Designation: D8302 – 20

Standard Test Method for Determination of Cycloparaffin Content in Saturated ATJ-SPK Jet Fuel Gas Chromatography[1]

This standard is issued under the fixed designation D8302; 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 cycloparaffin content by gas chromatography of the saturated ATJ-SPK jet fuel as specified in Specification D7566, section A5.4.1, derived from isobutanol and follows the fuel fingerprint described in the Annex of this test method.

1.2 The working range for the test method is for cycloparaffin content in the range of 1 % to 15 % by mass.

1.3 The test method has an interim precision and will be updated once an extended ILS is conducted.

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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.5 *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:*[2]

D2425 Test Method for Hydrocarbon Types in Middle Distillates by Mass Spectrometry

D6299 Practice for Applying Statistical Quality Assurance and Control Charting Techniques to Evaluate Analytical Measurement System Performance

D6300 Practice for Determination of Precision and Bias Data for Use in Test Methods for Petroleum Products, Liquid Fuels, and Lubricants

D7566 Specification for Aviation Turbine Fuel Containing Synthesized Hydrocarbons

D7372 Guide for Analysis and Interpretation of Proficiency Test Program Results

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 This test method references common gas chromatographic procedures, terms, and relationships which may be found in Practices E355 and E594.

3.2 *Definitions:*

3.2.1 *paraffins, n*—saturated, non-cyclic hydrocarbons.

3.3 *Abbreviations:*

3.3.1 *ATJ-SPK*—alcohol-to-jet synthetic paraffinic kerosene

3.3.2 *ASTM*—American Society for Testing and Materials

3.3.3 *FID*—flame ionization detector

3.3.4 *GC/MS*—gas chromatograph mass spectrometer

3.3.5 *IPC*—identified paraffin concentration

3.3.6 *m/z*—molecular mass to charge ratio of an ion

3.3.7 *PTP*—proficiency testing programs

3.3.8 *QC*—quality control

4. Summary of Test Method

4.1 A representative aliquot of ATJ-SPK jet fuel is introduced into a gas chromatograph equipped with a 5 % phenylmethylpolysiloxane bonded phase capillary column. 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 in boiling point order. The detector signal is processed by an electronic data acquisition system. The paraffins are identified by comparing their retention times to the ones reported in the method. Identification of the paraffins has been previously performed by analyzing reference samples and standards by mass spectrometry under conditions as indicated in the Annex. The concentrations of all components are determined in mass percent area by normalization of

[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 on Hydrocarbon Analysis.

Current edition approved July 1, 2020. Published July 2020. DOI: 10.1520/D8302-20.

[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.

the peak areas. The cycloparaffin content is determined as 100 % percent paraffins.

5. Significance and Use

5.1 This test method applies specifically to the ATJ-SPK jet fuel as specified in Specification D7566, section A5.4.1, derived from isobutanol and follows the fuel fingerprint described in the annex of this test method. It may not apply to other types of ATJ-SPK fuels.

5.2 Table A2.2 in Specification D7566 prescribes cycloparaffin concentration be a maximum of 15 % by mass.

5.3 Due to the nature of the chemical composition of ATJ-SPK jet fuel, standard analysis of the sample by Test Method D2425 for cycloparaffin content may yield a higher concentration of cycloparaffins than are actually present in the sample.

5.4 This method alleviates the potential for overestimating the cycloparaffin concentration by measuring the concentration of identified paraffins. Any remaining unidentified compounds are classified as potential cycloparaffins.

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, 200:1) 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. Pressure control devices and gauges shall be designed to attain the linear velocity required in the column used. A hydrogen flame ionization detector with associated gas controls and electronics, designed for optimum response with open tubular (capillary) columns, is required.

6.2 *Sample Introduction*—Manual or automatic liquid syringe sample injection to the splitting injector is employed. Devices capable of 0.1 µL to 0.5 µL injections are suitable. It should be noted that inadequate splitter design, poor injection technique and overloading the column may result in poor resolution and quantification.

TABLE 1 Typical Operating Conditions

Column Temperature Program	
Column Length	30 m
Initial Temperature	50 °C
Initial Hold Time	2 min
Program Rate	10 °C/min
Final Temperature	290 °C
Final Hold Time	0 min
Injector	
Temperature	200 °C
Split Ratio	200:1
Sample Size	0.1 µL
Detector	
Type	Flame Ionization
Fuel Gas	Hydrogen (35 mL/min)
Oxidizing Gas	Air (350 mL/min)
Make-up Gas	Nitrogen (12.6 mL/min)
Carrier Gas	
Type	Helium
Flow Rate	2.5 mL/min

6.3 *Column*—This test method utilizes a fused silica open tubular column with 5 %-Phenyl-methylpolysiloxane bonded (cross-linked) phase. A 30 m by 0.32 mm with a 0.25 µm film thickness was used to develop this method and all peak identifications described in this method were obtained with this column. Any column with equivalent polarity, improved chromatographic efficiency and selectivity as described in 6.3.1 may be used as long as the compounds of interest are readily identified.

6.4 *Electronic Data Acquisition System*—Any electronic 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 and using response factors,

6.4.2 Identification of individual components based on standards,

6.4.3 Noise and spike rejection capability,

6.4.4 Non-resolved peaks separated by perpendicular drop or tangential skimming as needed.

7. Reagents and Materials

7.1 *Carrier Gas,* helium, with a minimum purity of 99.95 % mol. Oxygen removal systems and gas purifiers are recommended. (**Warning—**Helium, compressed gas under high pressure.) Hydrogen carrier gas was not tested during development of this test method.

