



A Honeywell Company

Trace Impurities in Mixed Xylenes by GC

UOP Method 931-10

Scope

This method is for determining trace impurities in high-purity mixed xylenes by gas chromatography (GC). Specific trace impurities determined include non-aromatic hydrocarbons, benzene, toluene and individual C₉ and C₁₀ aromatic compounds. C₁₀ or higher non-aromatics, if present, may interfere with the determination of benzene, but it can be determined by UOP Method 543. The lower limit of quantitation for any single component is 1 mg/kg (mass-ppm). Impurities at concentrations above 500 mg/kg should be determined by UOP Method 744.

References

ASTM D4307, "Preparation of Liquid Blends for use as Analytical Standards," www.astm.org

UOP Method 543, "Non-aromatic Hydrocarbons in High-Purity Aromatics by Gas Chromatography," www.astm.org

UOP Method 744, "Aromatics in Hydrocarbons by Gas Chromatography," www.astm.org

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

Outline of Method

The sample is injected into a gas chromatograph that is equipped with an autoinjector, a fused silica capillary column internally coated with poly(ethylene glycol), and a flame ionization detector. The concentrations of individual or group impurities are determined by the external standard (ESTD) 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. See *Note* for alternative internal standard (ISTD) calibration and calculation techniques.

Definition

Mixed xylenes. For purposes of this method, mixed xylenes are defined to include ethylbenzene in addition to p-, m-, and o-xylene.

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).

© COPYRIGHT 1994, 2010 UOP LLC. All rights reserved.

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.

Apparatus

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

Balance, analytical, readable to 0.0001 g

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

Gas chromatograph, temperature programmable, built for capillary column chromatography, utilizing a split injection system having a glass injection port insert, and equipped with a flame ionization detector that will give a minimum peak height response of 10 times the background noise for 1 mg/kg benzene when operated at 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.

Leak detector, gas, Alltech Associates, Cat. No. 21-250

Refrigerator, flammable storage or explosion proof

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 *Note* and *Appendix*. 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, local supply

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

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

2-Ethyltoluene(1-methyl-2-ethylbenzene), 99% minimum purity, Sigma-Aldrich, Cat. No. E49401

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

n-Heptane, 99% minimum purity, Sigma-Aldrich Chemical, Cat. No. H219-8

Hydrogen, zero gas, 99.99% minimum purity, total hydrocarbons less than 0.5 ppm as methane, local supply

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

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

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

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

Toluene, 99.9% minimum purity, Sigma-Aldrich, Cat. No. E49401

n-Undecane, 99% minimum purity, Sigma-Aldrich, Cat. No. U407

Vials, 22-mL, with polyseal-lined caps, VWR, Cat. No. 16087-068

Vials, autosampler, for recommended sample injector, with caps, 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 benzene, toluene, n-undecane and 1-methyl-2-ethylbenzene in n-heptane. Thoroughly mix the solution by shaking. Record all weights to the nearest 0.1 mg.
 - Obtain the purest n-heptane possible to prepare the blend. Analyze it, looking for impurities that elute at the benzene, toluene, n-undecane and 1-methyl-2-ethylbenzene sites. If impurities in the heptane 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 n-heptane, if needed, using the technique in the Appendix of this method and determine the concentrations of benzene, toluene, n-undecane and 1-methyl-2-ethylbenzene in the n-heptane.
 - 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 1.5 mass-% of the stock solution in heptane. 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 benzene, toluene, n-undecane and 1-methyl-2-ethylbenzene in the calibration blend to the nearest mg/kg 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 benzene, toluene, n-undecane, or 1-methyl-2-ethylbenzene 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 benzene, toluene, n-undecane or 1-methyl-2-ethylbenzene, if any, in the n-heptane as analyzed as described in Appendix A; see first bullet under Step 1 above, mg/kg

M = concentration of benzene, toluene, n-undecane, or 1-methyl-2-ethylbenzene 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 benzene, toluene n-undecane and 1-methyl-2-ethylbenzene, to three significant figures, using Equation 2.

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

where:

L = absolute response factor for benzene, toluene, n-undecane, or 1-methyl-2-ethylbenzene
M = concentration of benzene, toluene, n-undecane, or 1-methyl-2-ethylbenzene in the calibration blend, from Equation 1, mg/kg
P = average peak area for benzene, toluene, n-undecane, or 1-methyl-2-ethylbenzene in the calibration blend

6. Determine the response factor daily or each time analyses are performed.
7. Use the absolute response factor for n-undecane to calculate the concentration of the non-aromatics. Use the absolute response factor for 1-methyl-2-ethylbenzene to calculate the concentration of all C₉, C₁₀, and heavy aromatics.

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 (Figures 1 and 2).

