Standard Method for Analysis of Benzene and Toluene Content in Hydrocarbon Waxes by Headspace Gas Chromatography
EWF METHOD 002/03
(Version 1 – Reviewed 2015)

1 Scope

1.1 This test method covers the qualitative and quantitative determination of the content of benzene and toluene in hydrocarbon wax.

1.2 This test method is applicable to all petroleum derived (paraffin/micro wax and slack waxes) and synthetic waxes, oxygenated waxes or natural products like beeswax or carnauba wax. The melting point of the products must not exceed 80°C. It is not tested for and not aimed at polyethylene waxes.

1.3 This method does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user to of this method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

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 profound knowledge of this technique.

2 Reference Documents

2.1 ASTM Standard D 4626: Practice for calculation of chromatographic response factors.

2.2 DIN 32 645: Chemical analysis; Decision limit, detection limit and determination limit; Estimation in case of repeatability

2.3 DIN 51 848: Testing of mineral oils; Precision of test methods

3 Summary of the Test Method

3.1 Weighed quantities of the test substance are filled into headspace vials and are hermetically sealed. The sample is equilibrated in a static headspace sampler at elevated temperature.

3.2 The equilibrated gas phase, which contains evaporated benzene and toluene, is transferred into a gas chromatographic column which separates the solvents by increasing boiling point. The column temperature is increased at a reproducible rate until the solvents are completely eluted from the column.

3.3 The eluted components are detected by a flame ionisation detector, recorded and integrated. The individual solvents are identified and quantified by comparing the retention times and peak areas obtained from standards with the retention times and peak areas of the wax sample.

4 Significance and Use

4.1 The determination of benzene and toluene contents in hydrocarbon wax can be used for control of production processes for intermediate products and for control of the purity of finished waxes.

5 Apparatus

5.1 *Static headspace sampler* – Any static headspace sampler that can be operated as sampler for the applied gas chromatograph described in chapter 5.2 and which can be operated at the conditions given in Table 1 may be employed.

5.2 *Chromatograph* – Any gas chromatographic instrument that can accommodate a capillary column, equipped with a flame ionisation 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 gas sample without fractionation, i.e. on-column or splitless injector.

5.3 *Column* – Any column used must meet the chromatographic resolution specification in 7.3. Capillary columns with thick (e.g. 5 µm) non polar or slightly polar cross-linked or bonded stationary phases and a length of at least 15 m are preferred.

5.4 *Integrator or Computer* – Means must be provided for recording and integrating the detector signal and summing the peak areas between specific time intervals. Peak areas can be measured by computer or electronic integration.

6 Reagents and Materials

6.1 *Carrier Gas* – Hydrogen, helium and nitrogen may be used. The minimum purity of the carrier gas used should be 99, 95 mol %.
Warning – Hydrogen, helium and nitrogen are compressed gases under high pressure. Hydrogen is an extremely flammable gas.

6.2 *Standards for identification and quantification* – Standard samples of benzene and toluene in wax are needed for establishing the retention times of the individual solvents and for quantitative calibration. Benzene and toluene used for calibration must be greater than 99,5 % purity.

6.3 *N-dodecane as diluent for benzene and toluene* – During the calibration procedure (chapter 9) n-dodecane is used to prepare standard solutions of benzene and toluene. The minimum purity of the n-dodecane should be 99 %.

6.4 *Solvent free wax* – A solvent free wax is needed for preparation of calibration standards with the relevant solvents. This wax should have similar physical and chemical properties like the wax to be analysed. The described analytical method should be used to check the absence of solvents.

6.5 *Preparation of solvent free wax* – Solvent free wax can be prepared by heating a sample in an oven over night at a temperature above the melting point (e.g. 80°C).

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 *Operation Conditions* – Set the chromatographic operating conditions (see Table 1) and allow the system to achieve all temperature set points. The 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 *Column Resolution* – Check the efficiency of the GC column by analysing a standard sample containing the wax and all relevant solvents. The column must be able to completely resolve all solvents.

8 Procedure

8.1 Prepare the wax sample for analysis as follows:

8.1.1 Accurately weigh 2 g solid wax sample into a 20 ml headspace vial and seal the vial with septum and crimp-on seal. The work shall be done quickly and all wax containers have to be kept sealed to avoid any evaporation of benzene and toluene.

8.1.2 Prepare the headspace sampler for the operating conditions as specified in Table 1 and load the sample vial into the sampler.