7.2 *Detector Gases,* hydrogen, air, and nitrogen. The minimum purity of the gases used should be 99.95 % mol for the hydrogen and nitrogen. The air should be hydrocarbon-free grade. Gas purifiers are recommended for the detector gases. (**Warning—**Hydrogen, extremely flammable gas under high pressure.) (**Warning—**Air and nitrogen, compressed gases under high pressure.)

7.3 *Standards for Calibration and Identification*—Standards of components to be analyzed are required for establishing identification by retention time. These standards shall be of highest purity, preferably ≥98 %. (**Warning—**These materials are flammable and may be harmful or fatal if ingested or inhaled.)

7.3.1 2, 2, 4-trimethylpentane, ≥99 % purity (**Warning—**Flammable and may be harmful or fatal, if ingested or inhaled.)

7.3.2 2,3,4-trimethylpentane, ≥98 % purity (**Warning—**Flammable and may be harmful or fatal, if ingested or inhaled.)

7.3.3 2,2,4,6,6-pentamethylheptane, ≥98 % purity (**Warning—**Flammable and may be harmful or fatal, if ingested or inhaled.)

7.3.4 2,2,4,4,6,8,8-Heptamethylnonane, ≥98 % purity (**Warning—**Flammable and may be harmful or fatal, if ingested or inhaled.)

8. Sampling

8.1 Transfer an aliquot of the sample to be analyzed into a vial and seal. Inject the test sample directly into the gas chromatograph, either manual or preferably using an automatic syringe injection.

9. Preparation of Apparatus

9.1 Install and condition column in accordance with manufacturer's or supplier's instructions. Check for leaks throughout the system and if leaks are found, tighten or replace fittings before proceeding.

9.2 Adjust the operating conditions of the gas chromatograph in accordance to Table 1 (6.4.4) and allow the system to equilibrate.

10. Calibration and Standardization

10.1 *Standard Identification*—Determine the retention times of 2,2,4-trimethylpentane, 2,3,4-trimethylpentane, 2,2,4,6,6-pentamethylheptane, and 2,2,4,4,6,8,8-heptamethylnonane.

10.2 *Unidentified Paraffin Peaks*—Additional small peaks surrounding the known 2,2,4,6,6-pentamethylheptane and 2,2,4,4,6,8,8-heptamethylnonane standard peaks have been determined to be paraffinic based on their mass fragmentation patterns from GC/MS analysis. Although the exact structures of these peaks have not been identified or confirmed by analysis of purchased standards, the peaks have been designated as paraffinic and are quantitated as such.

10.2.1 Additional data on how the GC/MS analysis was performed to determine that the unknown peaks were paraffinic may be found in Annex A1.

10.3 For each standard, inject 0.1 µL into the injection port and start the analysis, according to the conditions stated in Table 1.

10.3.1 To avoid peak overloading it may be necessary to dilute the standards in an appropriate non-interfering solvent.

10.4 Obtain a chromatogram and record the retention times of the paraffin standards and their corresponding unidentified paraffin peaks in a peak identification table for reference.

11. Procedure

11.1 *Analysis*—Introduce a representative aliquot of the sample into the gas chromatograph, using the same injection technique and conditions as used for the analysis of the standards.

11.2 *Interpretation of Chromatogram*—Obtain a chromatogram or integrated peak report, or both to compare the retention times of sample peaks to those of the standard analysis to determine the identities and integrated area of each detected component. Annex A2 gives an example chromatogram, calculation and report.

12. Calculation or Interpretation of Results

12.1 Record the total area of the identified peaks (all paraffinic compounds identified by standards or GC/MS analysis). See Annex A2 for example.

12.2 Divide the area of the identified peaks by total peak area reported and multiply by 100 to determine percent identified paraffin peaks. Subtract the result from 100 to determine maximum potential cycloparaffin concentration:

$$\text{Percent of Identified Paraffin Concentration (IPC)} = (\text{Area of Paraffinic Identified Peaks/Total Peak Area}) * 100 \quad (1)$$

$$\text{Maximum percent potential cycloparaffin concentration} = 100 - \text{IPC} \quad (2)$$

13. Quality Control of Test Method Performance

13.1 Confirm the test method performance via regular testing of quality control (QC) sample(s) following the guidance in Practice D6299.

13.1.1 The QC material should be representative of the samples analyzed routinely.

13.2 Use of a reference fuel or participation in appropriate proficiency testing programs (PTP), or both, is recommended for monitoring performance relative to industry and to verify that all compounds are identified correctly and that the instrument is properly optimized. Follow Practice D7372 for PTP.

14. Report

14.1 Report the maximum potential cycloparaffin concentration to the nearest 0.01 % by mass, and reference this test method. Report the total paraffin content IPC to 0.01 % by mass.

15. Precision and Bias

15.1 *Precision*—The current precision statement should be considered temporary until the inter-laboratory study is completed. The repeatability and reproducibility will be determined by an interlaboratory study in accordance with ASTM methodology.