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 50°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
Flow rate	2.3 mL/min
Head pressure @ 50°C	68 kPa gauge (10 psig)
Linear velocity @ 50°C	38 cm/sec
Split flow	50 mL/min
Injection port temperature	230°C
Column temperature program	
Initial temperature	50°C
Initial hold time	5 min
Programming rate	8°C/min
Final hold temperature	100°C
Final Time	0 min
Rate 2	2°C/min
Final Temperature 2	120°C
Final hold time 2	0 min
Rate 3	20°C/min
Final Temperature 3	230°C
Final hold time 3	5 min
Detector	flame ionization
Detector temperature	250°C
Hydrogen flow rate^a	38 mL/min
Air flow rate^a	450 mL/min
Makeup gas	nitrogen
Makeup gas flow rate^a	45 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 data system 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. CAUTION: Carbon disulfide is a flammable and toxic compound. Use appropriate care and personal protection equipment (PPE) when handling.
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 C9 and C10 aromatics region is expanded in Figure 2.
- Non-aromatics are determined as a composite group that includes all unidentified components eluting before ethylbenzene. The composite also includes benzene and toluene, if present. For some samples, benzene and/or toluene may be present and clearly separated from the non-aromatic components. In this case, benzene and/or toluene may be reported separately from the non-aromatics composite.
- The area of the n-propylbenzene peak must be measured by performing a tangent skim on the tail of the o-xylene peak.
- Heavy aromatics are defined as a composite group that includes all unidentified components eluting after o-xylene.

Calculations

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

$$\text{Component, mg/kg} = 0.795 \text{ LS} \quad (3)$$

where:

L = absolute response factor, previously defined, Equation 2

S = peak area of individual component or group of components

0.795 = correction for the difference in density between the n-heptane external standard and the xylenes sample, $0.684 \div 0.860$

Report each measured component or group of components to the nearest mg/kg.

