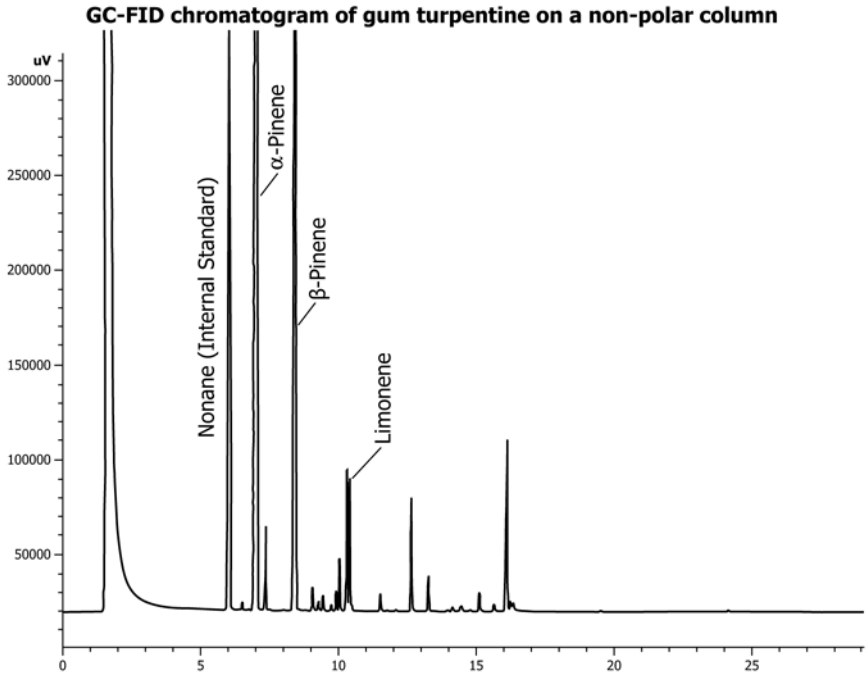

FIG. 1 (b)GC/FID Chromatograms *(continued)*

12. Analysis

12.1 Inject 0.1 to 1.0 µL of the test sample prepared in 11.1 to 11.2.

13. Calculation

13.1 Obtain the peak areas of all of the peaks needed from the chromatogram.

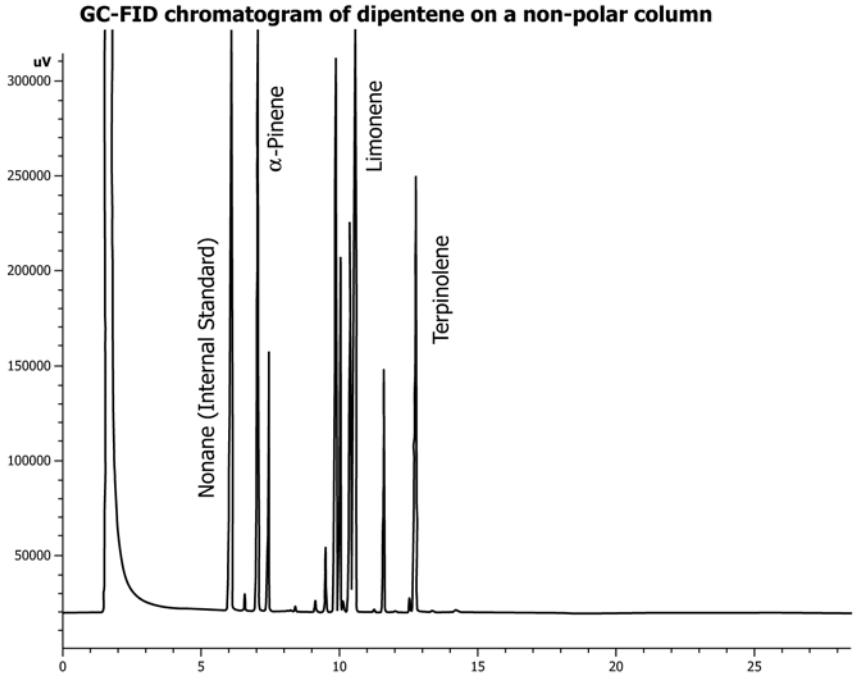

FIG. 1 (c)GC/FID Chromatograms *(continued)*

NOTE 6—See Fig. 1a through 1c for chromatograms of a typical pine oil, turpentine, and dipentene, respectively.

