Designation: D7974 − 15

Standard Test Method for Determination of Farnesane, Saturated Hydrocarbons, and Hexahydrofarnesol Content of Synthesized Iso-Paraffins (SIP) Fuel for Blending with Jet Fuel by Gas Chromatography[1]

This standard is issued under the fixed designation D7974; 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 This test method covers the determination of farnesane (2,6,10-trimethyldodecane), saturated hydrocarbons, and hexahydrofarnesol content in synthesized iso-paraffins (SIP) fuel for blending with jet fuel by gas chromatography.

1.2 Farnesane is determined from 96 % to 99.9 % by mass. Sum of saturated hydrocarbons including farnesane is determined from 97 % to 99.9 % by mass, and hexahydrofarnesol is determined from 0.02 % to 2.0 % by mass.

1.3 This test method does identify and quantify main impurities or group type of impurities but does not purport to identify all individual components that can be present in synthesized iso-paraffins (SIP) fuel for jet fuel blending.

1.4 This test method is inappropriate for impurities that boil at temperatures higher than 460 °C or for impurities that cause poor or no response in a flame ionization detector.

1.5 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.6 *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.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D4057 Practice for Manual Sampling of Petroleum and Petroleum Products

D4307 Practice for Preparation of Liquid Blends for Use as Analytical Standards

D7566 Specification for Aviation Turbine Fuel Containing Synthesized Hydrocarbons

E355 Practice for Gas Chromatography Terms and Relationships

E594 Practice for Testing Flame Ionization Detectors Used in Gas or Supercritical Fluid Chromatography

3. Terminology

3.1 *Definitions:*

3.1.1 This test method makes reference to many common gas chromatographic procedures, terms, and relationships. Detailed definitions can be found in Practices E355 and E594.

3.1.2 *saturated hydrocarbons, n*—paraffinic and naphthenic compounds.

4. Summary of Test Method

4.1 A representative aliquot of the synthesized iso-paraffins (SIP) fuel sample is introduced into a gas chromatograph equipped with a 5 % phenyl-methylpolysiloxane bonded phase capillary column. Helium or hydrogen carrier gas transports the vaporized aliquot through the column where the components are separated by the chromatographic process. Components are sensed by a flame ionization detector as they elute from the column. The detector signal is processed by an electronic data acquisition system. The farnesane and its impurities are identified by comparing their relative retention times to the ones reported in the method. Identification has been previously performed analyzing reference samples by mass spectrometry under identical conditions. The concentrations of all components are determined in mass percent area by normalization of the peak areas.

5. Significance and Use

5.1 Synthesized iso-paraffins (SIP) fuel are being approved for blending with jet fuel provided that they meet a purity specification of more than 97 % farnesane, more than 98 % saturated hydrocarbons, and less than 1.5 % hexahydrofarnesol in accordance with Specification D7566. This test method

---

[1] This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products, Liquid Fuels, and Lubricants and is the direct responsibility of Subcommittee D02.04.0L on Gas Chromatography Methods.

Current edition approved March 15, 2015. Published June 2015. DOI: 10.1520/D7974-15.

[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.

provides a method of determining the percentage of farnesane (purity) in the synthesized iso-paraffins (SIP) fuel for blending with jet fuel.

6. Apparatus

6.1 *Gas Chromatograph,* capable of operating at the conditions listed in Table 1. A heated flash vaporizing injector designed to provide a linear sample split injection (for example, 100:1) is required for proper sample introduction. Carrier gas controls shall be of adequate precision to provide reproducible column flows and split ratios in order to maintain analytical integrity. A hydrogen flame ionization detector with associated gas controls and electronics, designed for optimum response with open tubular columns, is required.

6.2 *Sample Introduction*—Manual or automatic liquid syringe sample injection to the splitting injector is employed. Devices capable of 1.0 µL injections are suitable.

6.3 *Column*—This test method utilizes a fused silica open tubular column with non-polar 5 % phenyl-methylpolysiloxane bonded (cross-linked) phase internal coating.

6.3.1 Open tubular column with a non-polar 5 % phenyl-methylpolysiloxane bonded (cross-linked) phase internal coating; a 30 m long by 0.25 mm internal diameter column with a 0.25 µm film thickness has been found to be suitable.

6.4 *Electronic Data Acquisition System*—Any data acquisition and integration device used for quantification of these analyses shall meet or exceed these minimum requirements:

6.4.1 Normalized percent calculation based on peak area,

6.4.2 Identification of individual components based on retention time,

6.4.3 Noise and spike rejection capability,

6.4.4 Sampling rate of 5 Hz.

7. Reagents and Materials

7.1 *Carrier Gas,* Helium or hydrogen, with a minimum purity of 99.9 % mol. Oxygen removal systems and gas purifiers should be used. (**Warning—**Helium, compressed gas under high pressure.) (**Warning—**Hydrogen, extremely flammable gas under high pressure.) The use of hydrogen sensors in the oven is strongly recommended that can shutoff the hydrogen source in case the hydrogen leaks.

