



Designation: D5442 – 17 (Reapproved 2021)

## Standard Test Method for Analysis of Petroleum Waxes by Gas Chromatography<sup>1</sup>

This standard is issued under the fixed designation D5442; 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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

### 1. Scope

1.1 This test method covers the quantitative determination of the carbon number distribution of petroleum waxes in the range from  $n$ -C<sub>17</sub> through  $n$ -C<sub>44</sub> by gas chromatography using internal standardization. In addition, the content of normal and non-normal hydrocarbons for each carbon number is also determined. Material with a carbon number above  $n$ -C<sub>44</sub> is determined by its difference from 100 % by mass and reported as C<sub>45+</sub>.

1.2 This test method is applicable to petroleum derived waxes, including blends of waxes. This test method is not applicable to oxygenated waxes, such as synthetic polyethylene glycols (for example, Carbowax<sup>2</sup>), or natural products such as beeswax or carnauba.

1.3 This test method is not directly applicable to waxes with oil content greater than 10 % as determined by Test Method D721.

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

1.5 *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 consult and establish appropriate safety, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.6 *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.*

<sup>1</sup> 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 D02.04.0H on Chromatographic Distribution Methods.

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<sup>2</sup> Carbowax is a registered trademark of Union Carbide Corp.

### 2. Referenced Documents

2.1 *ASTM Standards:*<sup>3</sup>

D721 Test Method for Oil Content of Petroleum Waxes

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

D4626 Practice for Calculation of Gas Chromatographic Response Factors

E260 Practice for Packed Column Gas Chromatography

E355 Practice for Gas Chromatography Terms and Relationships

### 3. Terminology

3.1 *Definitions of Terms Specific to This Standard:*

3.1.1 *carbon number, n*—a number corresponding to the number of carbon atoms in a hydrocarbon.

3.1.2 *cool on-column injection, n*—a sample introduction technique in gas chromatography where the sample is injected inside the front portion of a partition column at a temperature at or below the boiling point of the most volatile component in the sample.

3.1.3 *low volume connector, n*—a metal or glass union designed to connect two lengths of capillary tubing. Usually designed so that the tubing ends are joined with a minimum of either dead volume or overlap between them.

3.1.4 *non(normal paraffin)hydrocarbon (NON), n*—all other hydrocarbon types excluding those hydrocarbons with carbon atoms in a single length. Includes aromatics, naphthenes, and branched hydrocarbon types.

3.1.5 *normal paraffin, n*—a saturated hydrocarbon which has all carbon atoms bonded in a single length, without branching or hydrocarbon rings.

3.1.6 *wall coated open tube (WCOT), n*—a term used to specify capillary columns in which the stationary phase is coated on the interior surface of the glass or fused silica tube. Stationary phase may be cross-linked or bonded after coating.

### 4. Summary of Test Method

4.1 Weighed quantities of the petroleum wax and an internal standard are completely dissolved in an appropriate solvent and

<sup>3</sup> 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.

**TABLE 1 Typical Operating Conditions**

Column length (m):	25	30	15
Column inside diameter (mm):	0.32	0.53	0.25
Stationary phase:	DB-1 methyl silicone	RTX-1 methyl silicone	DB-5 5 % phenyl methyl silicone
Film thickness (µm):	0.25	0.25	0.25
Carrier gas:	Helium	Helium	Helium
Carrier flow (mL/min):	1.56	5.0	2.3
Linear velocity (cm/s):	33	35	60
Column initial temperature (°C):	80	80	80
Program rate (°C/min):	10	8	5
Final temperature (°C):	380	340	350
Injection technique:	cool on-column	cool on-column	cool on-column
Detector temperature (°C):	380	400	375
Sample size (µL):	1.0	1.0	1.0

introduced into a gas chromatographic column that separates the hydrocarbon components by increasing carbon number. The column temperature is linearly increased at a reproducible rate until the sample is completely eluted from the column.

4.2 The eluted components are detected by a flame ionization detector and recorded on a strip chart or computer system. The individual carbon numbers are identified by comparing the retention times obtained from a qualitative standard with the retention times of the wax sample. The percent of each hydrocarbon number through  $C_{44}$  is calculated via internal standard calculations after applying response factors.

4.3 For samples with final boiling points greater than 538 °C complete elution of all components may not be achieved under the specified conditions. For this reason, the  $C_{45+}$  material is determined by summing the concentrations of each individual carbon number through  $C_{44}$  and subtracting this total from 100 % by mass.

## 5. Significance and Use

5.1 The determination of the carbon number distribution of petroleum waxes and the normal and non-normal hydrocarbons in each can be used for control of production processes as well as a guide to performance in many end uses.

5.2 Data resulting from this test method are particularly useful in evaluating petroleum waxes for use in rubber formulations.

