



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 C₁₂ 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).
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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- μ L 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- μ L, 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-diisopropylbenzene 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-diisopropylbenzene 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.

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

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

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, n-propylbenzene, and 1,4-diisopropylbenzene to three significant figures, using Equation 2.

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

where:

L = absolute response factor for n-octane, benzene, n-propylbenzene, or 1,4-diisopropylbenzene

M = concentration of n-octane, benzene, n-propylbenzene, or 1,4-diisopropylbenzene 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.

Table 1
Recommended Operating Conditions

Carrier gas	hydrogen
Mode	constant flow
Head pressure	62 kPa gauge (9 psig)
Linear velocity @ 70°C	30 cm/sec
Equivalent flow @ 70°C	1.7 mL/min
Split flow	50 mL/min
Injection port temperature	250°C
Column temperature program	
Initial temperature	70°C
Initial hold time	0 min
Programming rate	2°C/min
Final hold temperature	200°C
Final Time	0 min
Rate 2	10°C/min
Final Temperature 2	230°C
Final hold time 2	7 min
Detector	flame ionization
Detector temperature	275°C
Hydrogen flow rate^a	35 mL/min
Air flow rate^a	350 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.

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 o-xylene peak must be measured by performing a tangent skim on the tail of the cumene peak.
 - Non-aromatics are determined as a composite group that includes all unidentified components eluting before cumene.

Calculations

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

$$\text{Component, mg/kg} = 1.002 \text{ LS} \quad (3)$$

where:

L = absolute response factor, previously defined, Equation 2

S = peak area of individual component or group of components

1.002 = correction for the difference in density between the toluene external standard and the cumene sample, $0.8640 \div 0.8623$

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

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

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 cumene to the nearest 0.01 mass-%.

Note

The external standard method of quantitation is preferred for best efficiency when analyzing multiple samples. It does, however, require the use of an autoinjector (or autosampler) for best precision. If an autoinjector is not available or if only one or two samples are to be analyzed, the internal standard or total normalization techniques are suitable alternatives.

In the internal standard technique, the peak areas for the impurity components are compared to the peak area for a known amount of internal standard weighed into each sample. The procedure for using the internal standard technique is described in *Appendix A* of this method.

Newer GCs may have a wide dynamic range such that sufficient sensitivity for the small impurities can be obtained without exceeding the instrument's capabilities to measure the major component. If that can be verified, see *Appendix B*, then the total normalization technique of quantitation may be used.

The external standard technique will be the reference in case of dispute.

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 cumene 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 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.

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.

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

<u>Component</u>	<u>Mean</u>	<u>Repeatability</u>		<u>Site Precision</u>	
		<u>Within-Day esd</u>	<u>Allowable Difference</u>	<u>Within-Lab esd</u>	<u>Allowable Difference</u>
Non-aromatics	15	1.3	4	2.2	7
Benzene	6	0.2	1	0.2	1
tert-Butylbenzene	44	0.4	1	0.4	1
m-Diisopropylbenzene	817	6.8	22	8.7	28
o-Diisopropylbenzene	51	0.4	1	0.5	2
p-Diisopropylbenzene	128	1.2	4	1.5	5
Cumene (mass-%)	99.87	0.001	0.01	0.001	0.01

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 1.5 hours. The labor requirement is 0.4 hour.

Suggested Suppliers

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

Aldrich, 1000 West Saint Paul Avenue, Milwaukee, WI 53233 (414-273-3850)
www.sigma-aldrich.com