13.2 Calculate the absolute value of each peak of interest, as follows:

$$\text{Terpene Compound, } \% = \frac{A_1 \times RRF_1 \times W_{IS}}{A_{IS} \times W_s} \times 100 \qquad (2)$$

where:

A_1 = peak area for terpene compound being determined;
RRF_1 = relative response factor for terpene compound being determined;
W_{IS} = weight of *n*-decane internal standard W_{IS} = weight used × purity;
A_{IS} = peak area of *n*-decane internal standard; and,
W_s = sample weight, g.

14. Report

14.1 Report the percentage of the individual terpene compound to the nearest 0.1 %.

15. Precision and Bias

15.1 *Internal Standard Method*—An interlaboratory study of the capillary GC determination of various terpenes and terpene alcohols in turpentine, dipentene, and pine oil was run in 1997 by seven laboratories using nonpolar columns. The design of the experiment was similar to that of Practice E691, and a within/between analysis of the date are given in ASTM Research Report: RR:D01-1111.[5]

15.1.1 *Test Result*—The precision information given below is based on three separate analyses of each individual sample.

15.1.2 *Precision for a Turpentine Material Containing about 50.0 % α-Pinene, about 31.7 % β-Pinene, and about 2.4 % Dipentene:*

15.1.2.1 *Repeatability Limit*—95 % for α-pinene = 0.4, for β-pinene = 0.3, and for dipentene = 0.2.

15.1.2.2 *Reproducibility Limit*—95 % for α-pinene = 3.5, for β-pinene = 5.4, and for dipentene = 0.7.

15.1.2.3 *Repeatability Standard Deviation*—% for α-pinene = 0.1, for β-pinene = 0.1, and for dipentene = 0.1.

15.1.2.4 *Reproducibility Standard Deviation*—% for α-pinene = 1.3, for β-pinene = 1.9, and for dipentene = 0.2.

15.1.3 *Precision for a Pine Oil Product Containing about 2.5 % Terpinolene, about 39.6 % α-Terpineol, and about 1.6 % γ-Terpineol:*

15.1.3.1 *Repeatability Limit*—95 % for terpinolene = 0.1, for α-terpineol = 1.5 and for γ-terpineol = 0.1.

15.1.3.2 *Reproducibility Limit*—95 % for terpinolene = 0.5, for α-terpineol = 9.2 and for γ-terpineol = 1.1.

15.1.3.3 *Repeatability Standard Deviation*—% for terpinolene = 0.03, for α-terpineol = 0.5 and for γ-terpineol = 0.03.

15.1.3.4 *Reproducibility Standard Deviation*—% for terpinolene = 0.2, for α-terpineol = 3.3 and for γ-terpineol = 0.4.

15.1.4 *Precision for a Dipentene Product Containing about 17.2 % α-Pinene, about 22.6 % Dipentene, and about 12.7 % Terpinolene:*

15.1.4.1 *Repeatability Limit*—95 % for α-pinene = 0.2, for dipentene = 0.8, and for terpinolene = 0.6.

15.1.4.2 *Reproducibility Limit*—95 % for α-pinene = 3.3, for dipentene = 4.4, and for terpinolene = 2.7.

15.1.4.3 *Repeatability Standard Deviation*—% for α-pinene = 0.07, for dipentene = 0.3 and for terpinolene = 0.2.

15.1.4.4 *Reproducibility Standard Deviation*—% for α-pinene = 1.2, for dipentene = 1.6 and for terpinolene = 0.9.

[5] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D01-1111. Contact ASTM Customer Service at service@astm.org.

15.1.5 *Bias*—Since there is no accepted reference material, method or laboratory suitable for determining the bias for the procedure in this test method for measuring component concentration, no statement on bias is being made.

