



Standard Test Method for Analysis of Petroleum Waxes by Gas Chromatography¹

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 (ϵ) 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 -C₁₇ through n -C₄₄ 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 -C₄₄ is determined by its difference from 100 mass % and reported as C₄₅₊.

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, Carbowax²), 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 and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*³

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

3.1.2 *cool on-column injection*—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*—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)*—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*—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)*—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 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

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² Carbowax is a registered trademark of Union Carbide Corp.

³ 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 |

retention times of the wax sample. The percent of each hydrocarbon number through C₄₄ 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 C₄₅₊ material is determined by summing the concentrations of each individual carbon number through C₄₄ and subtracting this total from 100 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 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 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 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 C₄₄) 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*-C₁₆ to *n*-C₄₄ 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*-C₁₆, *n*-C₄₄, 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 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 mass % $n\text{-C}_{16}$ in cyclohexane by accurately weighing approximately 0.4 g $n\text{-C}_{16}$ into a 100 mL volumetric flask. Add 100 mL of cyclohexane and reweigh. Record the mass of $n\text{-C}_{16}$ to within 0.001 g and the mass of solution (cyclohexane and $n\text{-C}_{16}$) to within 0.1 g.

7.6.2 Prepare a dilute solution of $n\text{-C}_{16}$ 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} = mass % $n\text{-C}_{16}$ internal standard in dilute solution,

W_{ISTD} = weight of $n\text{-C}_{16}$ from 7.6.1,

W_s = weight of cyclohexane plus $n\text{-C}_{16}$ from 7.6.1,

100 % = factor to convert weight fraction to 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 mass % solution of $n\text{-C}_{20}$ and $n\text{-C}_{24}$ 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 $n\text{-C}_{20}$ and $n\text{-C}_{24}$,

$W1$ = peak width (mm) at half height of $n\text{-C}_{20}$, and

$W2$ = peak width (mm) at half height of $n\text{-C}_{24}$.

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 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.

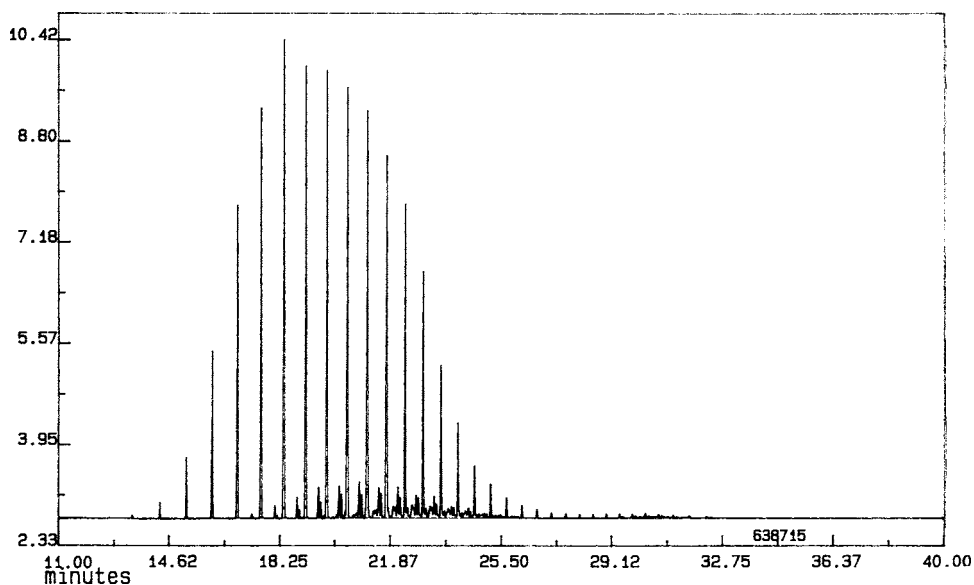


FIG. 1 Valley to Valley Integration for Area of Normal Paraffin

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 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 to 1.0 μL 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.

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. 1) 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 $n-C_{16}$ (hexadecane) internal standard peak that must be completely resolved (baseline separation) from the wax sample area.

11.4.2 Using a vertical drop to a horizontal baseline construction (see Fig. 2, Fig. 3), integrate the detector signal a second time. Sum the area of all the peaks of each carbon number and tabulate these totals. By convention, the peaks assigned the carbon number n are those that elute between the valley immediately following the normal paraffin peak (C_{n-1}) and the corresponding valley following the next normal paraffin peak (C_n).

11.4.3 To ensure proper and consistent integrations, plot the chromatogram with drawn in baseline after each integration and confirm that the baselines match Fig. 1 and Fig. 2.

