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Standard Test Method for Gas Chromatography Analysis of Petroleum Waxes Used in Equestrian Synthetic Surfaces¹

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1. Scope

1.1 The slack waxes typically used in equestrian surfaces comprise a blend of different waxes and oils, with various hydrocarbons, chain lengths and structures.

1.2 The blend of wax and oil determines the mechanical properties of the surface material, as well as the response of the wax to temperature. The combination of lower and higher carbon weight materials, oil content, and hydrocarbon structures also controls how the wax will endure over time. As the wax ages, it is expected that lower density components will be lost at a higher rate than higher density materials.

1.3 The gas chromatography (GC) test is used to determine the carbon number distribution in extracted wax samples for both normal and abnormal hydrocarbons (linear vs. non-linear carbon chains). This procedure is outlined in Test Method D5442. GC testing utilizes a chromatograph with a flame ionization detector and column.

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 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.*

¹ This test method is under the jurisdiction of ASTM Committee F08 on Sports Equipment, Playing Surfaces, and Facilities and is the direct responsibility of Subcommittee F08.28 on Equestrian Surfaces.

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2. Referenced Documents

2.1 *ASTM Standards:*²

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

D4626 Practice for Calculation of Gas Chromatographic Response Factors

D5442 Test Method for Analysis of Petroleum Waxes by Gas Chromatography

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

3.1.2 *cool on-column injection, n*—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*—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 linear chain. Includes aromatics, naphthenes, and branched hydrocarbon types.

3.1.5 *normal paraffin, n*—saturated hydrocarbon that has solely linearly bonded carbon atoms without branching or hydrocarbon rings.

3.1.6 *wall coated open tube (WCOT), n*—term used to specify capillary columns in which the stationary phase is

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.

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 Wax samples are thoroughly stirred, and 0.2 g of the wax is dissolved in 2.0 ml of cyclohexane. The solution is then sonicated for 15 min and transferred by pipette into a GC vial and sealed. A solvent blank GC vial of cyclohexane is also prepared. The wax-cyclohexane mixture is introduced into a gas chromatographic high-temperature column that separates the hydrocarbon components by increasing carbon number. The column temperature is increased at a reproducible rate until the sample is completely eluted from the column. The temperature of the column must be able to reach at least 400.0°C.

4.2 The eluted components are detected by a flame ionization detector (FID) 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 C₄₄ is calculated via internal standard calculations after applying response factors.

4.3 For samples with final boiling points greater than 538.0°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 100.00 mass %.

5. Significance and Use

5.1 The determination of the carbon number distribution of petroleum-based waxes used in synthetic equestrian tracks is useful for characterizing the overall molecular composition to aid in binder selection and replenishment. The test data is also very useful for comparing carbon number distributions between different binders and monitoring an existing track binder as it ages over time. The oil extracted from the wax can also be analyzed by this method. Track surface maintenance decisions can be aided by the results of this test.

6. Apparatus

6.1 *Chromatograph*—Any gas chromatographic instrument that can accommodate a WCOT column, equipped with a flame ionization detector, 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

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

provided the system meets the specification for linearity of response in 10.6. 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 any 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 10.5. 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 enough 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 FID. 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 weighted 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-C₁₆ in cyclohexane by accurately weighing approximately 0.4 g n-C₁₆ into a 100 mL volumetric flask. Add 100 mL of cyclohexane and reweigh. Record the mass of n-C₁₆ to within 0.001 g and the mass of solution (cyclohexane and n-C₁₆) to within 0.1 g.

7.6.2 Prepare a dilute solution of n-C₁₆ 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 the equation below:

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

where:

C_{ISTD} = mass % n-C₁₆ internal standard in dilute solution,
W_{ISTD} = weight of n-C₁₆ from 7.6.1,
W_S = weight of cyclohexane plus n-C₁₆ from 7.6.1,
100 % = factor to convert weight fraction to mass %, and
100 = dilution factor.

8. Hazards

8.1 Standard lab hazards are applicable in this test method and outlined in the procedure above.

9. Sampling, Test Specimens, and Test Units

9.1 To ensure homogeneity, completely mix the entire wax sample by heating it to 10.0°C above the temperature at which the wax is completely molten and then mix well by stirring. Using a clean transfer pipet, place a few drops on the surface of a clean aluminum foil sheet, 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.

9.2 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.

10. Preparation of Apparatus

10.1 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.

10.1.1 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.

10.2 Operating Conditions—Set the chromatographic operating conditions (see Table 1) and allow the system to achieve all temperature set points. 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.

10.3 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, recording device and 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 further conditioned or replaced.

10.3.1 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.

10.4 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.

10.5 Column Resolution—Check the efficiency of the GC column by analyzing, under conditions specified in 11.2, a 1 µL injection of 0.05 mass % solution of n-C₂₀ and n-C₂₄ in cyclohexane. The column resolution must not be less than 30 as calculated using Eq 2 below:

$$R = \frac{2d}{1.699(W_1 + W_2)} \quad (2)$$