TABLE 1 Typical Operating Conditions

Column Temperature Program	
Column length	30 m
Column inner diameter	0.25 mm
Film thickness	0.25 µm
Initial temperature	50 °C
Initial hold time	0 min
Program rate	3 °C ⁄ min
Final temperature	270 °C
Final hold time	20 min
Injector	
Temperature	300 °C
Split ratio	100:1
Sample size	1.0 µL
Detector	
Type	Flame ionization
Temperature	300 °C
Fuel gas	Hydrogen (≈40 mL/min)
Oxidizing gas	Air (≈400 mL/min)
Make-up gases	Helium (≈45 mL/min) or Nitrogen (≈45 mL/min)
Carrier Gas	
Type	Helium or Hydrogen
Flow rate	1 mL/min (Constant)

7.2 *Detector Gases,* Hydrogen, air, nitrogen, and helium. The minimum purity of the gases used should be 99.9 % mol for the hydrogen, nitrogen, and helium. The air should be hydrocarbon-free grade with a minimum purity of 99.0 % mol. Gas purifiers are recommended for the detector gases. (**Warning—**Hydrogen, extremely flammable gas under high pressure.) (**Warning—**Air and helium, compressed gases under high pressure.)

7.3 *Blank of Solvent,* n-Hexane with a minimum purity of 99.0 %.

7.4 *Validation Mixture for Apparatus Performance Checks:*

7.4.1 *Solvent,* n-Octane with a minimum purity of 99.0 %.

7.4.2 *Standards,* n-decane, n-dodecane, n-tetradecane, n-hexadecane with a minimum purity of 99.0 %.

8. Sampling

8.1 See Practice D4057 for general sampling. Transfer an aliquot of synthesized iso-paraffins (SIP) fuel sample into a septum vial and seal. Obtain the test sample for analysis directly from the sealed septum vial, for either manual or automatic syringe injection.

9. Preparation of Apparatus

9.1 Install and condition column in accordance with manufacturer's or supplier's instructions. After conditioning, attach column outlet to flame ionization detector inlet and check for leaks throughout the system. When leaks are found, tighten or replace fittings before proceeding.

9.1.1 When using hydrogen as carrier gas, column conditioning shall be performed after connecting the column to the detector.

9.2 Adjust the operating conditions of the gas chromatograph (Table 1) and allow the system to equilibrate.

9.3 *Performance Checks*—The apparatus shall be checked in regular intervals to make sure that it is in perfect working condition. Performance checks are realized by analyzing a calibration mixture in the analytical conditions defined in Table 1.

9.3.1 *Linearity Verification*—Verify linearity by analyzing a series of diluted standards or equivalent spread across the farnesane content range of the method in order to have at the minimums 15 degrees of freedom. Standard deviation of the residuals shall be less than 0.5 % which corresponds to a 95 % confidence interval of 1 %. Annex A1 gives an example of how linearity may be confirmed.

9.3.2 *Calibration Mixture Preparation*—Weigh the same amount of n-decane, n-dodecane, n-tetradecane, and n-hexadecane. Dilute the mixture in n-octane in order to obtain a concentration of 2 % mass of each component. See Practice D4307.

9.3.3 *Column Efficiency*—Calculate the number of theoretical plates on n-tetradecane peak using Eq 1:

$$n = 5.545(R\ t / W_{0.5})^2 \quad (1)$$

where:

n = the number of theoretical plates,
Rt = the retention time of n-tetradecane, and
$W_{0.5}$ = the peak width at half maximun of n-tetradecane, expressed in the same unit as the retention time.

9.3.3.1 The determined Number of theoretical plates shall be >500 000.

9.3.4 *Apparatus Performance Evaluation*—Percent mass of each component of the calibration mixture is determined from peak area percentages. Relative error percentage is determined from the known concentrations of the mixture using Eq 2:

$$\text{percent relative error}= \frac{100(|\text{calculated concentration} - \text{known concentration}|)}{\text{known concentration}} \quad (2)$$

9.3.4.1 Relative error shall be ≤5 %.

9.3.5 *Minimum Detectable Level (MDL)*—Minimum detectable level is determined by injecting the validation mixture preparation diluted in n-octane in order to obtain a concentration of 10 mg/kg of each component. The signal/noise ratio of each component shall be higher than 3. (S/N ratio = S (signal peak height)/N (noise in peak to peak)).

10. Gas Chromatographic Analysis Procedure

10.1 Set the instrument operating variables. See Table 1 for typical operating conditions.

10.2 Inject 1.0 µL of sample into the injection port and start the analysis. Obtain a chromatogram and peak integration report. Sample chromatograms are shown in Figs. 1-6.

10.3 A blank of solvent (for example n-hexane) shall be injected in between samples to remove memory effects.

11. Identification

11.1 Before execution of the final calculations, check the chromatogram for correct peak identification by comparison with those reported in Table 2 (see also Figs. 1-6, the reference chromatogram associated to those data).

12. Calculation

12.1 Determine the relative mass percent of the individual components by using the following Eq 3:

$$RM_i = \frac{A_i}{A_t} \times 100 \quad (3)$$

where:

RM_i = relative mass percentof the individual components,
A_i = area of the individual peak, and
A_t = total area of all detected peaks.

NOTE 1—There is no use of specific mass relative response factors that depend on the chemical nature or the molecular weight of the identified detected components.

NOTE 2—The large farnesane component being included in the calculation and its response linearity has been verified within the scope of the method to ensure that there is no column and/or detector overload which would lead to its purity underestimation. The results obtained are given in Annex A1.