11.4.4 Do not include, as part of the sample, any peaks resulting from the solvent or the internal standard.

NOTE 3—The total area for each carbon number can be measured by either pre-programming the integrator to sum the area of the peaks within the appropriate retention time windows or by analyzing the peak area data after the peak integration process is complete.

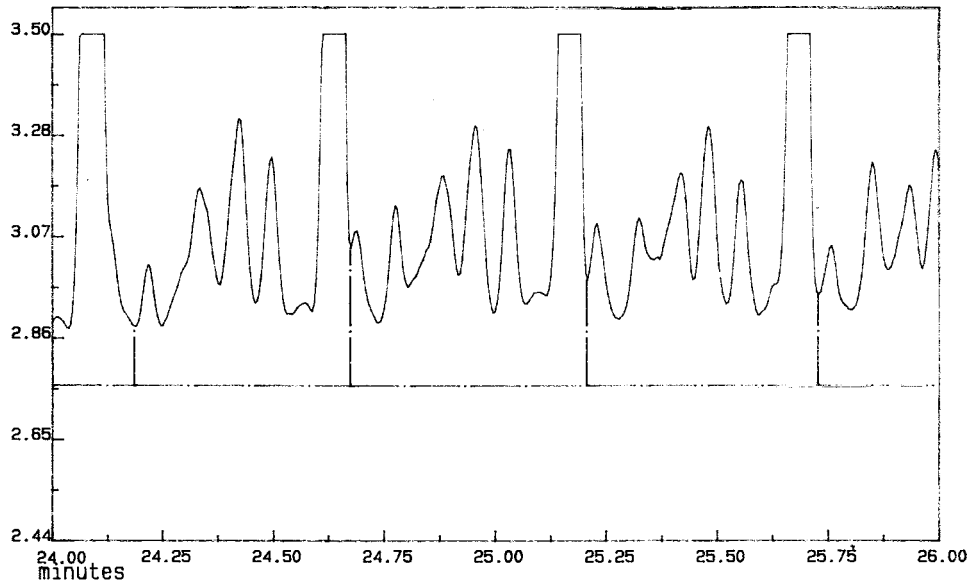


FIG. 2 Carbon Number Summation (Vertical Drop to Horizontal Baseline)

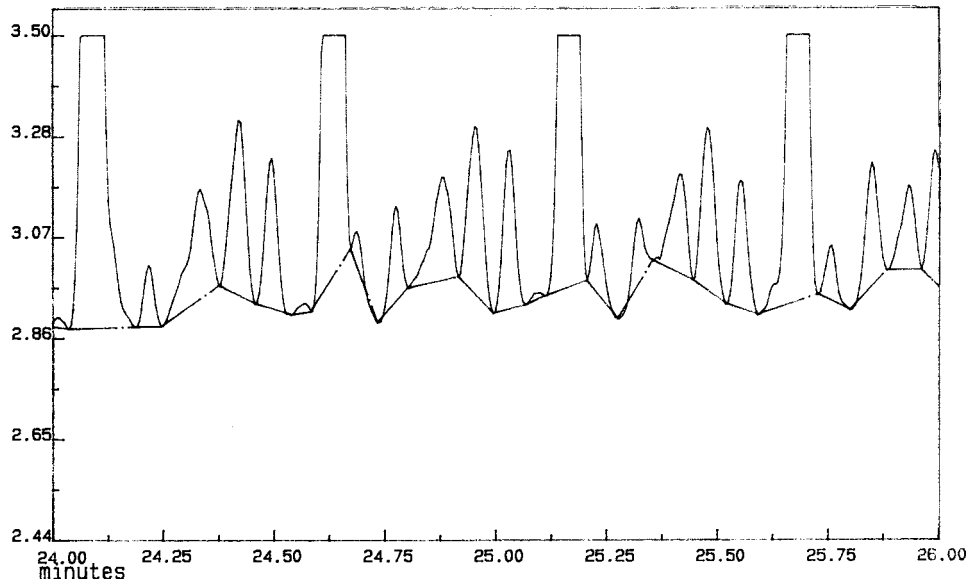


FIG. 3 Typical Wax Chromatogram

12. Calculation

12.1 *Each Carbon Number*—Calculate the mass % for each carbon number determined in 11.4.2 using Eq 3.

$$C_i = \frac{Area_i}{Area_{ISTD}} \times RRF_i \times \frac{MIX}{sample} \times C_{ISTD} \quad (3)$$

where:

- C_i = mass % of hydrocarbons with carbon number i ,
- $area_i$ = area sum of hydrocarbons with carbon number i ,
- $area_{ISTD}$ = area of n -C₁₆ internal standard peak,
- RRF_i = response factor, relative to n -C₁₆,
- MIX = weight of dilute internal standard/solvent mixture,

- $sample$ = weight of wax sample, and
- C_{ISTD} = mass % of n -C₁₆ in internal standard mixture.