## 6. Apparatus

6.1 *Chromatograph*—Any gas chromatographic instrument that can accommodate a WCOT column, equipped with a flame ionization detector (FID), and that can be operated at the conditions given in **Table 1** may be employed. The chromatograph should be equipped with a cool on-column inlet (or equivalent) for introducing appropriate quantities of sample without fractionation. In addition, the gas chromatograph must be capable of generating a chromatogram where the retention times of an individual peak have retention time repeatability within 0.1 min. Refer to Practices **E260** and **E355** for general information on gas chromatography.

6.2 *Sample Introduction System*—Any system capable of introducing a representative sample onto the front portion of a WCOT column may be employed. Cool on-column injection is preferred, however other injection techniques can be used provided the system meets the specification for linearity of response in **9.6**. For cool on-column injection, syringes with 0.15 mm to 0.25 mm outside diameter needles have been used successfully for columns 0.25 mm inside diameter or larger and standard 0.47 mm outside diameter syringe needles have been used for columns 0.53 mm inside diameter or greater.

6.2.1 Care must be taken that the sample size chosen does not allow some peaks to exceed the linear range of the detector or overload the capacity of the column.

6.3 *Column(s)*—Any column used must meet the chromatographic resolution specification in **9.5**. WCOT columns with 25 m to 30 m lengths and a stationary phase coating of methyl siloxane or 5 % phenyl methyl siloxane have been successfully used. Cross-linked or bonded stationary phases are preferred.

6.4 *Recorder*—A recording potentiometer or equivalent with a full-scale deflection of 5 mV or less for measuring the detector signal versus time. Full scale response time should be 2 s or less. Sensitivity and stability should be sufficient to generate greater than 2 mm recorder deflection for a hydrocarbon injection of 0.05 % by mass under the analysis conditions employed.

6.5 *Integrator or Computer*—Means must be provided for integrating the detector signal and summing the peak areas between specific time intervals. Peak areas can be measured by computer or electronic integration. The computer, integrator, or gas chromatograph must have the capability of subtracting the area corresponding to the baseline (blank) from the sample area, and have the ability to draw the baselines used for peak area integration.

## 7. Reagents and Materials

7.1 *Carrier Gas*—Carrier gas appropriate for the flame ionization detector. Hydrogen and helium have been used successfully. The minimum purity of the carrier gas used should be 99.95 mol %. (**Warning**—Hydrogen and helium are compressed gases under high pressure. Hydrogen is an extremely flammable gas.)

7.2 *n-hexadecane*—Hydrocarbon to be added to samples as an internal standard. Minimum purity of 98 % is required.

7.3 *Standards for Calibration and Identification*—Standard samples of normal paraffins covering the carbon number range (through  $C_{44}$ ) of the sample are needed for establishing the retention times of the individual paraffins and for calibration for quantitative measurements. Hydrocarbons used for standards must be greater than 95 % purity.

7.4 *Solvent*—A liquid (99 % pure) suitable for preparing a quantitative mixture of hydrocarbons and for dissolving petroleum wax. Cyclohexane has been used successfully. (**Warning**—Solvents are flammable and harmful if inhaled.)

7.5 *Linearity Standard*—Prepare a weighed mixture of *n*-paraffins covering the range between *n*- $C_{16}$  to *n*- $C_{44}$  and dissolve the mixture in cyclohexane. Use approximately equal

amounts of each of the paraffins and a balance capable of determining mass to within 1 % of the mass of each compound added. It is not necessary to include every *n*-paraffin in this mixture so long as the sample contains *n*-C<sub>16</sub>, *n*-C<sub>44</sub>, and at least one of every fourth *n*-paraffin. It will be necessary to prepare the standard sample in cyclohexane, so that the normal paraffins are completely dissolved in the solvent. Solutions of 0.01 % by mass *n*-paraffin have been used successfully. This sample must be capped tightly, to prevent solvent loss which will change the concentration of paraffins in the standard blend.

NOTE 1—Refer to Practice D4307 for details of how to prepare hydrocarbon mixtures.

**7.6 Internal Standard Solution**—Prepare a dilute solution of internal standard in cyclohexane in two steps as follows:

**7.6.1** Prepare a stock solution containing 0.5 % by mass *n*-C<sub>16</sub> in cyclohexane by accurately weighing approximately 0.4 g *n*-C<sub>16</sub> into a 100 mL volumetric flask. Add 100 mL of cyclohexane and reweigh. Record the mass of *n*-C<sub>16</sub> to within 0.001 g and the mass of solution (cyclohexane and *n*-C<sub>16</sub>) to within 0.1 g.