12.2 Determine the relative mass percent of saturated hydrocarbon group by summing the corresponding individual components determined as in 12.1, respecting the group assignment from Table 2.

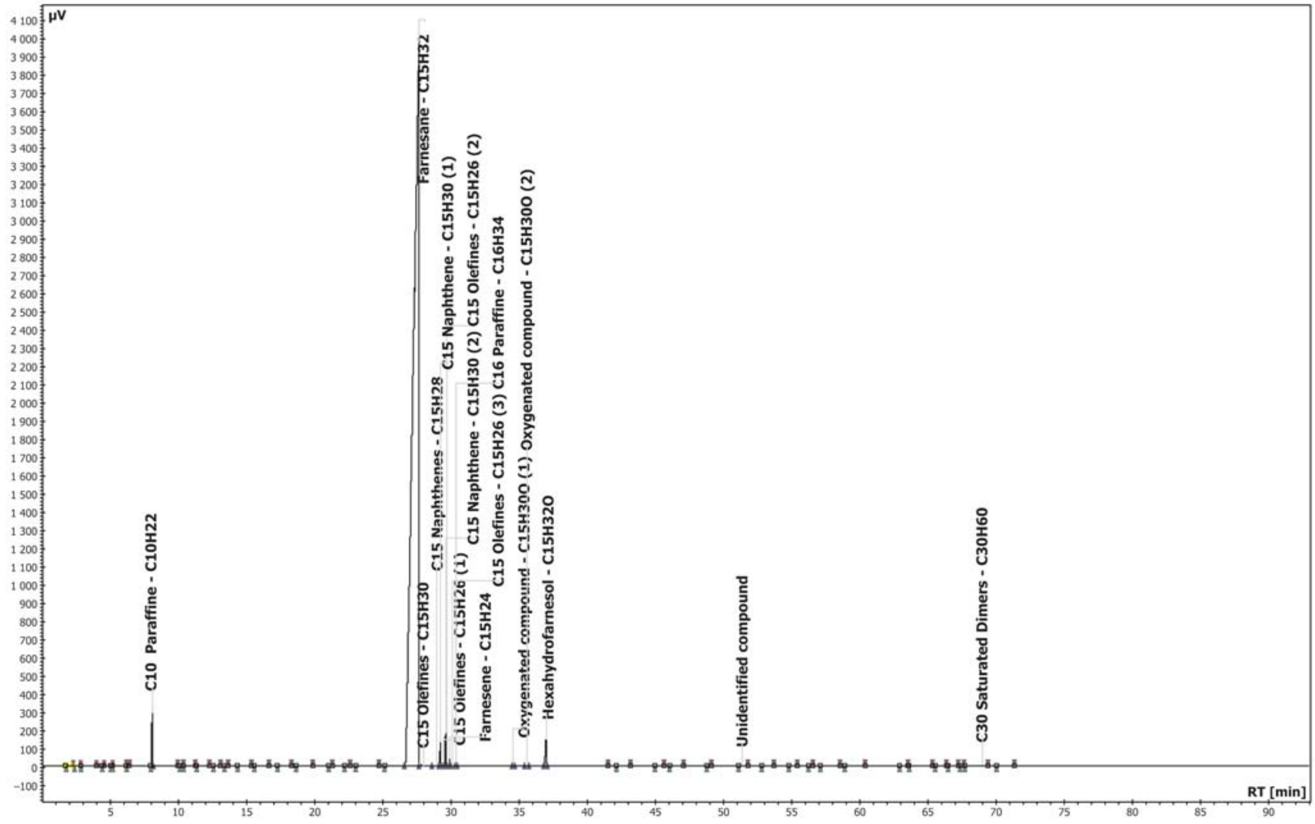
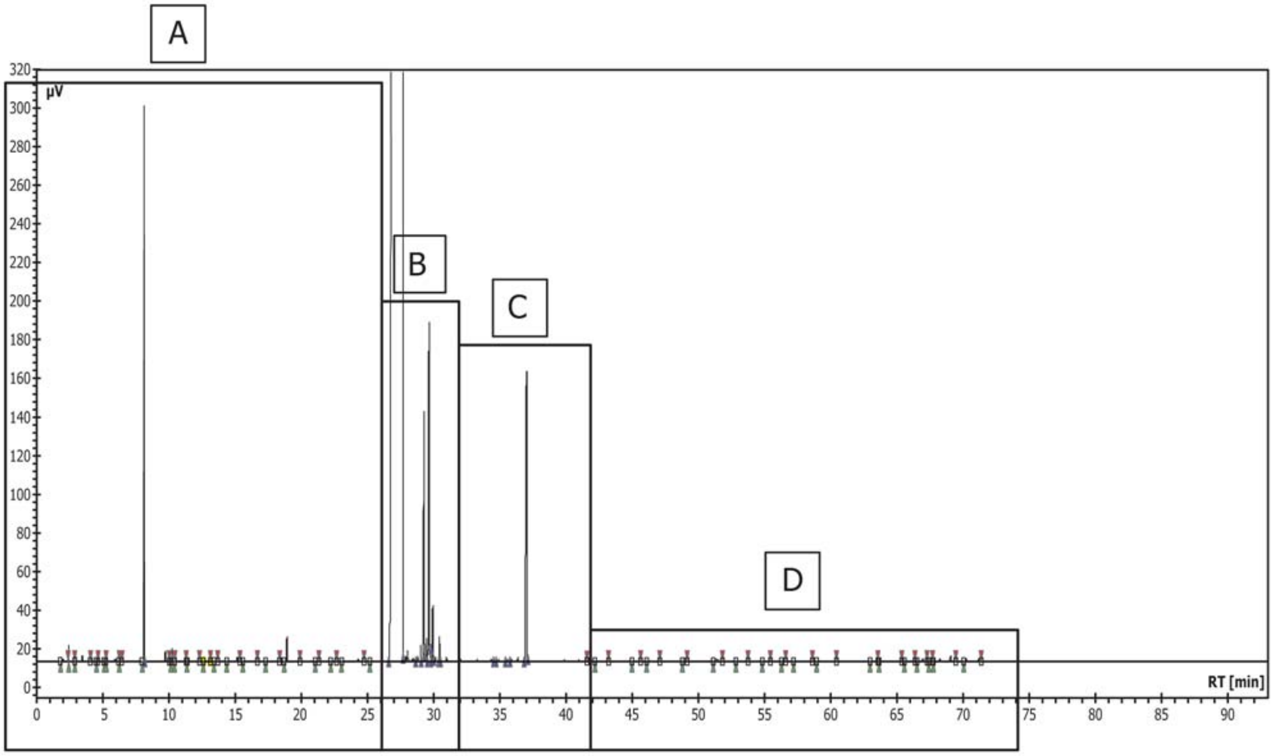