15.1.1 *Repeatability—Interim Repeatability*—The interim repeatability[3] carried out by a single laboratory on three ATJ-SPK jet fuel samples in accordance with Practice D6300, section 6.2.1.1, is as follows:

Average Mass Percent Cycloparaffins	Repeatability
1.12	0.0513
9.27	0.441
15.28	0.409

15.1.1.1 The precision of total paraffins has not been determined.

15.1.2 *Reproducibility*—To be determined.

15.2 *Bias*—At this time, there is no accepted reference material suitable for determining the bias for this test method, therefore no statement on bias is being made.

16. Keywords

16.1 ATJ-SPK jet fuel; butanol; butanols; cycloparaffin; gas chromatography; paraffin

[3] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-2000. Contact ASTM Customer Service at service@astm.org.

ANNEXES

(Mandatory Information)

A1. GC/MS ANALYSIS OF UNKNOWN PEAKS IN SATURATED ATJ-SPK JET FUEL

A1.1 Scope

A1.1.1 This annex provides GC/MS data which identifies unknown peaks in saturated ATJ-SPK jet fuel as either paraffins or cycloparaffins.

A1.2 Referenced Documents

A1.2.1 *ASTM Standards*:

D2425 Test Method for Hydrocarbon Types in Middle Distillates by Mass Spectrometry

A1.3 Terminology

A1.3.1 *Definitions*:

A1.3.1.1 Test Method D2425 defines paraffins and cycloparaffins based on the summation of characteristic mass fragments as follows:

Σ 71 (paraffins) = total peak height of *m/e* + 71 + 85

Σ 85 (mono or noncondensed polycycloparaffins, or both) = total peak height of *m/e* + 67 + 68 + 69 + 81 + 82 + 83 + 96 + 97

A1.4 GC/MS Analysis: Known Cycloparaffins

A1.4.1 Two known cycloparaffins, t-butylcyclohexane, 99 % purity and isopropylcyclohexane, 99 % purity, were chosen for GC/MS analysis to confirm characteristic mass spectrum m/z ratios as defined in Test Method D2425.

A1.4.2 The resulting mass spectra fragmentation patterns show a predominance of 67, 69, 82, and 83 mass fragments, which supports the characteristic mass groupings as defined by Test Method D2425 and indicate the cycloparaffinic nature of the compounds.

A1.5 GC/MS Analysis: Known Paraffins

A1.5.1 Two known paraffinic compounds present in the ATJ-SPK jet fuel, 2,2,4,6,6-pentamethylheptane, 98 % purity and 2,2,4,4,6,8,8-heptamethylnonane, 98 % purity, were analyzed by GC/MS to confirm characteristic mass spectrum m/z ratios as defined in Test Method D2425.

A1.5.2 The resulting mass spectra fragmentation pattern show a predominance of 71 and 85 mass fragments, which supports the characteristic mass groupings defined in Test Method D2425 and indicate the paraffinic nature of the compounds. They also both contain a large 99 mass fragment, which results from the -$CHCH_3CH_2C(CH_3)_3$ fragment in each compound.

A1.6 GC/MS Analysis: Known Peaks in Standard ATJ-SPK Jet Fuel

A1.6.1 GC/MS Analysis of the 2,2,4,6,6-pentamethylheptane peak found in a saturated, final product ATJ-SPK jet fuel sample shows similar abundances of m/z 71, 85, and 99 as those seen in the known 2,2,4,6,6-pentamethylheptane standard.

A1.6.2 GC/MS Analysis of the 2,2,4,4,6,8,8-heptamethylnonane peak found in a saturated, final product ATJ-SPK jet fuel sample shows similar abundances of m/z 71, 85, and 99 as those seen in the known 2,2,4,4,6,8,8-heptamethylnonane standard.

A1.7 GC/MS Analysis: Unknown Peaks in Saturated ATJ-SPK Jet Fuel

A1.7.1 Unidentified peaks are present in the C12-C16 region of saturated final product ATJ-SPK jet fuel, as determined by GC analysis. Analysis of the mass fragmentation patterns of the unknown peaks by GC/MS allows determination of which peaks are consistent with paraffin designation, as defined in Test Method D2425.

A1.7.2 Based on GC/MS analysis of the known C12 and C16 saturated acyclic hydrocarbons presented above, any unknown peaks reporting an apparent predominance of m/z 71 and 85, as confirmed by the abundances reported by GC/MS software, will be classified as a paraffin and quantitated as such.

Any unknown peaks reporting an apparent predominance of m/z 67, 68, 69, 81, 82, 83, 96, and 97, as confirmed by the abundances reported by GC/MS software, will not be classified and quantitated as paraffin.

A1.7.3 The GC/MS mass fragmentation patterns of eight unknown peaks in saturated ATJ-SPK jet fuel were analyzed.

A1.7.4 *Unknown Peak at 6.7 min*—The GC/MS results show a predominance of m/z 71, 85, and 99, as was seen in the known paraffin standards; therefore, this peak is classified as a paraffin.