**7.6.2** Prepare a dilute solution of *n*-C<sub>16</sub> internal standard by diluting one part of stock solution with 99 parts of cyclohexane. Calculate the concentration of internal standard in the dilute solution using Eq 1.

$$C_{ISTD} = \frac{W_{ISTD}}{W_s} \times \frac{100\%}{100} \quad (1)$$

where:

$C_{ISTD}$  = percent by mass *n*-C<sub>16</sub> internal standard in dilute solution,

$W_{ISTD}$  = weight of *n*-C<sub>16</sub> from 7.6.1,

$W_s$  = weight of cyclohexane plus *n*-C<sub>16</sub> from 7.6.1,

100 % = factor to convert weight fraction to percent by mass, and

100 = dilution factor.

## 8. Sampling

**8.1** To ensure homogeneity, completely mix the entire wax sample by heating it to 10 °C above the temperature at which the wax is completely molten and then mix well by stirring. Using a clean eyedropper, transfer a few drops to the surface of a clean sheet of aluminum foil, allow to solidify and break into pieces. The wax can either be used directly as described in Section 11 or placed in a sealed sample vial until ready for use.

**8.1.1** Aluminum foil usually contains a thin film of oil from processing. This oil must be removed by rinsing the foil with solvent such as hexane or mineral spirits, prior to use.

## 9. Preparation of Apparatus

**9.1 Column Conditioning**—Capillary columns with bonded (or cross-linked) stationary phases do not normally need to be conditioned; however, it is good chromatographic practice to briefly condition a new column as described below.

**9.1.1** Install the column in the chromatographic oven and connect one column end to the sample inlet system. Turn on the source of carrier gas and set the flow controller (or pressure regulator) to the flow rate to be used in the analysis. Increase the column temperature to the maximum value to be used in the

analysis and maintain this temperature for 30 min. Cool the column temperature to room temperature and connect the remaining column end to the detector. Care must be taken that the column terminates as close as possible to the tip of the FID jet. The temperature of the column between the column oven and the detector jet must be maintained above the maximum column temperature.

**9.2 Operating Conditions**—Set the chromatographic operating conditions (see Table 1) and allow the system to achieve all temperature setpoints. The recorder, computer or integrating device should be connected so that a plot of the detector signal versus time can be obtained. Make certain that the FID is ignited before proceeding.

**9.3 Baseline Blank**—After conditions have been set to meet performance requirements, program the column temperature upward to the maximum temperature to be used. Once the column oven temperature has reached the maximum temperature, cool the column to the selected starting temperature. Without injecting a sample, start the column temperature program, the recording device and the integrator. Make two baseline blank runs to determine if the baseline blank is repeatable. If the detector signal is not stable or if the baseline blanks are not repeatable, then the column should either be conditioned further or replaced.

**9.3.1 Baseline Bleed**—Observe the detector response from the blank run on the recorder. Some increase in detector response will be observed at the upper column temperatures due to stationary phase bleed. Column bleed is acceptable so long as the duplicate baseline blank analyses are repeatable. The baseline should be a smooth curve, free of any chromatographic peaks.

**9.4 Solvent Blank**—Make a 1 μL injection of the cyclohexane solvent and program the column oven. The solvent is of suitable purity if there are no detected peaks within the retention time range over which the wax samples elute.

**9.5 Column Resolution**—Check the efficiency of the GC column by analyzing, under conditions specified in 10.2, a 1 μL injection of 0.05 % by mass solution of *n*-C<sub>20</sub> and *n*-C<sub>24</sub> in cyclohexane. The column resolution must not be less than 30 as calculated using Eq 2.

$$R = \frac{2d}{1.699(W1 + W2)} \quad (2)$$

where:

$d$  = distance (mm) between the peak maxima of *n*-C<sub>20</sub> and *n*-C<sub>24</sub>,

$W1$  = peak width (mm) at half height of *n*-C<sub>20</sub>, and

$W2$  = peak width (mm) at half height of *n*-C<sub>24</sub>.

**9.6 Linearity of Response**—For quantitative accuracy, detector response must be proportional to the mass of hydrocarbon injected, and the response of the non-normal paraffins is assumed to be equivalent to the response of the *n*-paraffin with the same carbon number. In addition, sample injection technique and sample solution properties must be such that representative sample is introduced to the gas chromatograph