FIG. 1 Chromatogram of a Reference Distilled Farnesane



A Light compounds < Farnesane region
B Farnesane region
C Hexahydrofarnesol region
D Farnesane dimers region

FIG. 2 Chromatogram Identification Regions

13. Report

13.1 Report the purity of farnesane, hexahydrofarnesol, and sum of the saturated hydrocarbons (paraffins+naphthenes+saturated dimers) to the nearest 0.01 % mass, and reference this test method.

14. Precision and Bias

14.1 *Precision*—The precision of this test method as determined by the statistical examination of gas chromatographic test results from a single laboratory as follows:

14.1.1 *Repeatability*—The difference between successive results obtained by the same operator with the same apparatus under constant operating conditions on identical test materials wouldn't, in the long run, in the normal and correct operation of the test method exceed the following values only in one case in twenty.

Components	Repeatability, r (Mass percent)
Farnesane	0.06
Saturated hydrocarbons	0.07
Hexahydrofarnesol	0.02

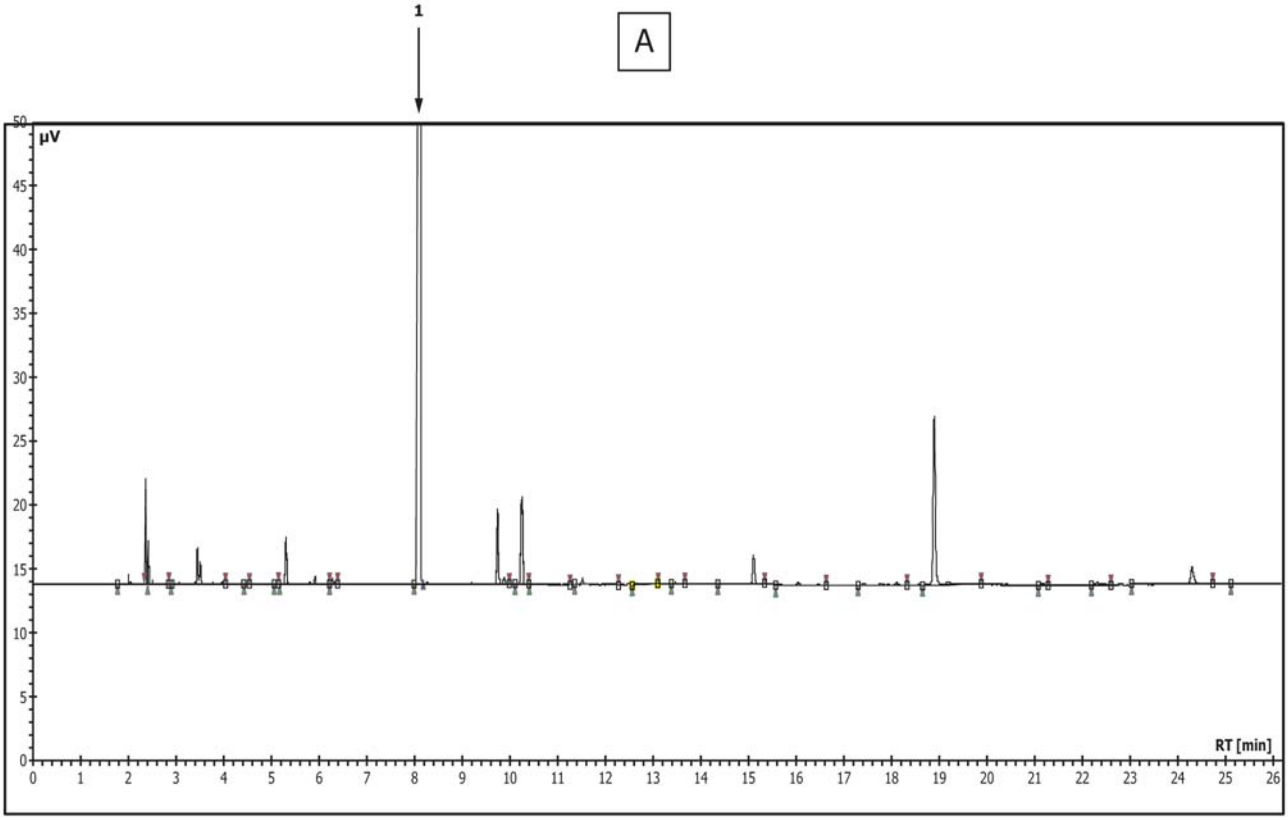
NOTE 3—Repeatability (95 % probability) has been calculated from 11 injections over a period of 2 weeks of a reference distilled farnesane sample.