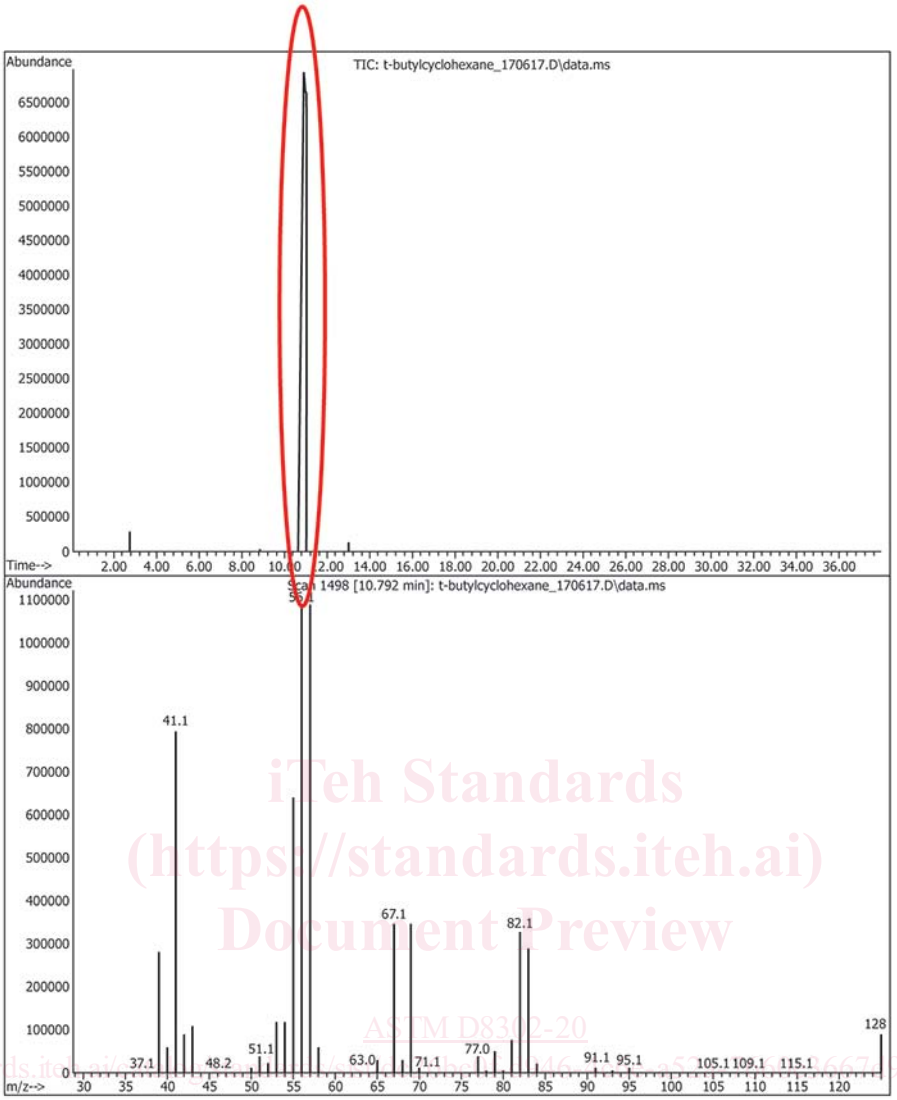
A1.7.5 *Unknown Peak at 6.8 min*—The GC/MS results show an apparent predominance of m/z 71 and 85, as confirmed by the abundances reported by the GC/MS software; therefore, this peak is classified as a paraffin.

A1.7.6 *Unknown Peak at 6.95 min*—The GC/MS results show an apparent predominance of m/z 71 and 85, as confirmed by the abundances reported by the GC/MS software; therefore, this peak is classified as a paraffin.

A1.7.7 *Unknown Peak at 7.64 min*—The GC/MS results show an apparent predominance of m/z 71 and 85, as confirmed by the abundances reported by the GC/MS software; therefore, this peak is classified as a paraffin.

A1.7.8 *Unknown Peak at 9.2 min*—The GC/MS results show a predominance of m/z 69, 83, and 97; therefore, this peak is not classified as a paraffin.

A1.7.9 *Unknown Peak at 9.27 min*—The GC/MS results show an apparent predominance of m/z 71 and 85, as confirmed by the abundances reported by the GC/MS software; therefore, this peak is classified as a paraffin.