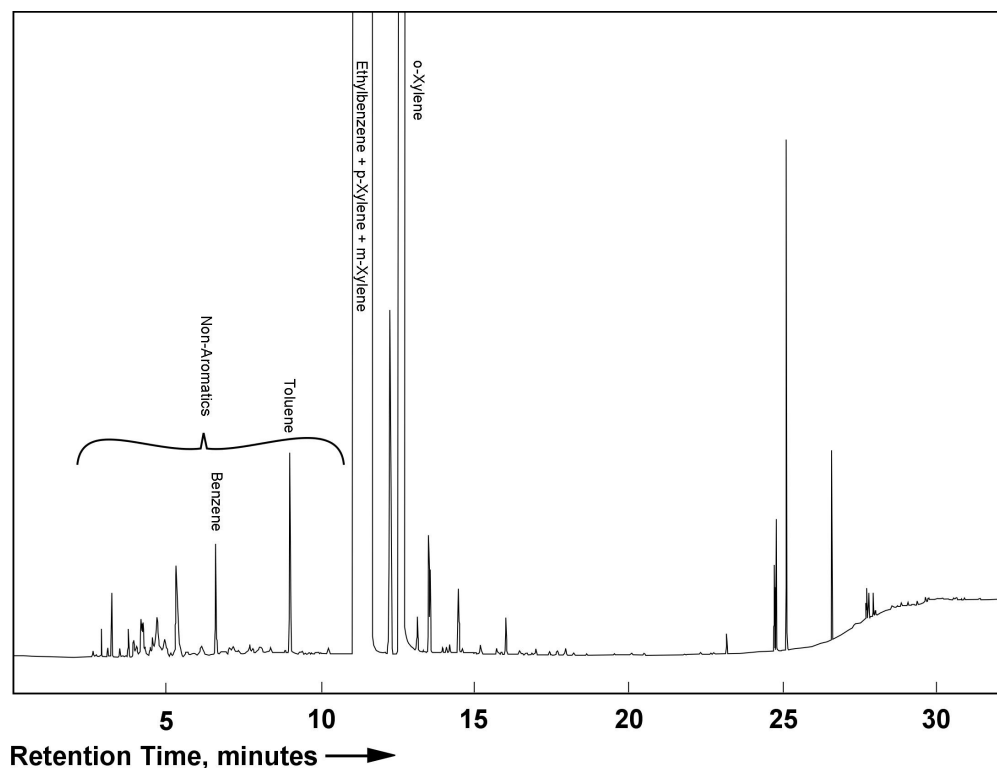


Figure 1
Xylene ESTD Chromatogram

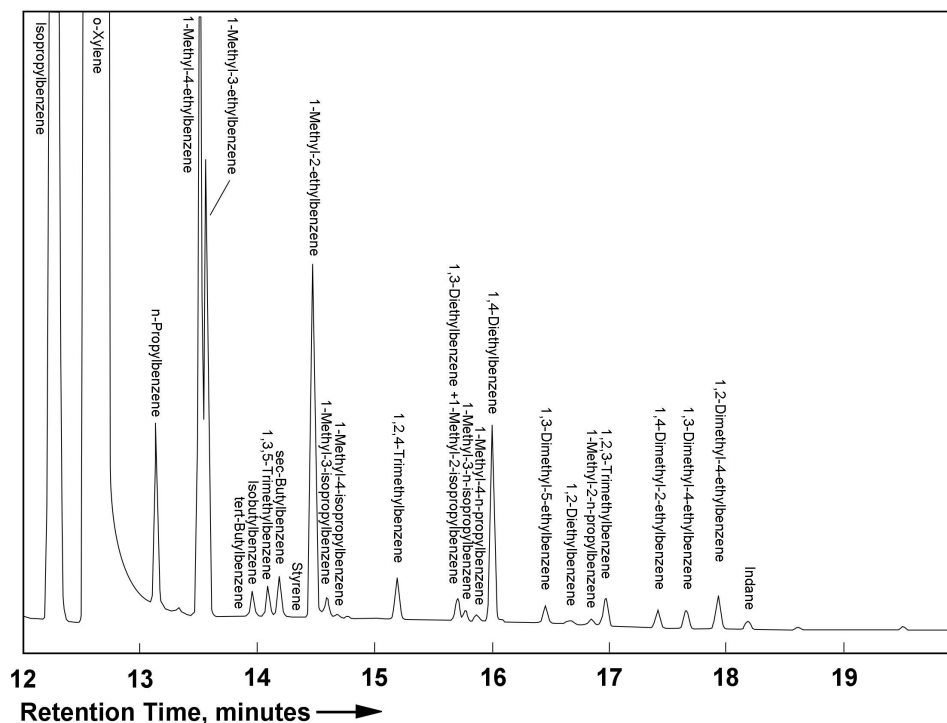


Figure 2
Xylene ESTD Chromatogram, C₉ and C₁₀ Aromatic Region

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 technique may be a suitable alternative. In this 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 the Appendix of this method.

The external standard technique will be the referee 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 mixed xylenes by two analysts, with each analyst performing analyses on two separate days, performing three analyses each day for a total of 12 analyses. Using a stepwise analysis of variance procedure, the within-day estimated standard deviations (esd) were calculated at the concentration means listed in Table 2. 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 2 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 2 with 95% confidence.

The data in Table 2 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.

Table 2
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	526.3	9.80	31.9	11.90	38.8
Toluene	127.1	0.84	2.8	1.43	8.7
Isopropylbenzene	371.4	2.03	6.6	2.93	11.5
n-Propylbenzene	18.1	0.17	0.6	0.18	0.6
1,2,4-Trimethylbenzene	4.9	0.05	0.2	0.05	0.2
1,2-Diethylbenzene	0.6	0.05	0.2	0.06	0.2
Indane	1.2	0.02	0.1	0.02	0.1
Heavy aromatics	350.7	2.85	9.3	3.95	13.7

Time for Analysis

The elapsed time for one analysis is 0.85 hour. The labor requirement is 0.35 hour.

Suggested Suppliers

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

Grace, 2051 Waukegan Rd., Deerfield, IL 60015 USA (847-948-8600)
www.discoverysciences.com

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

Restek, 110 Benner Cir., Bellefonte, PA 16823 USA (814-353-1300) www.restek.com
Sigma-Aldrich, 1000 West Saint Paul Ave., Milwaukee, WI 53233 USA (414-273-3850)
www.sigma-aldrich.com

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

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

Appendix

Alternative Calibration and Analysis Using Internal Standard

Scope

This Appendix describes an alternative means of calibration and calculation for the analysis of impurities in high-purity mixed xylenes. 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 is injected into a gas chromatograph that is equipped with a fused silica capillary column, internally coated with poly(ethylene glycol), and a flame ionization detector. The mg/kg concentration of the impurities is obtained on an absolute basis by the internal standard method of quantitation, wherein the peak areas for the impurities are compared to the peak area for a known amount of internal standard.

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 in addition or substitution to that listed in the body of the method.

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 as it does to the internal standard, response factors are required to relate the peak areas of the recorded impurities to mg/kg. 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.

Check instrument performance as follows:

1. Weigh the internal standard into an aliquot of the calibration blend prepared in the body of the method (as described in *Sample Preparation*, below) and analyze it as described in *Sample Analysis*, below.

2. Compare the calibration blend concentrations from Equation 1 in the body of the method to the concentrations determined by the analysis of the calibration blend.
3. If the results differ by more than 10% relative, check the apparatus, the operating conditions, and the blend composition.