14.1.2 *Reproducibility*—Reproducibility was not determined for this test method at this time.

14.1.3 *Bias*—Bias was not determined for this test method at this time.

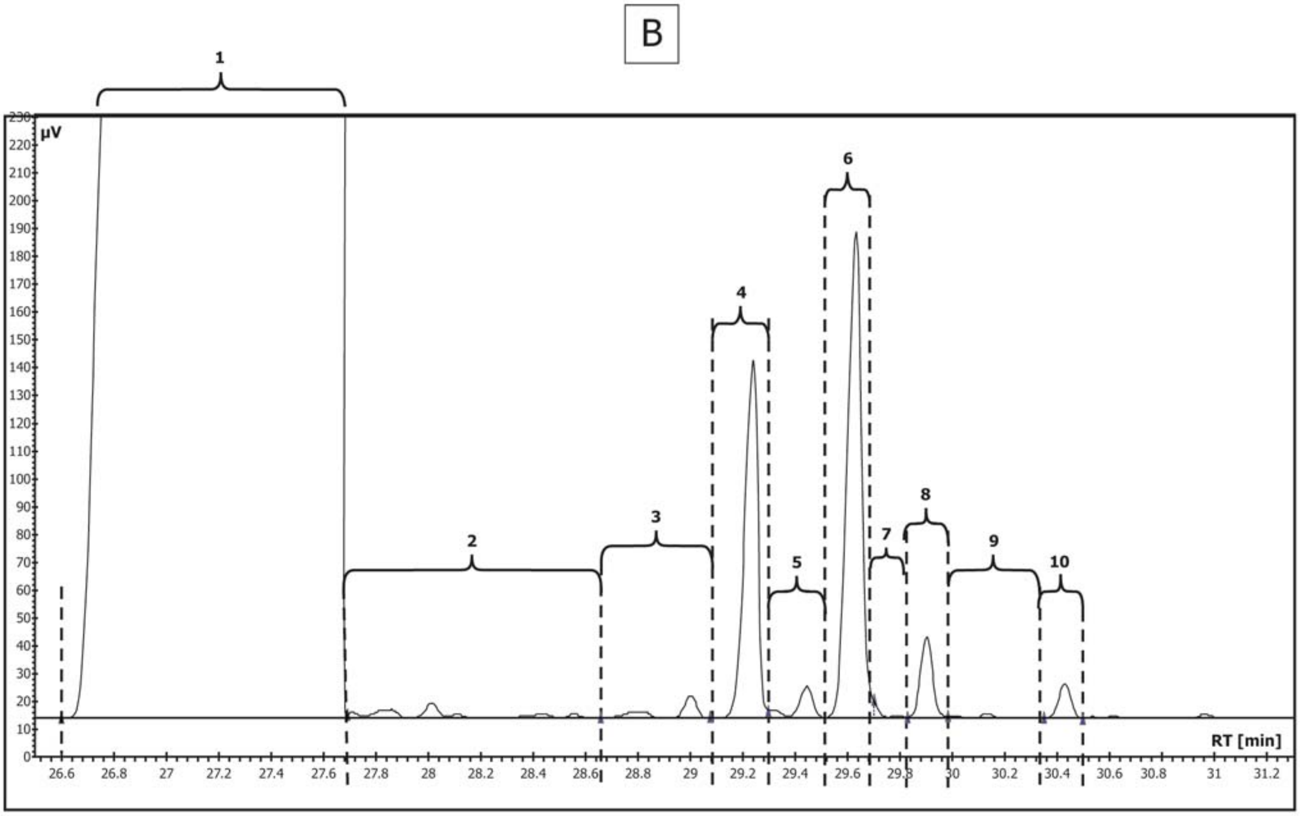
15. Keywords

15.1 farnesane; gas chromatography; hexahydrofarnesol; jet fuel grade; saturated hydrocarbons; synthesized iso-paraffins (SIP) fuel