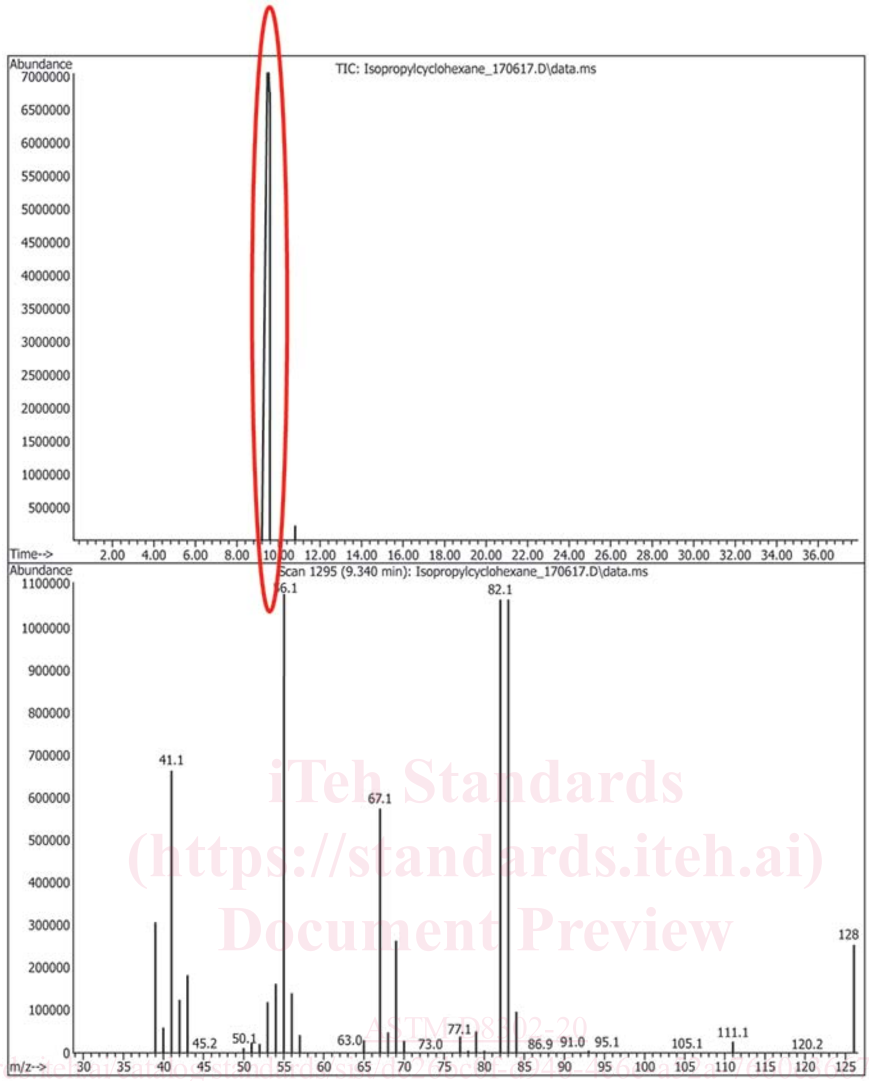


Name: Scan 1498 (10.792 min): t-butylcyclohexane_170816.D\data.ms
MW: N/A ID#: 2641 DB: Text File
Comment: t-butylcyclohexane
10 largest peaks:
56 999 | 57 767 | 41 499 | 55 401 | 67 219 | 69 211 | 82 205 | 83 179 | 39 176 | 54 75 |
Synonyms:
no synonyms.

FIG. A1.1 GC/MS m/z Abundance Report: Aldrich Standard "t-butylcyclohexane"

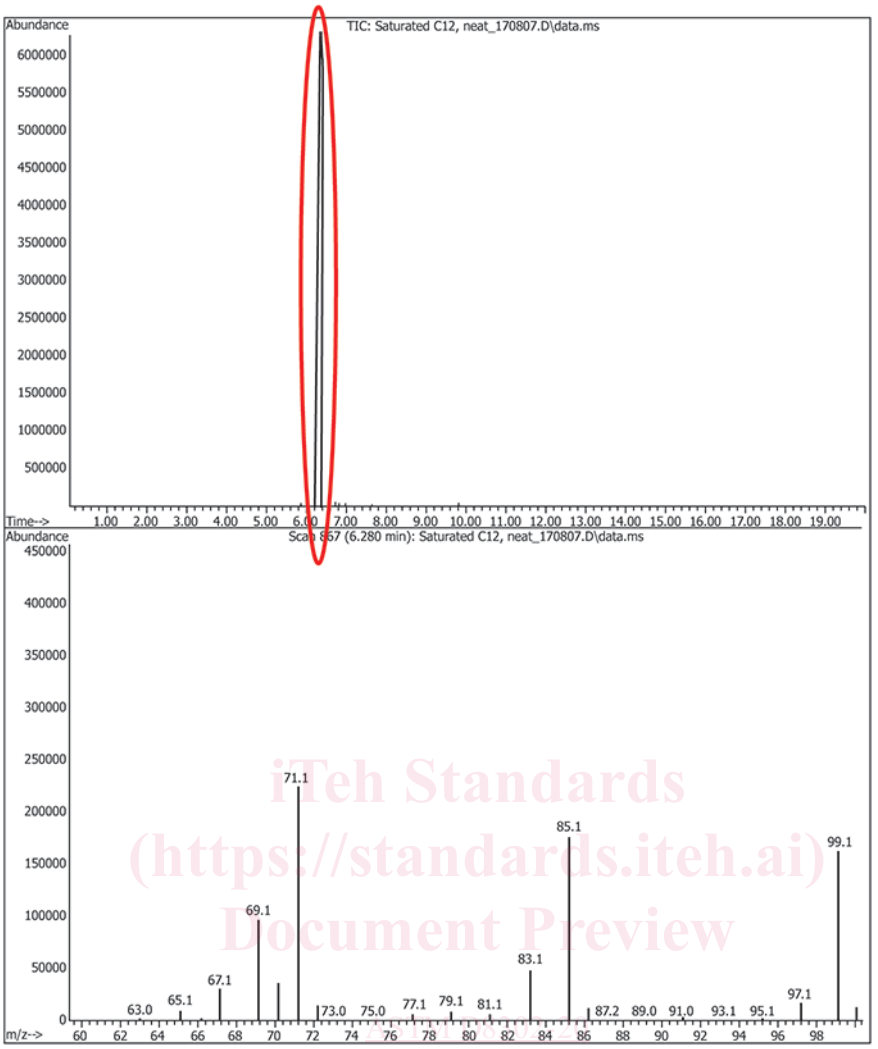
A1.7.10 *Unknown Peak at 9.73 min*—The GC/MS results show an apparent predominance of m/z 71 and 85, as confirmed by the abundances reported by the GC/MS software; therefore, this peak is classified as a paraffin.

