Standard Test Method for Analysis of Hydrocarbon Waxes by Gas Chromatography EWF METHOD 001/03

(Version 1 – Reviewed 2015)

1. Scope

1.1 This test method provides for the determination of the carbon number distribution of hydrocarbon waxes in the range from C16 to approx. C100. In addition the qualitative and quantitative content of normal and non-normal hydrocarbons for each carbon number is determined.

1.2 This test method is applicable to petroleum derived waxes and synthetic waxes from a Fischer Tropsch or similar process. This process is not applicable to oxygenated waxes, such as polyethylene glycols, or natural products such as beeswax or carnauba.

1.3 This test method does not address all safety problems. It is the responsibility of the user of this method to establish appropriate health and safety practices.

1.4 It is not the intention of this method to describe basic principles of the technique of gas chromatography. It is assumed that the user of this method has a pro- found knowledge of this technique.

Detailed description of hard and soft ware is omitted, considering the constant development in this field

2. Referenced Documents

2.1 ASTM Standard D4626
Practice for Calculation of Chromatographic Response Factors

3. Summary of the Test Method

3.1 Weighed quantities of the hydrocarbon wax are completely dissolved in cyclohexane and introduced into a gas chromatographic column which sepa- rates 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.

3.2 The eluted components are detected by a flame ionization detector and recorded. 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 percentages of each hydrocarbon number is calculated via the areas of the individual hydrocarbons or by using an internal standard if applicable.

4. Significance and Use

4.1 The determination of carbon number distribution and the content of normal and non-normal hydrocarbons can be used for control of production processes and as a guide to performance in various end uses.

4.2 This method can also be used to determine total hydrocarbon content of waxes as required by EU regulations or JECFA recommendations for food additives and or food contact materials.

5. Apparatus

5.1 Chromatograph - Any gas chromatographic instrument that can accommodate a capillary column, equipped with a flame ionization detector (FID), and which can be operated at the conditions given in Table 1 may be employed. The chromatograph should be equipped with a suitable inlet for introducing appropriate quantities of sample without fractionation.

5.2 Sample Introduction System - Any system capable of introducing a representative sample onto the front portion of a capillary column may be employed. On-column injection is preferred, however other injection techniques can be used provided the system meets the specification for linearity of response in 7.6.

5.3 Column(s) - Any column used must meet the chromatographic resolution specification in 7.5. Cross-linked or bonded stationary phases are preferred.

5.4 Recorder - A recording potentiometer or equivalent with a full-scale deflection of 5 millivolt or less for measuring the detector signal versus time. Full scale response time should be 2 seconds 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.

5.5 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.

6. Reagents and Materials

6.1 Carrier Gas - 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.

6.2 For n-hexadecane - or squalane to be added to samples if an internal standard

is used, minimum purity of 98% is required. The solution is prepared according to good laboratory practice.

6.3 Standards for Identification - Standard samples or normal paraffins covering the carbon number range of the sample are needed for establishing the retention times of the individual paraffins. Hydrocarbons used for standards must be greater than 95% purity. The standard must contain as a minimum hydrocarbons up to C_{60}.

6.4 Solvent - Cyclohexane is the preferred solvent (99% pure).

6.5 Linearity Standard - Prepare a weighed mixture of n-paraffins covering the range between n-C_{16} to as a minimum n-C_{60} and dissolve the mixture in cyclohexane. It is not necessary to include every n-paraffin in this mixture so long as the sample contains n-C_{16}, n-C_{60} and at least one of every fourth n-paraffin.

7. Preparation of Apparatus

7.1 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.

7.2 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 vs time can be obtained. Make certain that the FID is ignited before proceeding.

7.3 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.

7.3.1 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.

7.4. Solvent Bank - 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.

7.5. Column Resolution - Check the efficiency of the GC column by analyzing, a 1 µl injection of 0.05 mass % solution of n-C_{20} and n-C_{24} in cyclohexane. The column

resolution must not be less than 30 as calculated using following equation

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

Where:

d = distance (mm) between the peak maxima of n-C_{20} and n-C_{24}
W1 = peak width (mm) at half height of n-C_{20}
W2 = peak width (mm) at half height of n-C_{24}

7.6. 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 must be equivalent to the response of the n-paraffin with the same carbon number. The analysis system must be shown to conform to these requirements as specified in 7.6.1.