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

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

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

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

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

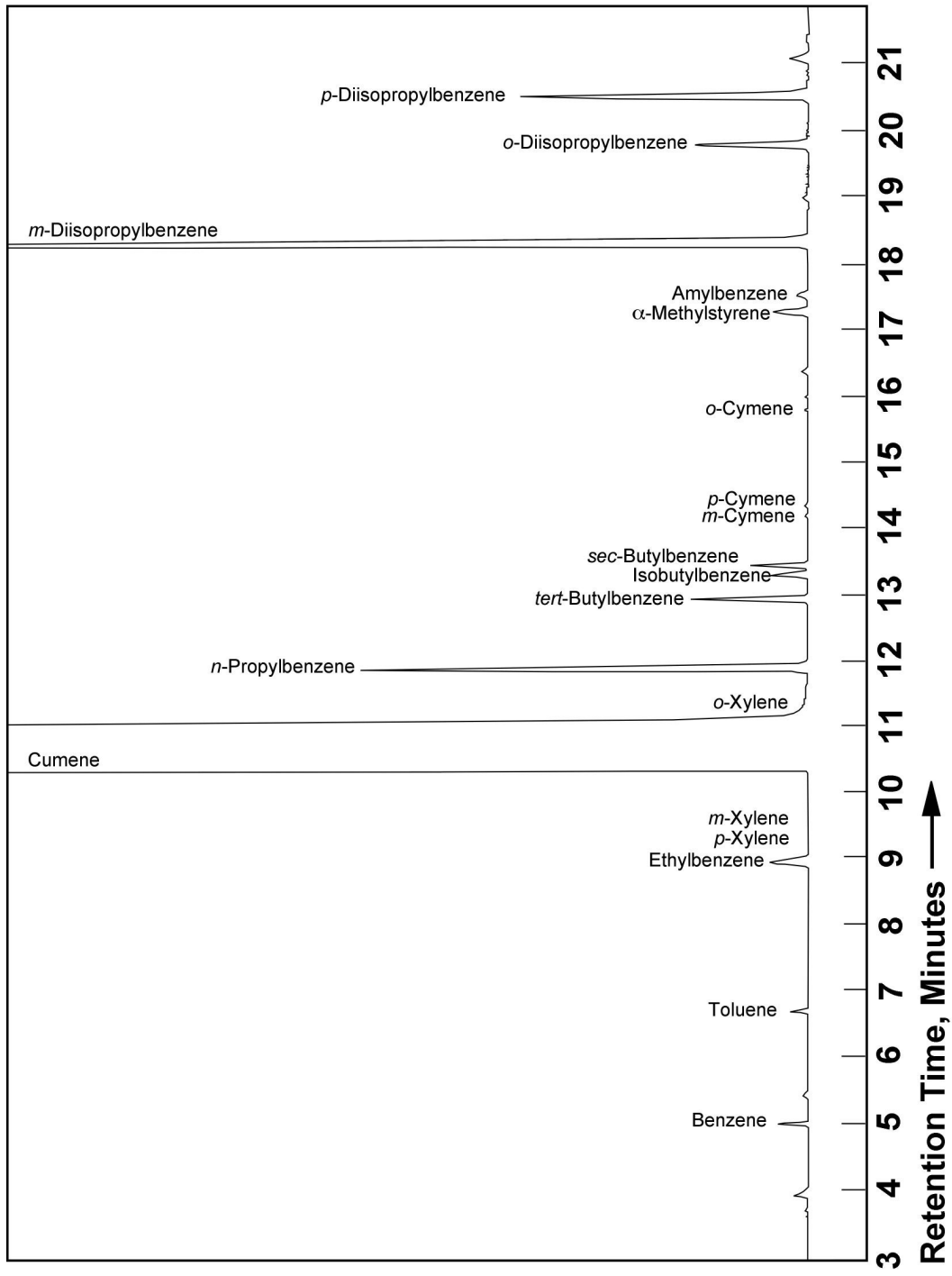


Figure 1
Typical Chromatogram

UOP Method 702

Appendix A

Alternative Calibration and Analysis Using Internal Standard

Scope

This Appendix describes an alternative means of calibration and calculation for the analysis of high purity cumene. It is useful when no autoinjector is available or only a few samples are to be analyzed.

Reference

Scanlon, J. T. and Willis, D. E., *Journal of Chromatographic Science*, **23**, 333-340 (1985)

Outline of Method

The sample to be analyzed is injected into a gas chromatograph that is equipped with a fused silica capillary column. The mass-% concentration of the impurities in the cumene sample are obtained on an absolute basis by the internal standard method of quantitation, wherein the peak areas for the impurity components are first corrected for response and then compared to the peak area for a known amount of internal standard. The cumene purity is then determined by subtracting the total impurities from 100%.

Apparatus

The apparatus required is the same as that listed in the body of the method, except that the use of an autosampler or autoinjector is not mandatory.

