A Honeywell Company

Impurities in Distilled High Purity Cumene by GC

UOP Method 702-09

Scope

This method is for determining trace impurities in distilled, high purity cumene by gas chromatography (GC). Benzene and toluene may not be separated from the non-aromatic impurities by this method but, if required, may be determined individually by UOP Method 543. Isoparaffins and/or olefins in the C_{12} range may interfere with the determination of ethylbenzene. The lower limit of detection for any single component is 5 mg/kg (mass-ppm).

References

ASTM Practice D4307, “Preparation of Liquid Blends for Use as Analytical Standards,” www.astm.org

UOP Method 543, “Trace Non-Aromatic Hydrocarbons in High-Purity Aromatics by Gas Chromatography,” www.astm.org

UOP Method 999, “Precision Statements in UOP Methods,” www.astm.org

Outline of Method

The sample to be analyzed is injected into a GC that is equipped with a capillary injection port, a fused silica capillary column, and a flame ionization detector (FID). The concentrations of individual or group impurities are determined by the external standard method of quantitation, wherein peak areas of the sample components are compared to the peak areas of a calibration blend analyzed under identical conditions and injection volumes. The concentration of the major component is then determined by subtracting the total impurities from 100%. See *Note* for alternative means of calibration and calculation.

Apparatus

References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used.

Balance, readability 0.1-mg

Chromatographic column, 60 m of 0.32-mm ID fused silica capillary, internally coated to a film thickness of 0.50 µm with cross-linked poly(ethylene glycol), Restek, Cat. No. 10642

IT IS THE USER'S RESPONSIBILITY TO ESTABLISH APPROPRIATE PRECAUTIONARY PRACTICES AND TO DETERMINE THE APPLICABILITY OF REGULATORY LIMITATIONS PRIOR TO USE. EFFECTIVE HEALTH AND SAFETY PRACTICES ARE TO BE FOLLOWED WHEN UTILIZING THIS PROCEDURE. FAILURE TO UTILIZE THIS PROCEDURE IN THE MANNER PRESCRIBED HEREIN CAN BE HAZARDOUS. MATERIAL SAFETY DATA SHEETS (MSDS) OR EXPERIMENTAL MATERIAL SAFETY DATA SHEETS (EMSDS) FOR ALL OF THE MATERIALS USED IN THIS PROCEDURE SHOULD BE REVIEWED FOR SELECTION OF THE APPROPRIATE PERSONAL PROTECTION EQUIPMENT (PPE).

Nonconfidential UOP Methods are available from ASTM International, 100 Barr Harbor Drive, P.O. Box C700, West Conshohocken, PA 19428-2959, USA. The UOP Methods may be obtained through the ASTM website, www.astm.org, or by contacting Customer Service at service@astm.org, 610.832.9555 FAX, or 610.832.9585 PHONE.

Gas chromatograph, temperature programmable, built for capillary column chromatography, utilizing a split injection system having a glass injection port insert and equipped with an FID that will give a minimum peak height response of five times the background noise for 5 mg/kg n-propylbenzene when operated under the recommended conditions, Agilent Technologies, Model 7890

Data system, electronic, for obtaining peak areas. This device must integrate areas at a sufficiently fast rate so that narrow peaks typically resulting from use of a capillary column can be accurately measured. Agilent Technologies, ChemStation.

Refrigerator, explosion-proof or flammable storage, VWR, Cat. No. 55700-340

Regulator, air, two-stage, high purity, delivery pressure range 30-700 kPa (4-100 psi), Matheson Tri-Gas, Model 3122-590

Regulator, hydrogen, two-stage, high purity, delivery pressure range 30-700 kPa (4-100 psi), Matheson Tri-Gas, Model 3122-350

Regulator, nitrogen, two-stage, high purity, delivery pressure range 30-700 kPa (4-100 psi), Matheson Tri-Gas, Model 3122-580

Sample injector, any syringe or injector capable of injecting a repeatable 0.5-µL volume of sample. The use of an automatic injection device is required to achieve necessary repeatable injection volumes. See *Appendixes*. Agilent Technologies, Model 7683.

Reagents and Materials

References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used.

Air, total hydrocarbons less than 2.0 ppm as methane (zero gas)

Benzene, 99.9% minimum purity, Aldrich, Cat. No. 270709

Carbon disulfide, low organic impurity, VWR, Cat. No. AA40910-AP

1,4-Diisopropylbenzene, 97% minimum purity, Aldrich, Cat. No. 126276

Gas purifier, for hydrogen, to remove oxygen and moisture from carrier gas, VICI Mat/Sen, Cat. No. P200-1

Hydrogen, 99.95% minimum purity, total hydrocarbons less than 0.5 ppm as methane (zero gas)

Nitrogen, 99.99% minimum purity, total hydrocarbons less than 0.5 ppm as methane (zero gas)

n-Octane, 99.9% minimum purity, Aldrich, Cat. No. 296988

Pipet bulbs, VWR, Cat. No. 15001-362

Pipets, disposable, Pasteur, VWR, Cat. No. 14673-043

n-Propylbenzene, 98% minimum purity, Aldrich, Cat. No. P5240-7

Syringe, replacement, for recommended sample injector, 5-µL, Agilent Technologies, Cat. No. 5181-1273

Toluene, >99.9% minimum purity, Aldrich, Cat. No. 89680, (Note 2)

Vials, autosampler, for recommended sample injector, Agilent Technologies, Cat. No. 5182-0864

Calibration

Preparation of Calibration Blend

Quantitative results are based on the injection of repeatable volumes of both the calibration blend and the sample. Absolute response factors, derived from the calibration blend, are used to relate the peak areas of each known component to mg/kg.