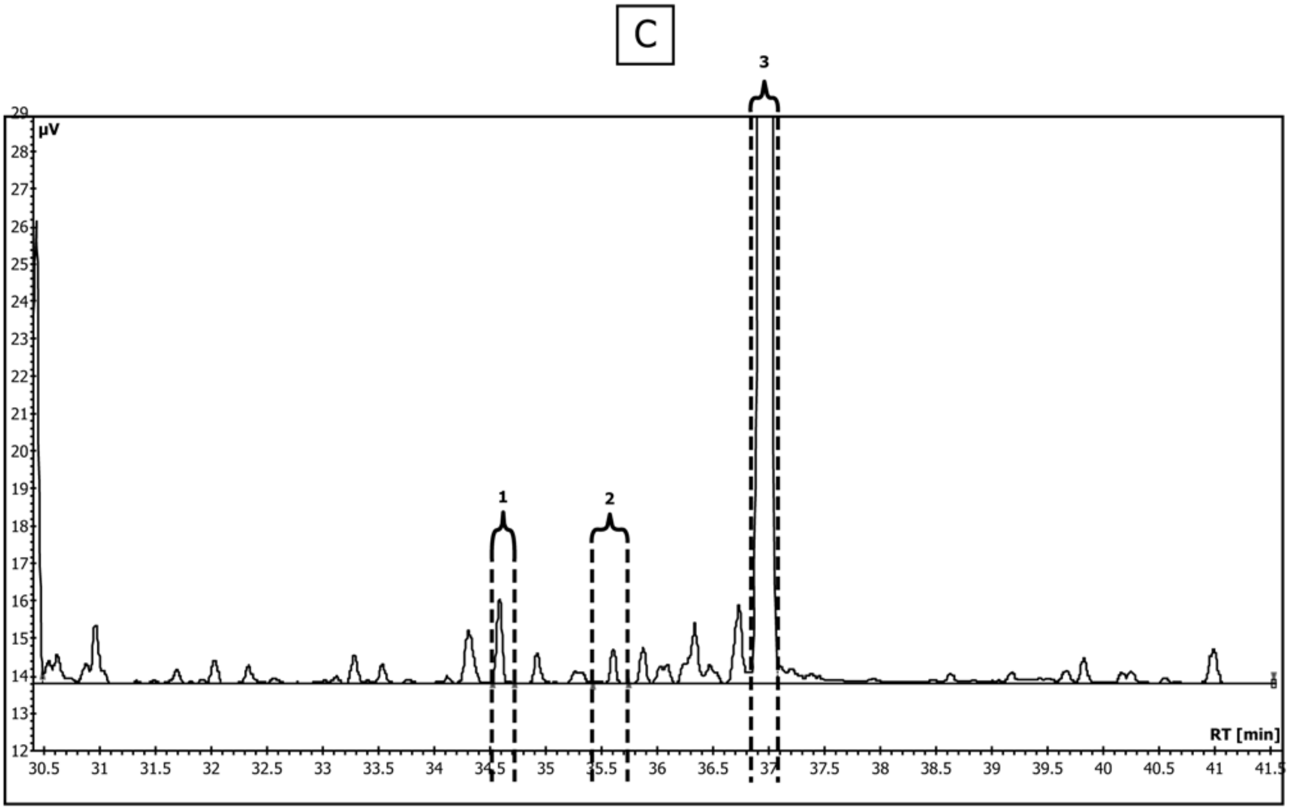
1 C_{10} Paraffine ($C_{10}H_{22}$)

FIG. 3 Zoom Chromatogram of Region A (0 min to 26 min)



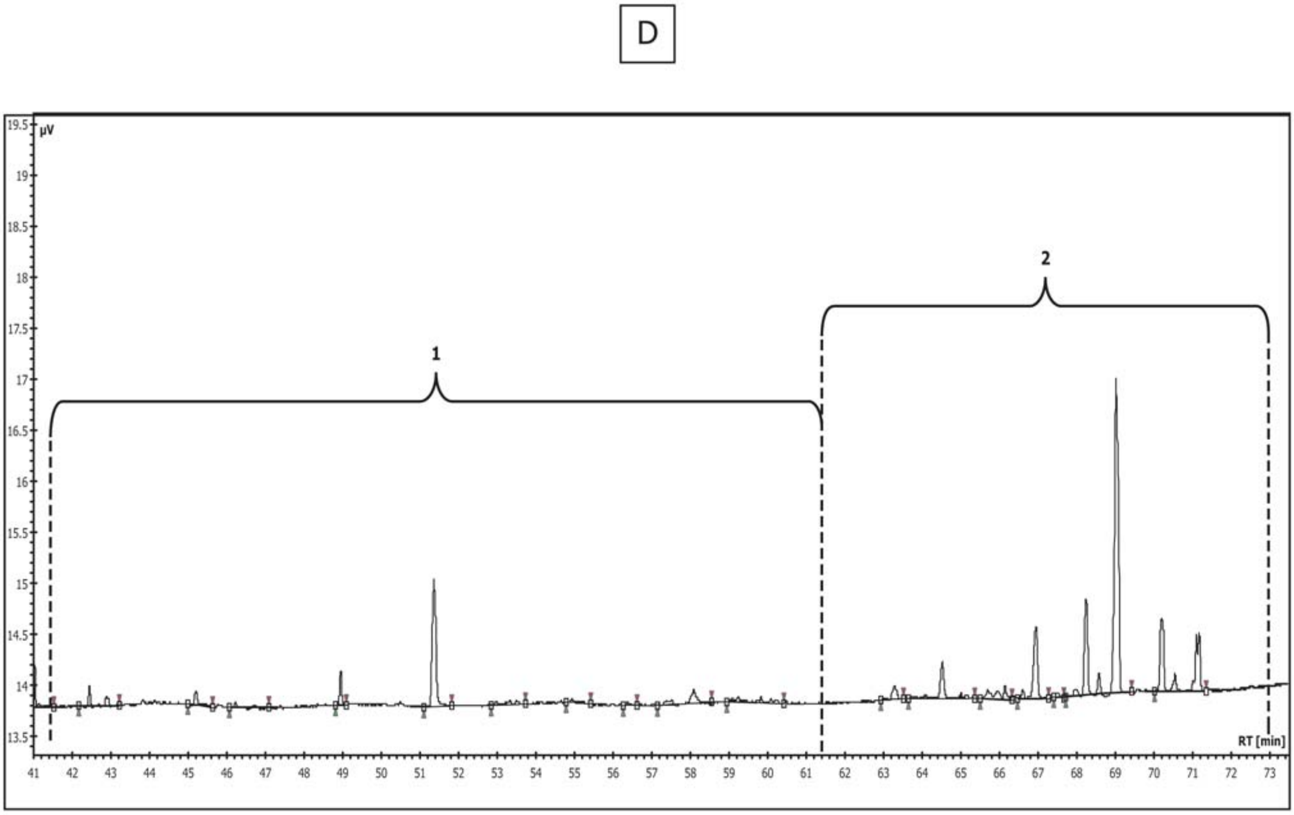
1 Farnesane ($C_{15}H_{32}$)
2 C_{15} Olefins ($C_{15}H_{30}$)
3 C_{15} Naphthenes ($C_{15}H_{28}$)
4 C_{15} Naphthene ($C_{15}H_{30}$)
5 C_{15} Olefins ($C_{15}H_{26}$)
6 C_{15} Naphthene ($C_{15}H_{30}$)
7 C_{15} Olefins ($C_{15}H_{26}$)
8 Farnesene ($C_{15}H_{24}$)
9 C_{15} Olefins ($C_{15}H_{26}$)
10 C_{16} Paraffin ($C_{16}H_{34}$)

