



Designation: D 6387 – 99

Standard Test Methods for Composition of Turpentine and Related Terpene Products by Capillary Gas Chromatography¹

This standard is issued under the fixed designation D 6387; 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 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 *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. Subcommittee D01.34 will be working on this problem prior to the next version of this test method.

2. Referenced Documents

2.1 ASTM Standards:

- D 13 Specification for Spirits of Turpentine²
- D 801 Test Methods for Sampling and Testing Dipentene²
- D 802 Test Methods for Sampling and Testing Pine Oil²
- D 804 Terminology Relating to Naval Stores, Including Tall Oil and Related Products²
- D 3009 Test Method for Composition of Turpentine by Gas Chromatography²

¹ These test methods are under the jurisdiction of ASTM Committee D-01 on Paint and Related Coatings, Materials, and Applications and are the direct responsibility of Subcommittee D01.34 on Naval Stores.

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² *Annual Book of ASTM Standards*, Vol 06.03.

E 691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method³

3. Terminology

3.1 For definitions see Terminology D 804.

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. Alternatively, 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 D 13 and Test Methods D 801 and D 802, and packed column gas chromatography for the major constituents (for example, α -pinene, β -pinene) as in Test Method D 3009. 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.

³ *Annual Book of ASTM Standards*, Vol 14.02.

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 non-polar (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 Society⁴, 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.

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.

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.

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.

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

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

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