Reagents and Materials

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

The following reagents and materials are an addition or substitution to that listed in the body of the method.

Cumene, 99.9% minimum purity, Fisher, Cat. No. 32973 5000

1,3,5-Triethylbenzene, 97+%, Aldrich, Cat. No. 132071-25G

Vial, 15-mL, with screw cap, VWR, Cat. No. 16087-062

Procedure

Calibration

An internal standard is added to the sample in order to accurately quantitate the low levels of impurities expected. Since the flame ionization detector does not respond equally on a mass basis to the components determined and the internal standard, response factors are required to relate the peak areas of the recorded impurities to mass-%. It has been found that using effective carbon number factors, sometimes called theoretical factors, provides accurate quantitation. The theoretical relative response factors were calculated using the effective carbon number (ECN) concept as described by Scanlon and Willis. These factors are listed in Table A1 and are used in the *Calculations* portion of Appendix A.

Prepare a hydrocarbon calibration blend, containing components in cumene, as described in ASTM Method D4307, whose composition is similar to the samples to be analyzed. The pure compounds listed in the body of the method may be used as representative of typical impurities in the cumene. Add the internal standard to the pure cumene and the calibration blend as described in *Procedure, Sample Preparation*. Analyze the cumene and the calibration blend. If any blend components are present in the pure cumene, add their concentrations to the calculated concentrations of the calibration blend. Compare these corrected concentrations to the concentrations determined by the analysis of the calibration blend. If the results differ by more than 10% relative, check the apparatus, the operating conditions, and the blend composition.

Table A1**Theoretical Relative Response Factors, Mass Basis**

1,3,5-Triethylbenzene (Internal Standard)	1.000
Non-aromatics	1.052
Benzene*	0.963
Toluene*	0.973
C₈ Aromatics	0.981
C₉ Aromatics	0.988
C₁₀ Aromatics	0.993
C₁₁ Aromatics	0.997
C₁₂+ Aromatics	1.000

*Use the response factors for benzene and toluene only if they are clearly separated from the non-aromatic components.

Sample Preparation

- Transfer approximately 10 g of the sample to be analyzed to a tared vial and weigh to the nearest 0.1 mg.
 - The sample is deposited in the center of the vial with a Pasteur pipet so that the liquid does not contact the neck.
- Add approximately 0.1 g of 1,3,5-triethylbenzene internal standard using a Pasteur pipet and quickly reweigh to the nearest 0.1 mg.
 - The internal standard is added to the vial while on the balance pan and deposited into the center of the liquid — not on the side of the vial.
- Cap the vial and mix well by inverting several times.

Sample Analysis

- Follow the *Chromatographic Technique*, Steps 1 through 5, as described in the body of the method.
- Inject nominally 0.5 μ L of sample containing the internal standard into the gas chromatograph and start the integrator and the column oven programming sequence.
- Identify the components in the resultant chromatogram and determine the areas of the non-aromatics group, the individual aromatic impurities, and the 1,3,5-triethylbenzene peaks.
 - A chromatogram is shown in Figure A1.

- The area of the o-xylene peak must be measured by performing a tangent skim on the tail of the cumene peak.
- Non-aromatics are determined as a composite group that includes all unidentified components eluting before cumene.

Calculations

Calculate the concentration of each impurity or group of impurities in the cumene sample to the nearest mg/kg using Equation A1:

$$\text{Impurity, mg/kg} = 10^6 \frac{DFG}{JH} \quad (\text{A1})$$

where:

D = peak area of component of interest
F = component response factor from Table A1
G = mass of 1,3,5-triethylbenzene added to sample, g
H = mass of sample, g
J = peak area of the 1,3,5-triethylbenzene
10⁶ = factor to convert to mg/kg

Calculate the purity of the cumene by subtracting the sum of the impurity concentrations from 100% using Equation A2:

$$\text{Cumene, mass-\%} = 100 - \frac{\sum_{i=1}^n V}{10^4} \quad (\text{A2})$$

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 cumene to the nearest 0.01-mass-%. Also state that the analysis was performed by the internal standard technique.

Precision

Precision statements were determined using UOP Method 999 from precision data obtained using an autosampler.