A1.7.11 *Unknown Peak at 9.91 min*—The GC/MS results show an apparent predominance of m/z 71 and 85, as confirmed by the abundances reported by the GC/MS software; therefore, this peak is classified as a paraffin.



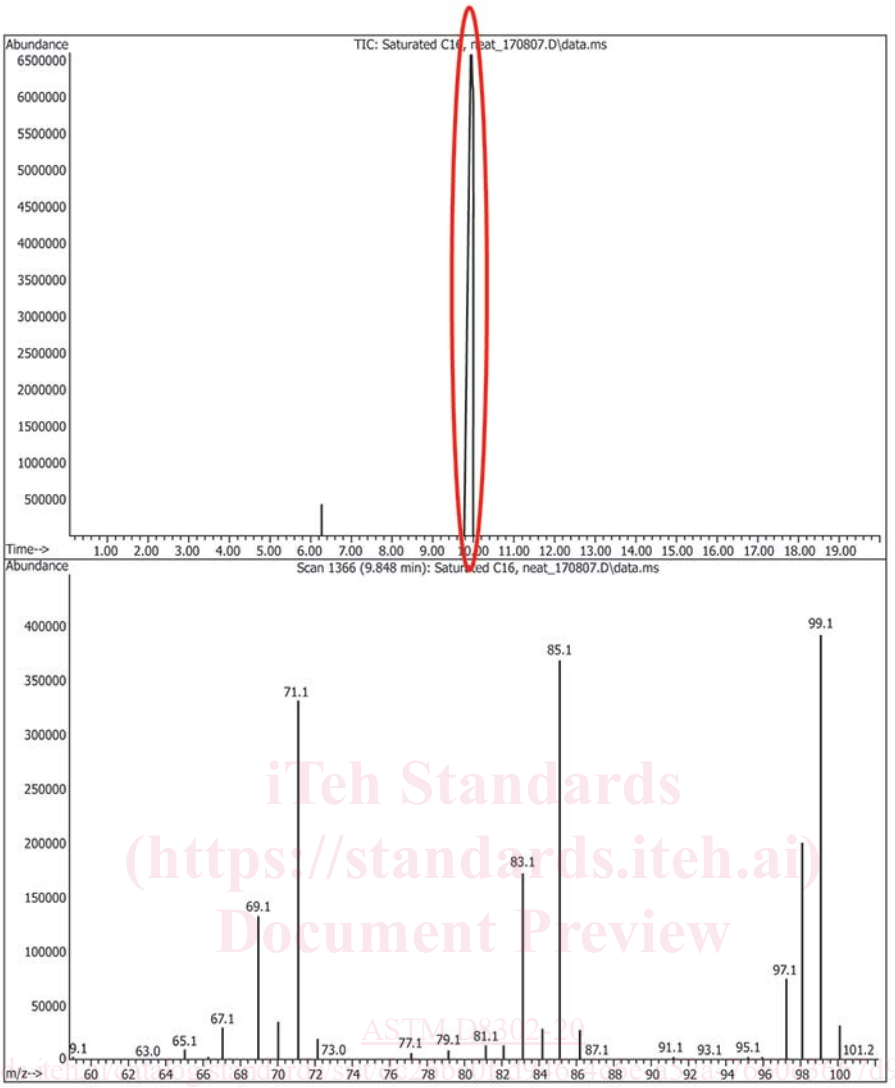
Name: Scan 1295 (9.340 min): Isopropylcyclohexane_170817.D\data.ms
MW: N/A ID#: 2643 DB: Text File
Comment: Isopropylcyclohexane
10 largest peaks:
82 999 | 83 991 | 55 976 | 41 544 | 67 463 | 39 251 | 69 218 | 126 209 | 43 149 | 54 136 |
Synonyms:
no synonyms.

FIG. A1.2 GC/MS m/z Abundance Report: Aldrich Standard "Isopropylcyclohexane"