FIG. 4 Zoom Chromatogram of Region B (26.5 min to 31.2 min)



1 Oxygenated compound ($C_{15}H_{30}O$)
2 Oxygenated compound ($C_{15}H_{30}O$)
3 Hexahydrofarnesol ($C_{15}H_{32}O$)

FIG. 5 Zoom Chromatogram of Region C (30.5 min to 41.5 min)



1 Unidentified compounds
2 C_{30} Saturated Dimers ($C_{30}H_{60}$)

FIG. 6 Zoom Chromatogram of Region D (41 min to 73 min)

TABLE 2 List of Compounds in Distilled Farnesane and their Retention Times (Rt)

Components	Rt (min)	Saturated Hydrocarbons
Light compounds unidentified < Farnesane	< 27.6	
C_{10} Paraffin ($C_{10}H_{22}$)	8.1	x
Farnesane ($C_{15}H_{32}$)[A]	27.6	x
C_{15} Olefins ($C_{15}H_{30}$)	from 27.7 to 28.7	
C_{15} Naphthenes ($C_{15}H_{28}$)	from 28.7 to 29.1	
C_{15} Naphthene ($C_{15}H_{30}$)	29.2	x
C_{15} Olefins ($C_{15}H_{26}$)	from 29.3 to 29.5	
C_{15} Naphthene ($C_{15}H_{30}$)	29.6	x
C_{15} Olefins ($C_{15}H_{26}$)	from 29.7 to 29.8	
Farnesene ($C_{15}H_{24}$)[B]	29.9	
C_{15} Olefins ($C_{15}H_{26}$)	from 30 to 30.35	
C_{16} Paraffin ($C_{16}H_{34}$)	31.4	x
Oxygenated compound $C_{15}H_{30}O$ (1)	34.6	
Oxygenated compound $C_{15}H_{30}O$ (2)	35.4	
Hexahydrofarnesol ($C_{15}H_{32}O$)[C]	37.0	
Unidentified compound	51.4	
C_{30} Saturated Dimers ($C_{30}H_{60}$)	from 62.5 to 72.5	x
Sum of the other unidentified compounds		

[A] Farnesane is an iso-paraffin with chemical formula: $C_{15}H_{32}$, chemical name: 2,6,10-trimethyldodecane and CAS Registry Number: 3891-98-3.

[B] Farnesene is a branched alkene with chemical formula: $C_{15}H_{24}$, chemical name: (6E)-7,11-dimethyl-3-methylene-1,6,10-dodecatriene and CAS Registry Number: 18794-84-8.

[C] Hexahydrofarnesol is an alkyl alcohol with chemical formula: $C_{15}H_{32}O$, chemical name: 3,7,11-trimethyl-1-dodecanol and CAS Registry Number: 6750-34-1.

ANNEX

(Mandatory Information)

A1. FARNESANE RESPONSE LINEARITY

INTRODUCTION

The following description and procedure satisfies the verification of linearity when setting up the instrument.

A1.1 A series of six standards with known farnesane contents spread across the farnesane content range of the method (96 % to 99.9 % mass) has been analyzed three times under the operating conditions of the method.

A1.2 These standards have been prepared by diluting in n-heptane a reference farnesane of which purity has been determined at 98.73 % mass after five analyses using the present method.

A1.3 The average of the three farnesane peak areas obtained has been plotted with the known farnesane content in percent mass.

