



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-μL, 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

10⁶ = 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, o-xylene, and cumene to three significant figures, using Equation 2.

$$L = \frac{M}{P} \quad (2)$$

where:

L = absolute response factor for n-octane, benzene, o-xylene, or cumene

M = concentration of n-octane, benzene, o-xylene, or cumene in the calibration blend, from Equation 1, mg/kg

P = average peak area for n-octane, benzene, o-xylene, or cumene in the calibration blend

6. 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 o-xylene to calculate the concentration of p-xylene, m-xylene, and o-xylene. Use the absolute response factor for cumene to calculate the concentration of cumene, n-propylbenzene, each of the three diethylbenzene isomers, and the C₉+ aromatics composite of all the unidentified peaks eluting after cumene.

Procedure

The analyst is expected to be familiar with general laboratory practices, the technique of gas chromatography, and the equipment being used. Dispose of used reagents, materials, and samples in an environmentally safe manner according to local regulations.

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 80°C.
6. Mix the sample by shaking. Fill an autosampler vial with an aliquot of the sample and place it 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.
7. Inject nominally 0.5 µL (repeatable) of sample into the gas chromatograph and start the integrator and the column oven programming sequence.
 - The use of an autoinjector or autosampler automates the injection of the sample into the GC, starts the data system, and the GC oven program simultaneously.

- To minimize cross contamination in trace level analyses, an injection of carbon disulfide is to be made between each sample or blend. Also, use carbon disulfide in the syringe wash vial, and replace it after every series of injections.
8. Identify the components in the resultant chromatogram and determine the areas of the impurity peaks.
- A typical chromatogram is shown in Figure 1.
 - The area of the p-xylene peak must be measured by performing a tangent skim on the tail of the ethyl benzene peak as shown in Figure 2.
 - Non-aromatics are determined as a composite group that includes all unidentified components eluting before cumene.
 - The C₉+ aromatics are determined as a composite group that includes all unidentified components eluting after cumene.

Table 1
Recommended Operating Conditions

Carrier gas	hydrogen
Mode	constant pressure
Head pressure	68.9 kPa gauge (10 psig)
Linear velocity @ 80°C	22 cm/sec
Equivalent flow @ 70°C	0.7 mL/min
Split flow	50 mL/min
Injection port temperature	230°C
Column temperature program	
Initial temperature	80°C
Initial hold time	24 min
Programming rate	20°C/min
Final hold temperature	230°C
Final time	13 min
Detector	flame ionization
Detector temperature	240°C
Hydrogen flow rate^a	35 mL/min
Air flow rate^a	375 mL/min
Makeup gas	nitrogen
Makeup gas flow rate^a	30 mL/min
Sample size	0.5 µL, repeatable

^aConsult the manufacturer's instrument manual for suggested flow rates.

Calculations

Obtain peak areas for each individual component or group of components except ethyl benzene and calculate the composition of the sample to the nearest mg/kg using Equation 3:

$$\text{Component, mg/kg} = 1.000 \text{ LS} \quad (3)$$

where:

L = absolute response factor, previously defined, Equation 2

S = peak area of individual component or group of components

1.000 = correction for the difference in density between the toluene external standard and the ethyl benzene sample, $0.8669 \div 0.8670$

Calculate the concentration of ethyl benzene in the sample by subtracting the sum of all the measured components from 100% using Equation 4.

$$\text{Ethyl benzene, mass-\%} = 100 - \frac{\sum_{i=1}^n V}{10^4} \quad (4)$$

where:

V = concentration of individual component or group of components, mg/kg
100 = 100%
10⁴ = factor to convert mg/kg to mass-%

Report each measured component or group of components to the nearest mg/kg. Report the concentration of ethyl benzene to the nearest 0.01 mass-%.

Precision

Precision statements were determined using UOP Method 999, "Precision Statements in UOP Methods," from precision data obtained using an autosampler.

Repeatability and Site Precision

A nested design was carried out for determining impurities in ethyl benzene by four analysts, with each analyst performing analyses on two separate days, performing two analyses each day for a total of 16 analyses. Using a stepwise analysis of variance procedure, the within-day and within-lab estimated standard deviations (esd) were calculated at the concentration means listed in Table 3. Two analyses performed in one laboratory by the same analyst on the same day should not differ by more than the repeatability allowable differences shown in Table 3 with 95% confidence. Two analyses performed in one laboratory by different analysts on different days should not differ by more than the site precision allowable differences shown in Table 3 with 95% confidence.

Table 3
Repeatability and Site Precision, mg/kg (mass-% for Ethylbenzene)

Component	Mean	Repeatability		Site Precision	
		Within-Day esd	Allowable Difference	Within-Lab esd	Allowable Difference
Non-aromatics	351	6.3	21	10.4	34
Benzene	482	2.5	8	3.2	11
Toluene	150	1.2	4	1.3	4
p-Xylene	8	0.4	1	0.5	2
m-Xylene	2	0.5	2	0.6	2
o-Xylene	78	1.1	4	1.4	5
Cumene	1	0.4	1	0.5	2
C₉+ Aromatics	68	2.8	9	3.6	12
Ethylbenzene (mass-%)	99.886	0.0008	0.002	0.0014	0.005

The data in Table 3 represent short-term estimates of the repeatability of the method. When the test is run routinely, use of a control standard and a control chart is recommended to generate an estimate of long-term repeatability.

Reproducibility

There is insufficient data to calculate the reproducibility of the test at this time.

Time for Analysis

The elapsed time for one analysis is 1.0 hour. The labor requirement is 0.4 hour.