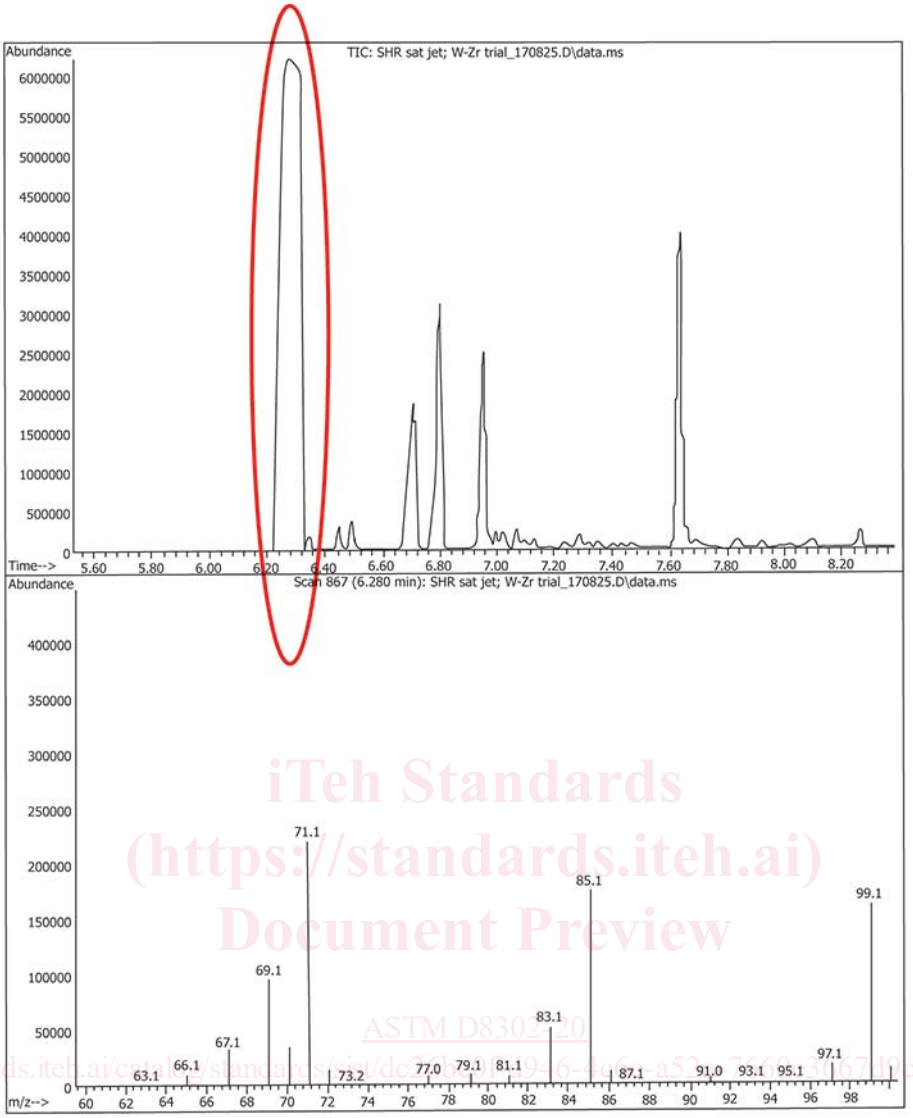
Name: Scan 867 (6.280 min): Saturated C12, neat_170807.D\data.ms
MW: N/A ID#: 2644 DB: Text File
Comment: Saturated C12, neat
10 largest peaks:
57 999 | 56 563 | 41 378 | 43 167 | 55 142 | 71 107 | 39 92 | 85 84 | 99 78 | 58 71 |
Synonyms:
no synonyms.

FIG. A1.3 GC/MS m/z Abundance Report: Aldrich Standard "2,2,4,6,6-pentamethylheptane"



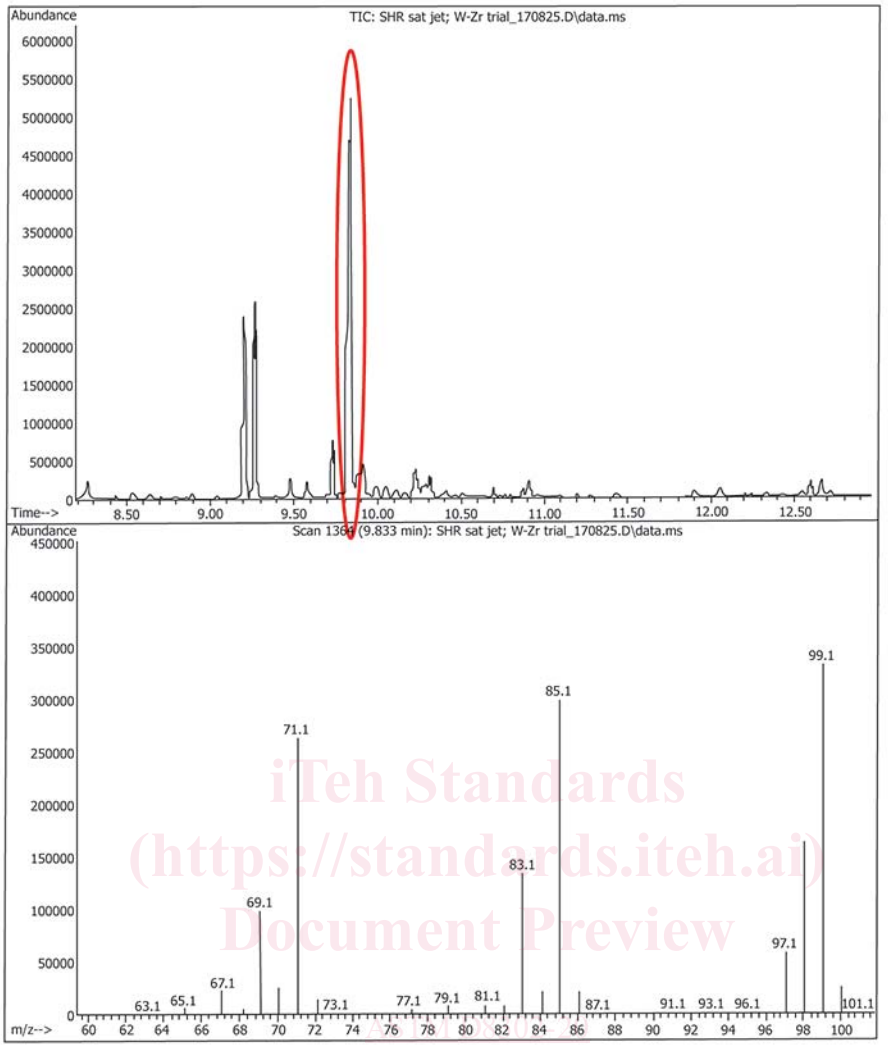
Name: Scan 1366 (9.848 min): Saturated C16, neat_170807.D\data.ms
MW: N/A ID#: 2645 DB: Text File
Comment: Saturated C16, neat
10 largest peaks:
57 999 | 41 281 | 99 186 | 85 173 | 56 160 | 71 156 | 113 149 | 43 142 | 55 139 | 98 94 |
Synonyms:
no synonyms.