7.6.1 Analyze the linearity standard described in 6.5 and calculate the relative mass response factors according to practice ASTM D4626. Response factors calculated relative to hexadecane must be between 0.90 and 1.10.

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

8. Procedure

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

8.1.2 Accurately weigh 20 mg of the wax specimen into a suitable glass vial and dissolve the wax in 20 ml cyclohexane. Agitate the vial until the wax is dissolved, using gentle heating if necessary. The solution should be clear when injected.

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

8.2 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 minutes. Without injecting any material, initiate a blank run using operating conditions as per Table I. Store a record of this blank run in the computer or integration device for subtraction from the sample area.

Some gas chromatographs have software routines to make the baseline correction directly to the detector signal. With such systems, no computer subtraction of the blank is necessary.

8.3 Following the same procedure as for the blank run (8.2), inject 1.0 µl of the wax sample solution from 8.1 into the injection port. Immediately start the temperature program, the recorder, and the integrator, and store the acquired detector signal.

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

8.4.1 Using a valley to valley construction, integrate the detector signal to obtain an area (Figure1) for each peak in the chromatogram.

8.4.2 For carbon number summation use a vertical drop to a horizontal baseline construction (Figure 2).
By definition: The non-normal hydrocarbon is followed by the normal hydrocarbon of the same carbon number.

8.4.3 Do not include, as part of the sample, any peaks resulting from the solvent.

8.4.4 Peaks with areas below 0.1 % are not included into the calculation.

8.4.5 For calculating and integration the common base line ends at the last C-normal peak with an area of 0.1 area %.

9. Calculations

9.1 Content of normal and non-normal hydrocarbons

9.1.1 Determination of total area (normal and non-normal) A_{TS}, using the corrected horizontal baseline

9.1.2 Area calculation or normal paraffin with a carbon number i by valley/valley method = A_{NV}

9.1.3 Area of a non-normal paraffin with a carbon number i
$N_{NON} = A_i - A_{NV}$

9.1.4 Caclulation of area % of a normal paraffin with carbon number i

$$A_{ANi} = \frac{100 \times A_{NV}}{A_{TS}}$$

9.1.5 Calculation of area % of a non-normal paraffin with a carbon number i
$C_{ANONi} = C_{Ai} - C_{ANi}$

By definition: The non-normal hydrocarbon peaks and the following peak consisting of normal and non-normal hydrocarbons are of the same carbon number. (Figure 1)

9.2 Carbon Number Summation

(normal and non-normal content for each carbon number)

Use vertical drop to baseline.
By definition: The non-normal hydrocarbon is followed by the normal hydrocarbon of the same carbon number. (Figure 2)

$A_i = A_{NONPD} + A_{NPD}$

$$C_{Ai} = \frac{100 \times A_i}{A_{TS}}$$

A_i = Area of normal and non-normal paraffin with a carbon number i

A_{NONPD} = Area of a non-normal paraffin with a carbon number i, perpendicular drop calculation

A_{NPD} = Area of non-normal paraffin with a carbon number i, perpendicular drop calculation

A_{TS} = Total area of sample

C_{Ai} = Area of a paraffin with carbon number i (normal and non-normal)

This method can be used for quick scanning and if information of % of total hydrocarbons e.g. up to C_{25} is required.

Note: By using good laboratory practice it is possible to condition and control the gas chromatograph in such a way that response factors (see 7.6.1) are nearly 1.0.

If the response factor is 1.0 or deviating to a small extent only (± 0.05) the calculated area percentages will equal weight percentages and a qualitative result is obtained.
The use of an internal standard can be omitted. For practical reasons, therefore, the calculations 9. will result in area percentages. If control of the response factor cannot be obtained, an internal standard (6.2) is necessary.