Repeatability and Site Precision

A nested design was carried out for determining impurities in cumene by two analysts, with each analyst performing analyses on two separate days, performing two analyses each day for a total of eight analyses. Using a stepwise analysis of variance procedure, the within-day estimated standard deviations (esd) were calculated at the concentration means listed in Table A2. 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 A2 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 A2 with 95% confidence.

The data in Table A2 is a short-term estimate of precision. When the test is run routinely, a control standard and chart should be used to develop a better estimate of the long-term precision.

Reproducibility

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

Table A2
Repeatability and Site Precision, mg/kg

<u>Component</u>	<u>Mean</u>	<u>Repeatability</u>		<u>Site Precision</u>	
		<u>Within-Day esd</u>	<u>Allowable Difference</u>	<u>Within-Lab esd</u>	<u>Allowable Difference</u>
Non-aromatics	2824	121.9	478	163.7	737
Ethylbenzene	21	1.6	6	1.7	7
n-Propylbenzene	204	8.1	32	11.7	53
tert-Butylbenzene	815	31.3	123	45.5	204
sec-Butylbenzene	116	4.7	18	6.6	30
α-Methylstyrene	107	4.0	16	6.0	27

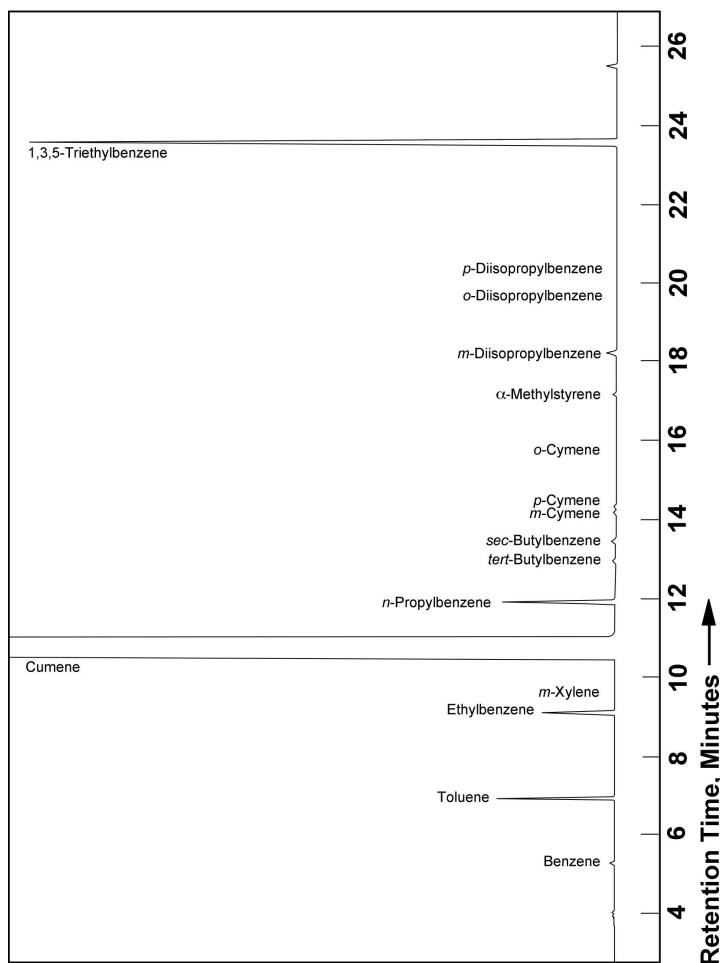


Figure A1
Typical Chromatogram

UOP Method 702

Appendix B

Alternative Calibration and Analysis Using Total Normalization

Scope

This Appendix describes an alternative means of calibration and calculation for the analysis of high purity cumene. It may only be applied when the GC used has a wide dynamic range such that sufficient sensitivity for the small impurities can be obtained without exceeding the instrument's capabilities to measure the major component.

Reference

Scanlon, J. T. and Willis, D. E., *Journal of Chromatographic Science*, **23**, 333-340 (1985)

Outline of Method

The sample to be analyzed is injected into a gas chromatograph that is equipped with a fused silica capillary column. The mass-% composition of the sample is obtained by the total normalization technique, wherein the peak areas of the entire sample are first corrected for differences in response and then normalized to 100%.