FIG. A1.4 GC/MS m/z Abundance Report: Aldrich Standard "2,2,4,4,6,8,8-heptamethylnonane"



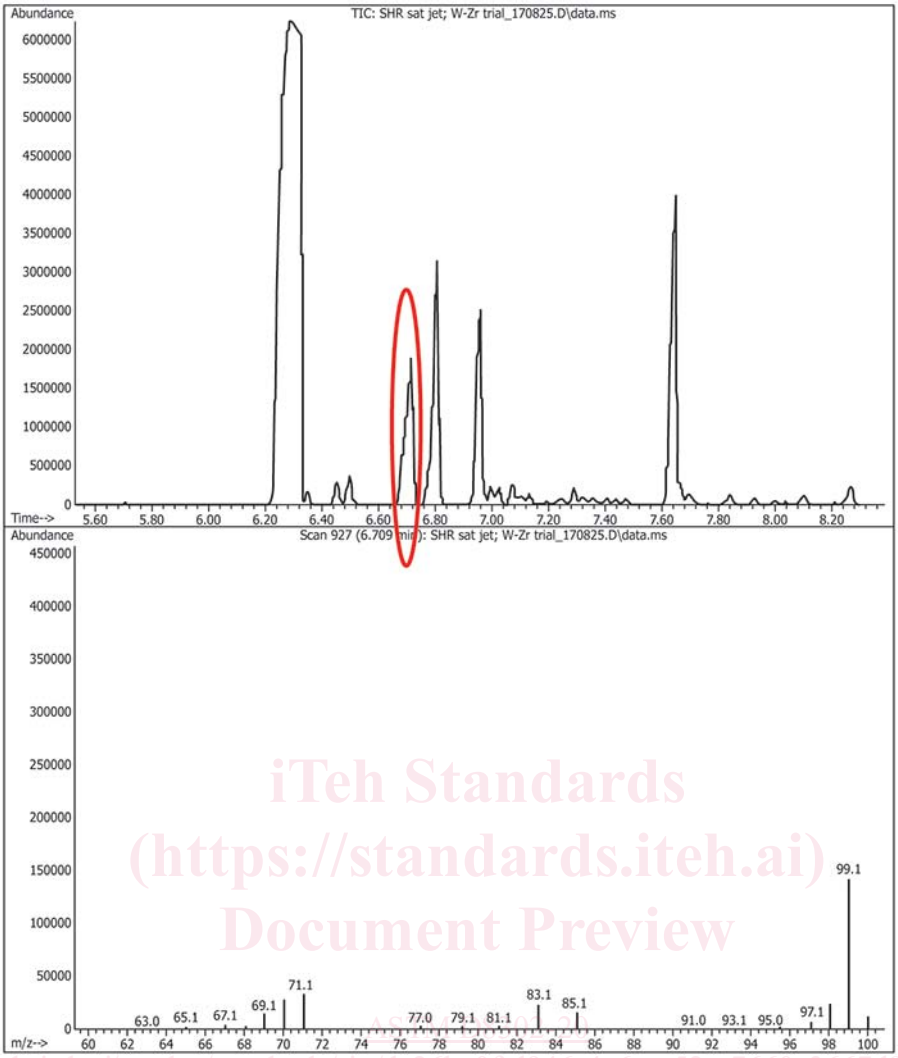
Name: Scan 867 (6.280 min): SHR sat jet; W-Zr trial_170825.D\data.ms
MW: N/A ID#: 2646 DB: Text File
Comment: SHR sat jet; W-Zr trial
10 largest peaks:
57 999| 56 557| 41 374| 43 163| 55 142| 71 106| 39 91| 85 84| 99 78| 58 70|
Synonyms:
no synonyms.

FIG. A1.5 GC/MS m/z Abundance Report: Saturated ATJ-SPK-Jet Fuel Peak "2,2,4,6,6-pentamethylheptane"



Name: Scan 1364 (9.833 min): SHR sat jet; W-Zr trial_170825.D\data.ms
MW: N/A ID#: 2651 DB: Text File
Comment: SHR sat jet; W-Zr trial
10 largest peaks:
57 999| 41 227| 99 182| 85 164| 113 154| 71 144| 56 131| 43 116| 55 115| 98 90|
Synonyms:
no synonyms.

FIG. A1.6 GC/MS m/z Abundance Report: Saturated ATJ-SPK-Jet Fuel Peak "2,2,4,4,6,8,8-heptamethylnonane"



Name: Scan 927 (6.709 min): SHR sat jet; W-Zr trial_170825.D\data.ms
MW: N/A ID#: 2647 DB: Text File
Comment: SHR sat jet; W-Zr trial
10 largest peaks:
57 999 | 41 177 | 99 164 | 56 145 | 43 139 | 113 70 | 55 62 | 58 48 | 71 39 | 39 38 |
Synonyms:
no synonyms.

FIG. A1.7 GC/MS m/z Abundance Report: Unknown Peak at 6.7 min