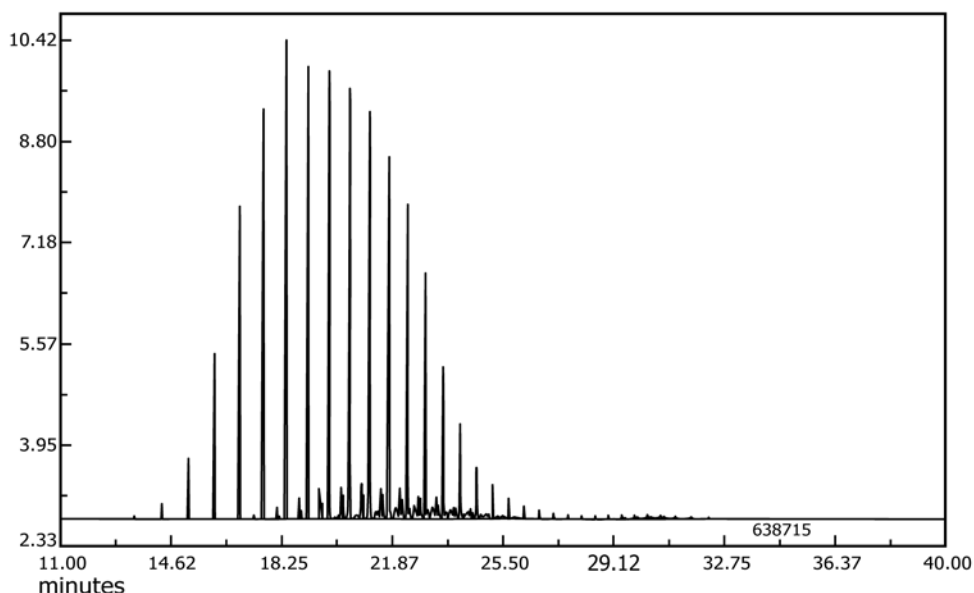


FIG. 1 Typical Wax Chromatogram

without discrimination. Before use, the analysis system must be shown to conform to these requirements as specified in 9.6.1.

9.6.1 Analyze the linearity standard described in 7.5 and calculate the relative mass response factors according to Practice D4626. Response factors calculated relative to hexadecane must be between 0.90 and 1.10.

9.6.2 If relative response factors are not within the limits stated above, take appropriate action and reanalyze the linearity standard to ensure linearity and the absence of discrimination.

9.7 *Retention Time Repeatability*—Check the retention time repeatability by analyzing the linearity standard in duplicate. Retention times for duplicate analyses must not differ by more than 0.10 min between duplicate runs.

## 10. Calibration and Standardization

10.1 *n-Paraffin Identification*—Determine the retention time of each *n*-paraffin in the range from  $C_{16}$  to  $C_{44}$  by injecting small amounts of each paraffin either separately or in known mixtures. Completely dissolve samples in cyclohexane.

10.2 *Standardization*—Inject the linearity standard described in 7.5 and measure the peak area of each *n*-paraffin by electronic integrator or computer.

10.2.1 Calculate the response per unit mass of the detector for each component in the linearity standard, relative to  $n-C_{16}$ , according to Practice D4626.

## 11. Procedure

11.1 Prepare a solution of the petroleum wax sample for analysis as follows:

11.1.1 Obtain a petroleum wax sample specimen as directed in 8.1.

11.1.2 Accurately weigh about 0.0100 g of the wax specimen into a glass vial of approximately 15 mL capacity. Add approximately 12 mL of the dilute internal standard solution

(0.005 % by mass  $n-C_{16}$  in cyclohexane), cap the vial and determine the exact weight of dilute internal standard solution added. Record both weights.

11.1.3 Agitate the vial until the wax is dissolved, using gentle heating if necessary.

11.1.4 For manual syringe injections, fill the syringe directly from this vial. For automatic syringe injections, transfer a suitable aliquot to the appropriate autosampler vial.

11.2 Before analyzing wax samples, program the column temperature to the maximum temperature used. Once the column temperature has reached the maximum, cool the column to the selected starting temperature, and allow it to equilibrate at this temperature for at least 3 min. Without injecting any material, initiate a blank run by starting the temperature program, recorder, and integrator and allow to continue until at least 2 min after the retention time of  $n-C_{44}$ . Store a record of this blank run in the computer or integration device for subtraction from the sample area.

NOTE 2—Some commercially available gas chromatographs have software routines as part of their standard systems to make the baseline correction directly to the detector signal. With such systems, no computer subtraction of the blank is necessary.

11.3 Following the same procedure as for the blank run (see 11.2), inject 0.5  $\mu$ L to 1.0  $\mu$ L of the wax sample solution from 11.1 into the cool on-column injection port. Immediately start the temperature program, the recorder, and the integrator, and store the acquired detector signal. Typical Chromatogram is shown in Fig. 1.

11.4 Integrate the stored detector signal twice, using the baseline construction parameters as directed below.

11.4.1 Using a valley to valley baseline construction, integrate the detector signal to obtain an area (see Fig. 2) for each peak in the chromatogram. Based on the retention times determined in 10.1, identify the normal paraffin peaks and tabulate only their areas. Also record the area of the  $n-C_{16}$