8.2 Set the GC operation conditions as specified in Table 1 and run a blank without injecting a sample. If there are any peaks or baseline drift, take appropriate action to remedy the problems.

8.3 After equilibrating the GC for at least 3 min at the starting temperature, the gas sample from the headspace sampler can be injected. Immediately start the temperature programme and the recording and storing of the acquired detector signal.

8.4 Using a vertical drop to a horizontal baseline construction, integrate the detector signal to obtain an area for the benzene and toluene peak in the chromatogram.

8.5 Calculate the individual benzene and toluene concentrations from the peak areas applying the calibration curves or response factors which have to be determined as described in 9.

9 Calibration

9.1 Prepare calibration standards with a solvent free wax that is representative for the waxes to be analysed as follows:

9.1.1 Prepare standard solutions of 1000 ppm benzene and toluene in n-dodecane.

9.1.2 Accurately weigh 2 g solvent free wax samples into 20 ml headspace vials and seal the vials with septum and crimp-on seal.

9.1.3 Inject the standard solution though the septum into the vial applying an appropriate syringe: 1.3 µl for a 0.5 ppm standard, 2.7 µl for a 1.0 ppm standard, 13.3 µl for a 5.0 ppm standard. Standards with other concentrations can be prepared accordingly.

9.2 Prepare the headspace sampler for the operating conditions as specified in Table 1 and load the sample vial into the sampler like normal samples.

9.3 Analyse the standards with the GC like normal samples.

9.4 Determine the calibration curves applying your GC software system or calculate response factors from peak areas and the applied concentration in the standards.

10 Precaution

10.1 The main source of error while sampling, preparation of standards and handling of samples and standards is evaporation. Pay attention to gas-tight sealed glasses and vials, a high filling level of sampling and storage containers (to minimise evaporation into the gas phase over the wax) and a quick handling of opened containers to minimise this error.

10.2 If the sample contains additional low boiling hydrocarbons or solvents, the benzene and toluene peaks can be shifted to slightly different retention times. In such a case the identification has to be checked by other means, e.g. by standard addition or by using a MS detector.

11 Precision

11.1 *Detection limit according to DIN 32 645* - The detection limit is the minimum content of benzene or toluene that can be detected qualitatively at a confidence level of 99 %. Applying the operation parameters of table 1, the following detection limits have been determined under repeatability conditions (same operator, same instrument, constant operating conditions, identical test material):

Benzene: 0.06 ppm (mg/kg)
Toluene: 0.18 ppm (mg/kg)

11.2 *Determination limit according to DIN 32 645* – The determination limit is the minimum content of benzene or toluene that allows a quantitative determination. Applying the operation parameters of table 1, the following determination limits have been calculated under repeatability conditions:

Benzene: 0.2 ppm (mg/kg)
Toluene: 0.3 ppm (mg/kg)

11.3 *Repeatability according to DIN 51 848 part 1* – The difference between two test results , obtained by the same operator with the same apparatus under constant operating conditions on identical material would in the long run, in the normal and correct operation of the test method, exceed the following values only in one case in twenty:

Benzene: 0.04 ppm (mg/kg)*
Toluene: 0.09 ppm (mg/kg)*

*: These repeatability data are only valid for analysis results close to the determination limit.

11.4 *Reproducibility* – The difference between two singe and independent results obtained by different operators working in different laboratories on identical test material has not yet been investigated.

Table 1

Typical Gas Chromatographic Parameters (Examples)

Column:	Capillary column with thick non polar or slightly polar cross-linked or bonded stationary phase, at least 15 m long. E.g.: CP Sil 5-CB, 15 m, 0, 32 µm I.D., 3 µm film thickness
Carrier gas:	H_2, 6 psi, 2 ml/min (or helium or nitrogen at appropriate flow rate)
Detector:	FID, 325°C
Make-up gas:	N_2, 25 ml/min
Burning gas:	H_2, 30 ml/min, air 280 ml/min
Temperature program:	5°C/min from 60°C to 130°C
Injection:	HP Headspace Sampler 7694 (or other suitable instrument)
Temperature:	Oven = 80°C, Loop = 100°C, Transfer Line = 100°C
Event Times:	Vial Equilibration Time = 30 min, Pressure Time = 0.13 min, Loop Fill Time = 0.15 min, Loop Equilibration Time = 0.13 min, Inject Time: 0.13 min.
Vial Pressure:	20.0 psi
Carrier Pressure:	6.0 psi
Vial Shaking:	Low