Suggested Suppliers

Agilent Technologies, 2850 Centerville Rd., Wilmington, DE 19808-1610, USA, 1-302-633-8000,
www.agilent.com

Aldrich, 1000 West Saint Paul Ave., Milwaukee, WI 53233, USA, 1-414-273-3850,
www.sigma-aldrich.com

Fisher Scientific, 711 Forbes Ave., Pittsburgh, PA 15219-4785, USA, 1-412-490-8300,
www.fishersci.com

Matheson Tri-Gas, 166 Keystone Drive, Montgomeryville, PA 18936, USA, 1-215-641-2700,
www.mathesontrigas.com

Restek, 110 Benner Circle, Bellefonte, PA 16823, USA, 1-814-353-1300, www.restek.com

VICI Mat/Sen, 7806 Bobbitt, Houston, TX 77055, USA, 1-713-688-9345, www.vicimatsen.com

TCI Fine Chemicals, 9211 N. Harborage Street, Portland, OR 97203, USA, 1-800-423-8616,
www.TCIchemicals.com

VWR International, 1310 Goshen Parkway, West Chester, PA 19380, USA, 1-610-431-1700,
www.vwr.com

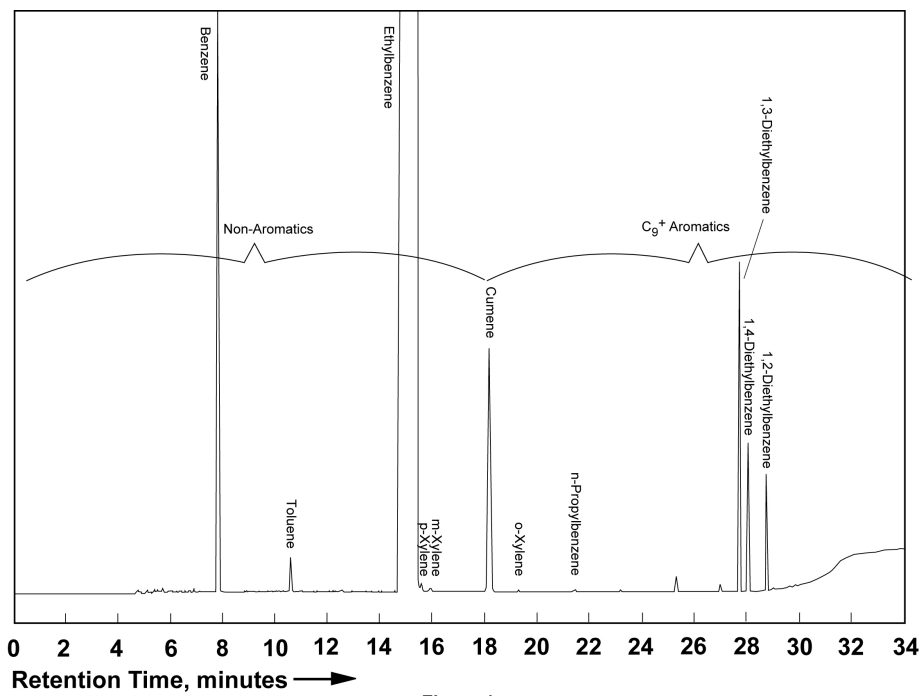


Figure 1
Typical Chromatogram
Total Sample

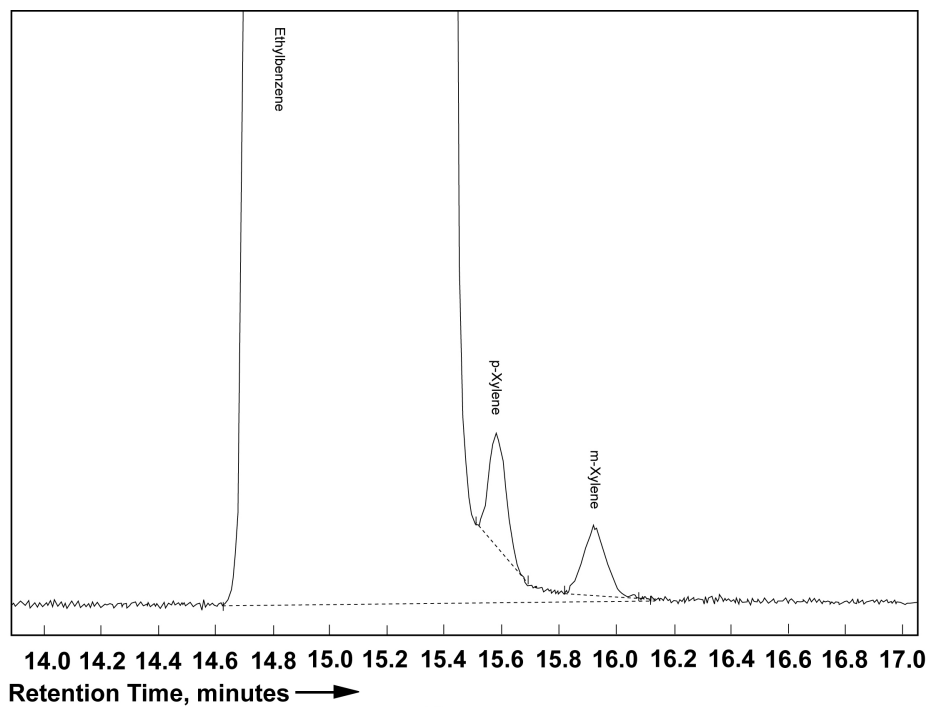


Figure 2
Typical Chromatogram
Detailed view illustrating how to measure p-xylene using tangent skim event