A1.4 The result is a linear response of farnesane over the range considered (Fig. A1.1) according to the least square straight line obtained:

$$A_F = 19.626\ C_F - 141.4 \qquad \text{(A1.1)}$$

where:

A_F = area of farnesane peak, and
C_F = content of farnesane component in percent mass.

A1.4.1 The correlation coefficient, R^2 is equal to 0.9927.

A1.4.2 This equation has then been used to recalculate for each standard its farnesane content in percent mass like if it was an unknown sample.

A1.4.3 Standard deviation of the residuals is less than 0.5 % which corresponds to a 95 % confidence interval of 1 %.

A1.5 *Remark*—Farnesane response linearity across a broader range (50 % to 99.9 %) has also been verified (Fig. A1.2) by adding to the previous results five standards spread across the range 50 % to 90 % mass of farnesane. The response linearity is also verified according to equation $A_F = 18.547\ C_F - 36.113$ with a correlation coefficient R^2 equal to 0.9998. In this case, standard deviation of the residuals is less than 0.5 % which corresponds to a 95 % confidence interval of 1 %.

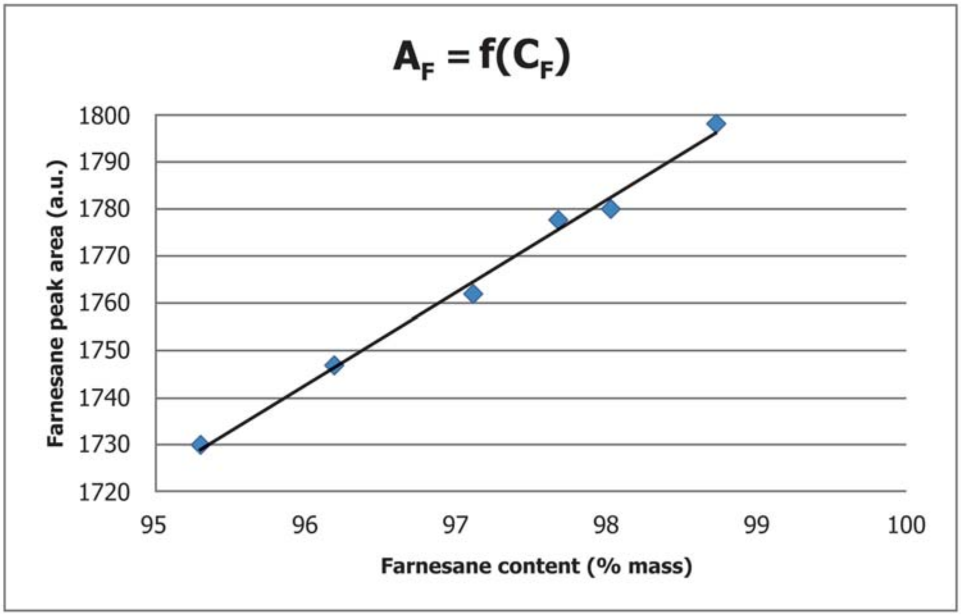


FIG. A1.1 Farnesane Response Linearity across the Farnesane Content Range of the Method (96 % to 99.9 % mass)

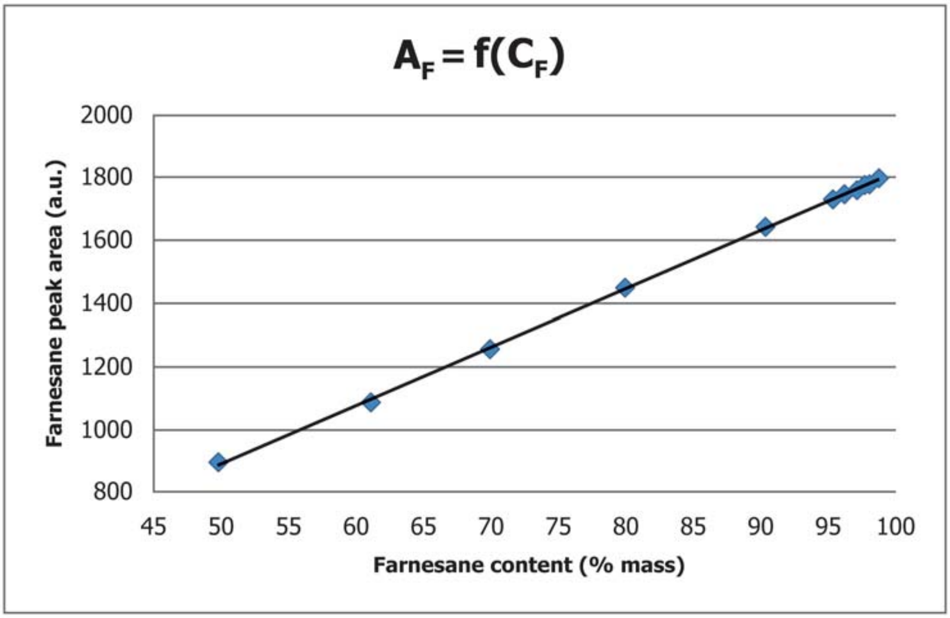


FIG. A1.2 Farnesane Response Linearity across the Farnesane Content Range (50 % to 99.9 % mass)

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 (e-mail); or through the ASTM website (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/