Designation: D5442 – 17 (Reapproved 2021)

Standard Test Method for Analysis of Petroleum Waxes by Gas Chromatography[1]

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*-C_{17} through *n*-C_{44} 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_{44} is determined by its difference from 100 % by mass and reported as C_{45+}.

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[2]), 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.*

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, 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

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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

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