AREA PERCENT METHOD

16. Preparation of Retention Time Standard

16.1 Prepare similar to 8.1 except that only approximate weights need to be used.

17. Set-Up of Gas Chromatograph

17.1 Set conditions as described in 9.1.

18. Preparation of Test Sample

18.1 Preparation described in 11.1 and 11.2 except that an internal standard is not added.

19. Analysis

19.1 Inject 0.1 to 1.0 µL of the test sample prepared in 18.1.

20. Calculation

20.1 Sum the areas of all the individual peaks, exclusive of the solvent peak, to obtain the total peak area.

NOTE 7—See Fig. 1a, 1b, or 1c for chromatograms of a typical turpentine, dipentene, and pine oil, respectively.

20.2 Calculate the relative percent of each terpene compound present, as follows:

$$\text{Terpene, \%} = (A \times 100)/TA \quad (3)$$

where:

A = peak area for terpene compound being determined, and
TA = sum of areas of all peaks, except solvent peak.

21. Report

21.1 Report the area percent of the individual terpene compounds to the nearest 0.1 %.

22. Precision and Bias

22.1 *Area Percent Method*—An interlaboratory study of the capillary GC determination of various terpenes and terpene alcohols in turpentine, dipentene, and pine oil was run in 1997 by seven laboratories using nonpolar columns. The design of the experiment was similar to that of Practice E691, and a within/between analysis of the date are given in ASTM Research Report RR:D01-1111.[5]

22.1.1 *Test Result*—The precision information given below is based on three separate analyses of each individual sample.

22.1.2 *Precision for a Turpentine Material Containing about 51.1 % α-Pinene, about 28.8 % β-Pinene, and about 2.7 % Dipentene:*

22.1.2.1 *Repeatability Limit*—95 % for α-pinene = 0.3, for β-pinene = 0.1 and for dipentene = 0.1.

22.1.2.2 *Reproducibility Limit*—95 % for α-pinene = 2.1, for β-pinene = 0.5, and for dipentene = 0.2.

22.1.2.3 *Repeatability Standard Deviation*—% for α-pinene = 0.1, for β-pinene = 0.04, and for dipentene = 0.03.

22.1.2.4 *Reproducibility Standard Deviation*—% for α-pinene = 0.7, for β-pinene = 0.2, and for dipentene = 0.1.

22.1.3 *Precision for a Pine Oil Product Containing about 2.9 % terpinolene, about 37.9 % α-Terpineol, and about 1.7 % γ-Terpineol:*

22.1.3.1 *Repeatability Limit*—95 % for terpinolene = 0.1, for α-terpineol = 0.3, and for γ-terpineol = 0.02.

22.1.3.2 *Reproducibility Limit*—95 % for terpinolene = 0.6, for α-terpineol = 3.8, and for γ-terpineol = 0.4.

22.1.3.3 *Repeatability Standard Deviation*—% for terpinolene = 0.02, for α-terpineol = 0.1, and for γ-terpineol = 0.03.

22.1.3.4 *Reproducibility Standard Deviation*—% for terpinolene = 0.2, for α-terpineol = 3.3 and for γ-terpineol = 0.01.

22.1.4 *Precision for a Dipenetene Product Containing about 17.6 % α-Pinene, about 23.0 % Dipentene, and about 12.9 % Terpinolene:*

22.1.4.1 *Repeatability Limit*—95 % for α-pinene = 0.2, for dipentene = 0.7 and for terpinolene = 0.1.

22.1.4.2 *Reproducibility Limit*—95 % for α-pinene = 0.9, for dipentene = 2.3, and for terpinolene = 0.5.

22.1.4.3 *Repeatability Standard Deviation*—% for α-pinene = 0.1, for dipentene = 0.2, and for terpinolene = 0.1.

22.1.4.4 *Reproducibility Standard Deviation*—% for α-pinene = 0.3, for dipentene = 0.8, and for terpinolene = 0.2.

22.1.5 *Bias*—Since there is no accepted reference material, method, or laboratory suitable for determining the bias for the procedure in this test method for measuring component concentration, no statement on bias is being made.

23. Keywords

23.1 capillary column; dipentene; gas chromatography; pine oil; turpentine