Table 1

Test method for hydrocarbon waxes with carbon numbers up to approx. C100

TYPICAL GAS CHROMATOGRAPHIC PARAMETERS

GC HP 5890/II + Integrator 3396A, Agilent 6890 + Chemstation software or other suitable instrument

Injection System:	On - Column or other methods (see 5.2) (automatic sampler recommended)
Detector:	FID
Column:	Capillary Column e.g. SGE HT 5 Alu clad 25 m, 0.32 mm I.D., 0.1 µm film thickness or similar (see 5.3)
Sample Preparation:	20 mg wax in 20 ml cyclohexane
Injection:	1 µl
Temperature Program:	70 °C - 200 °C, rate 25 °C/min. 200 °C - 325 °C, rate 12 °C/min 325 °C - 425 °C, rate 8 °C/min.
Final Temperature:	425 °C 15 min. isotherm
Detector Temperature:	430 °C
Required Gases:	H_2, N_2, synth. air (He)
Carrier Gas:	H_2 0.5 psi = approx. 1 ml H_2/min. Also helium has been used successfully
Make-Up Gas:	N_2 approx. 25 ml/min.
Burning Gas:	H_2 approx. 30 ml/min. synth. air 280 ml/min.

FIG 1: Content of normal and non - normal hydrocarbons

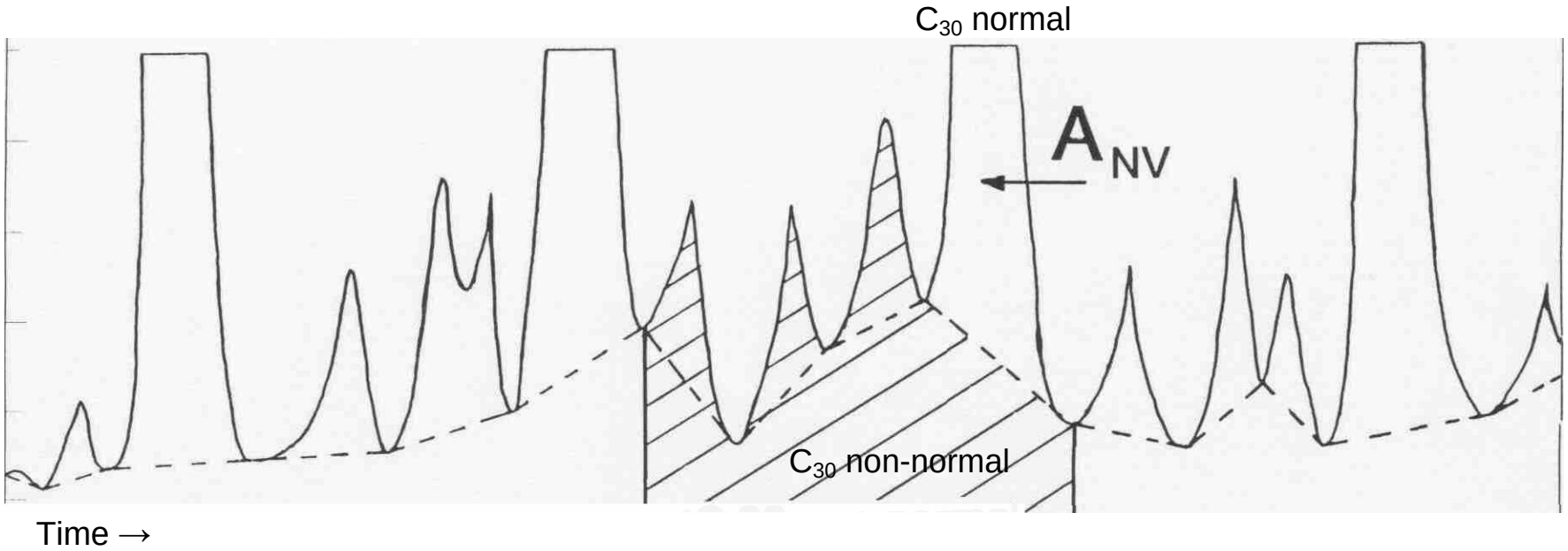

FIG. 2: Carbon number summation (Vertical drop to horizontal baseline)