Apparatus

The apparatus required is the same as that listed in the body of the method, except that the use of an autosampler or autoinjector is not mandatory. Additionally, the gas chromatograph must meet the dynamic range and linearity requirements described in *Calibration*, Steps 2 through 4.

Procedure

Calibration

The GC system must first be validated to confirm that its dynamic range is sufficient to measure the smaller components at the required sensitivity without exceeding the dynamic range for the major component (cumene).

1. Prepare a calibration blend as described in the body of the method under *Calibration*.
2. Establish the operating conditions at the required sensitivity as described in the body of the method under *Chromatographic Technique*, Steps 1 through 5. If the data system gives an over-range warning when a sample of cumene is analyzed, stop. Do not use the total normalization technique.
3. Visually inspect the top of the cumene peak at a magnification not less than 10X full scale. If the top of the peak shows any flattening or other deformity, the dynamic range of the system has been exceeded. Stop. Do not use the total normalization technique.
4. If there is no visible indication of the dynamic range being exceeded, analyze the calibration blend in triplicate. Calculate the results as described in *Calculations* below. If the values for each of the components do not repeat within 3%, and if the average of the results is not within 3% of the calculated concentration of the calibration blend, stop. Do not use the total normalization technique.

5. If all of the above conditions are satisfied, proceed with the analysis of samples as described in the body of the method under *Chromatographic Technique* Steps 7 and 8.

Since the flame ionization detector does not respond equally on a mass basis to the components determined, response factors are required to relate the peak areas of the recorded impurities to mass-%. It has been found that using effective carbon number factors, sometimes called theoretical factors, provides accurate quantitation. The theoretical relative response factors were calculated using the effective carbon number (ECN) concept as described by Scanlon and Willis. These factors are listed in Table B1 and are used in the *Calculations* portion of this method.

Table B1
Theoretical Relative Response Factors, Mass Basis

Non-aromatics	1.064
Benzene*	0.975
Toluene*	0.986
C₈ Aromatics	0.994
Cumene and other C₉ Aromatics	1.000
C₁₀ Aromatics	1.005
C₁₁ Aromatics	1.009
C₁₂+ Aromatics	1.013

*Use the response factors for benzene and toluene only if they are clearly separated from the non-aromatic components.

Calculations

Obtain peak areas for each individual component or group of components including cumene. Calculate the components or group of components in the sample, other than cumene, to the nearest mg/kg using Equation B1. Calculate the concentration of cumene in the sample to the nearest 0.01 mass-% using Equation B2.

$$\text{Component, mg/kg} = 10^6 \frac{PR}{T} \quad (\text{B1})$$

where:

P = peak area of individual component or group of components (the group components are shown in Figure 1 in the body of the method)

R = relative response factor, previously defined

T = sum of the products, **PR**, of all the recorded peaks

10⁶ = factor to convert to mg/kg

$$\text{Cumene, mass-\%} = \frac{V}{10^4} \quad (\text{B2})$$

where:

V = concentration of cumene, mg/kg

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 cumene to the nearest 0.01-mass-%. Also state that the analysis was performed by the total normalization technique.

Precision

Precision statements were determined using UOP Method 999 from precision data obtained using an autosampler.

Repeatability and Site Precision

A nested design was carried out by two analysts, with each analyst performing analyses on two separate days, performing two analyses each day for a total of eight analyses. Using a stepwise analysis of variance procedure, the within-day estimated standard deviations (esd) were calculated at the concentration means listed in Table B2. 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 B2 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 B2 with 95% confidence.

The data in Table B2 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.

Table B2
Repeatability and Site Precision, mass-ppm (mass-%)

<u>Component</u>	<u>Mean</u>	<u>Repeatability</u>		<u>Site Precision</u>	
		<u>Within-Day esd</u>	<u>Allowable Difference</u>	<u>Within-Lab esd</u>	<u>Allowable Difference</u>
Non-aromatics	413	5.0	20	8.3	50
Toluene	58	5.0	20	5.0	22
Ethylbenzene	1851	3.5	14	3.5	14
Cumene (mass-%)	99.36	0.003	0.01	0.003	0.01

Reproducibility

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