1. Prepare a stock solution as described in ASTM Method D4307 to contain approximately 1.5 mass-% each of n-octane, benzene, n-propylbenzene, and 1,4-diisopropylbenzenene in toluene. Thoroughly mix the solution by shaking. Record all weights to the nearest 0.1 mg.
   - Obtain the purest toluene possible to prepare the blend. Analyze it, looking for impurities that elute at the n-octane, benzene, n-propylbenzene, and 1,4-diisopropylbenzenene sites. If impurities in the toluene are present at any of the sites, their concentrations must be accounted for in the calculation of the respective concentrations of the named components in the blend. Analyze the toluene, if needed, using the technique in Appendix A of this method and determine the concentrations of n-octane, benzene, n-propylbenzene, and 1,4-diisopropylbenzene in the toluene.
   - This blend will be used as the stock solution in the preparation of the actual calibration blend. Label this mixture as the stock solution.
2. Prepare the calibration blend to contain approximately 3.0 mass-% of the stock solution in toluene. Thoroughly mix the calibration blend by shaking. Record all weights to the nearest 0.1 mg.
   - If refrigerated, the stock solution and calibration blend should remain stable for several months.
3. Calculate the concentration of n-octane, benzene, n-propylbenzene, and 1,4-diisopropylbenzene in the calibration blend to the nearest 0.0001 mass-% using Equation 1. Using the above dilutions, the resulting calibration blend should contain approximately 230 mg/kg of each added component.

$$\mathbf{M} = \frac{\mathbf{10^6\ AB}}{\mathbf{CD}} + \mathbf{E} \qquad \mathbf{(1)}$$

where:

A = mass of n-octane, benzene, n-propylbenzene, or 1,4-diisopropylbenzene in the stock solution, g
B = mass of stock solution in the calibration blend, g
C = total mass of the stock solution prepared, g
D = total mass of the calibration blend prepared, g
E = concentration of n-octane, benzene, n-propylbenzene, or 1,4-diisopropylbenzene, if any, in the toluene as analyzed as described in Appendix A; see bullet under Step 1, *Preparation of Calibration Blend*, mg/kg
M = concentration of n-octane, benzene, n-propylbenzene, or 1,4-diisopropylbenzene in the calibration blend, mg/kg
$\mathbf{10^6}$ = factor to convert to mg/kg

4. Analyze the calibration blend in triplicate as described under *Chromatographic Technique*.
   - The peak areas from each of the triplicate runs should not deviate from the average by more than 3% (relative) of the value. If greater deviations occur, make certain that there are no problems with the equipment and then make additional runs until the required repeatability is obtained on three consecutive runs.
   - Confirm the stability of the chromatographic system by analyzing the calibration blend again at the end of a series of analyses. If the results differ by more than 5% from the average of the triplicate runs, a problem has developed with the chromatographic system, and the series of samples must

be rerun after the problem is resolved. Typical problems to look for include a leaky septum and a dirty or partially plugged syringe.

5. Use the average peak areas to calculate the absolute response factor for n-octane, benzene, n-propylbenzene, and 1,4-diisopropylbenzene to three significant figures, using Equation 2.

$$L = \frac{M}{P} \tag{2}$$

where:

L = absolute response factor for n-octane, benzene, n-propylbenzene, or 1,4-diisoproplybenzene
M = concentration of n-octane, benzene, n-propylbenzene, or 1,4-diisoproplybenzene in the calibration blend, from Equation 1, mg/kg
P = average peak area for n-octane, benzene, n-propylbenzene, or 1,4-diisopropylbenzene in the calibration blend

Use the absolute response factor for n-octane to calculate the concentration of the non-aromatics. Use the absolute response factor for benzene to calculate the concentration of benzene and toluene. Use the absolute response factor for n-propylbenzene to calculate the concentration of ethylbenzene, p-xylene, m-xylene, o-xylene, isopropylbenzene, n-propylbenzene and α-methylstyrene. Use the absolute response factor for 1,4-diisopropylbenzene to calculate the concentration of the composite of all peaks eluting after n-propylbenzene, not including α-methylstyrene.

Procedure

The analyst is expected to be familiar with general laboratory practices, the technique of gas chromatography, and the equipment being used.

Chromatographic Technique

1. Install the gas purifier in the supply line between the carrier gas source and the carrier gas inlets on the gas chromatograph.
   - Column life is significantly reduced if the gas purifier is not used.
2. Install the fused silica capillary column in the gas chromatograph according to the column and gas chromatograph manufacturer's instructions.
   - *CAUTION*: Hydrogen leakage into the confined volume of the column oven can cause a violent explosion. Therefore, it is mandatory to check for leaks each time a connection is made and periodically thereafter.
3. Establish the recommended operating conditions as given in Table 1.
   - Different conditions may be used provided they produce the required sensitivity and chromatographic separations equivalent to those shown in the Typical Chromatogram (Figure 1).
4. Program the column oven to 240°C (see Table 1) and maintain this temperature until a stable baseline has been obtained at the required sensitivity.
5. Cool the column oven to a stabilized 70°C.
6. Mix the sample by shaking. Fill an autosampler vial with an aliquot of the sample and place in the autosampler (or autoinjector) tray.
   - Multiple samples may be prepared in advance for unattended operation. Samples are stable in the vials for several hours.