12.2 *Normal Paraffin*—Calculate the mass % of each normal paraffin hydrocarbon from the individual areas determined in 11.4.1 using Eq 4.

$$N_i = \frac{Area_i}{Area_{ISTD}} \times RRF_i \times \frac{MIX}{sample} \times C_{ISTD} \quad (4)$$

where:

- N_i = mass % of normal paraffin with carbon number i ,
- $area_i$ = peak area of normal paraffin with carbon number i ,
- $area_{ISTD}$ = area of n -C₁₆ internal standard peak,

RRF_i = response factor, relative to $n\text{-C}_{16}$,
 MIX = weight of dilute internal standard/solvent mixture,
 $sample$ = weight of wax sample, and
 C_{ISTD} = mass % of $n\text{-C}_{16}$ in internal standard mixture.

12.3 Non-Normal Paraffin Hydrocarbon—The non-normal paraffin hydrocarbons are calculated as the difference between the mass percent of hydrocarbons with carbon number i (C_i) and the mass percent of the n -paraffin with carbon number i (N_i):

$$NON_i = C_i - N_i \quad (5)$$

where:

$NON(i)$ = mass percent of the non-normal paraffin hydrocarbons of each carbon number.

12.3.1 The response for all components in a carbon number is assumed to be the same as the response for the normal paraffin of the same carbon number as determined in **10.2**.

12.3.2 Relative response factors for individual n -paraffins between those determined from the calibration mixture are obtained by interpolation.

12.4 Calculate the mass percent Of C_{45+} according to Eq 6:

$$mass \% C_{45+} = 100 \% - \Sigma C_i \quad (6)$$

where:

ΣC_i = the sum of the mass % of all detected hydrocarbons.

13. Report

13.1 Report the concentration in mass percent of the normal (N_i) and non-normal (NON_i) hydrocarbons for each carbon number in the sample to the nearest 0.01 mass percent. Report also the amount of residual as % C_{45+} .

14. Precision and Bias ⁴

14.1 Precision—The precision of this test method as determined by statistical examination of interlaboratory test results is as follows:

⁴ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report D02-1316.

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TABLE 2 Repeatability and Reproducibility

| Carbon Number | Range, mass % | Repeatability ^A | Reproducibility ^A |
|----------------------|---------------|----------------------------|------------------------------|
| C ₂₁ | 0.11–0.25 | 0.014 | 0.039 |
| C ₂₃ | 0.04–2.90 | 0.0463 $X^{0.30}$ | 0.1663 $X^{0.30}$ |
| C ₂₆ | 0.01–8.94 | 0.0785 $X^{0.56}$ | 0.4557 $X^{0.56}$ |
| C ₂₉ | 0.04–8.15 | 0.0872 $X^{0.31}$ | 0.3984 $X^{0.62}$ |
| C ₃₂ | 0.44–5.05 | 0.1038 $X^{0.50}$ | 0.6472 $X^{0.50}$ |
| C ₃₅ | 2.52–5.62 | 0.1737 X | 0.4540 X |
| C ₃₈ | 0.44–3.61 | 0.1131 ($X + 0.1069$) | 0.5476 ($X + 0.1069$) |
| C ₄₁ | 0.06–2.96 | 0.1600 X | 0.5460 X |
| C ₄₄ | 0.02–2.26 | 0.4990 $X^{0.60}$ | 0.9220 $X^{0.60}$ |
| Total n -paraffins | 18.73–79.52 | 2.64 | 26.03 |

^A Where X is the mass % of the component.

14.1.1 Repeatability—The difference between the two test results, obtained by the same operator with the same apparatus under constant operating conditions on identical test material, would, in the long run, in the normal and correct operation of the test method, exceed the values in **Table 2** only in one case in twenty.

14.1.2 Reproducibility—The difference between two single and independent results, obtained by different operators working in different laboratories on identical test materials would, in the long run, in the normal and correct operation of the test method, exceed the values in **Table 2** only in one case in twenty.

14.2 Bias—Bias cannot be determined because there is no reference material suitable for determining the bias of the procedure in this test method.

15. Keywords

15.1 gas chromatography; non-normal paraffin hydrocarbons; normal paraffin; paraffin wax; petroleum wax