



A Honeywell Company

Trace Impurities in High Purity Ethyl Benzene by GC

UOP Method 755-13

Scope

This method is for determining trace impurities in high purity ethyl benzene by gas chromatography (GC). Specific impurities identified include benzene, toluene, p-xylene, m-xylene, o-xylene, cumene, n-propylbenzene, 1,2-diethylbenzene, 1,3-diethylbenzene, and 1,4-diethylbenzene. Non-aromatics and unidentified C₉+ aromatics are determined as composites. 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, "Trace Non-Aromatic Hydrocarbons in High-Purity Aromatics by Gas Chromatography." The lower limit of detection for any single component is 2 mg/kg (mass-ppm) except for p-xylene, which has a lower detection limit of 10 mg/kg.

References

ASTM Method D4052, "Density and Relative Density of Liquids by Digital Density Meter,"
www.astm.org

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 internally coated with poly(ethylene glycol), 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%.

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Apparatus

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

Balance, readable to 0.0001 g

Chromatographic column, 60 m of 0.25-mm ID fused silica capillary, internally coated to a film thickness of 0.50 μm with cross-linked poly(ethylene glycol), Restek, Cat. No. 10641

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 2 mg/kg o-xylene 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. 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, zero gas, total hydrocarbons less than 2.0 ppm as methane

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

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

Cumene, 99.0% minimum purity, TCI, Cat. No. C0687

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

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

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

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

o-Xylene, 97% minimum purity, Aldrich, Cat. No. 294780

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

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

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

Toluene, >99.9% minimum purity, Aldrich, Cat. No. 89680

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 Practice D4307 to contain approximately 1.0 mass-% each of n-octane, benzene, o-xylene, and cumene in toluene. Thoroughly mix the solution by shaking. Record all weights to the nearest 0.0001 g.
 - Obtain the purest toluene possible to prepare the blend. Analyze it, looking for impurities that elute at the n-octane, benzene, o-xylene, and cumene 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.
 - 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 1.0 mass-% of the stock solution in toluene. Thoroughly mix the calibration blend by shaking. Record all weights to the nearest 0.0001 g.
 - If refrigerated, the stock solution and calibration blend should remain stable for several months.
3. Calculate the concentration of n-octane, benzene, o-xylene, and cumene in the calibration blend to the nearest 1 mg/kg using Equation 1. Using the above dilutions, the resulting calibration blend should contain approximately 100 mg/kg of each added component.

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

where:

A = mass of n-octane, benzene, o-xylene, or cumene 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, o-xylene, or cumene, if any, in the toluene, mg/kg

M = concentration of n-octane, benzene, o-xylene, or cumene in the calibration blend, mg/kg

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.