Table A1**Theoretical Response Factors, Relative to the Internal Standard, Mass Basis**

n-Undecane (Internal Standard)	1.000
Non-aromatics	1.003
Benzene*	0.916
Toluene*	0.926
C₉ Aromatics	0.933
C₁₀ Aromatics	0.938
Heavy aromatics	0.942

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

Sample Preparation

1. 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.
2. Add approximately 0.1 g of n-undecane 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.
3. Cap the vial and mix well by inverting several times.

Sample Analysis

1. Follow the *Chromatographic Technique*, Steps 1 through 5, as described in the body of the method.
2. Inject nominally 0.5 μ L of sample containing the internal standard into the gas chromatograph and start the data system and the column oven programming sequence.
 - If an autoinjector or autosampler is used, it automates the injection of the sample into the GC, starts the data system, and the GC oven program simultaneously.
3. Identify the components in the resultant chromatogram and determine the areas of the non-aromatics group, the individual aromatic impurities, and the n-undecane peaks.
 - A typical chromatogram is shown in Figure 1 in the body of the method. The C₉ and C₁₀ aromatics region is expanded in Figure 2 in the body of the method. The location of the n-undecane internal standard is shown in Figure A1.
 - Non-aromatics are determined as a composite group that includes all unidentified components eluting before ethylbenzene. The composite also includes benzene and toluene, if present. For some samples, benzene and/or toluene may be present and clearly separated from the non-aromatic components. In this case, benzene and/or toluene may be reported separately from the non-aromatics composite.

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

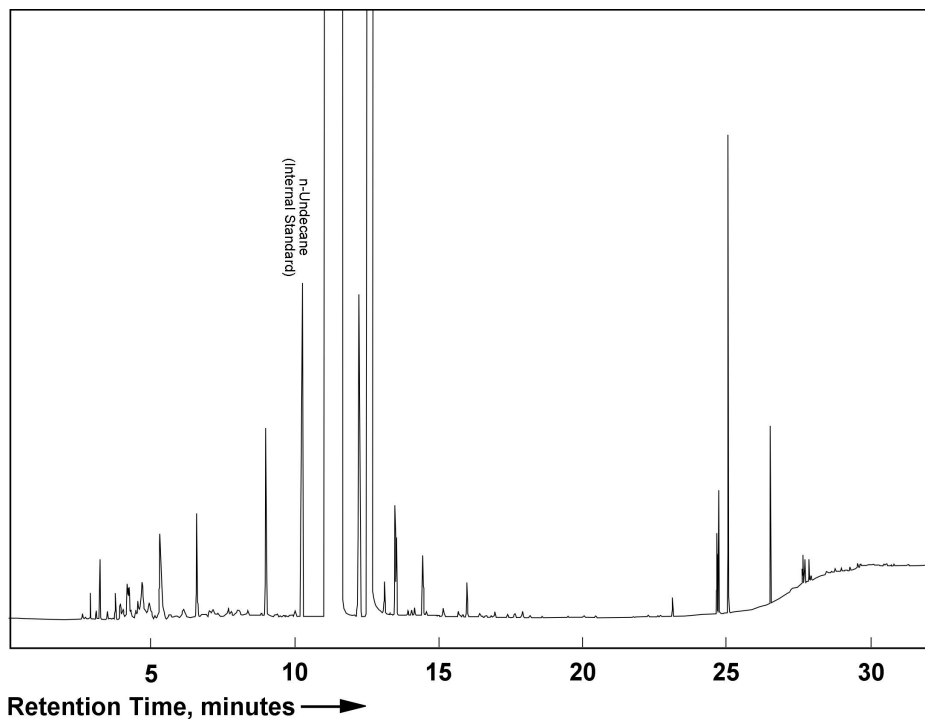


Figure A1
Xylene ISTD Chromatogram

Calculations

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

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

where:

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

Report each measured component or group of components to the nearest mg/kg. Also state that the analysis was performed by the internal standard technique.

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 mixed xylenes by two analysts, with each analyst performing analyses on two separate days, performing three analyses each day for a total of 12 analyses. Using a stepwise analysis of variance procedure, the within-day estimated standard deviations (esd) were calculated at the concentration means listed in Table A1. 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 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 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	551.8	6.95	22.7	8.73	31.7
Toluene	130.7	0.19	0.6	0.40	1.6
Isopropylbenzene	376.6	1.22	4.0	1.53	6.9
n-Propylbenzene	18.4	0.09	0.3	0.09	0.3
1,2,4-Trimethylbenzene	5.2	0.06	0.2	0.07	0.2
1,2-Diethylbenzene	0.5	0.04	0.1	0.04	0.1
Indane	1.4	0.06	0.2	0.07	0.4
Heavy aromatics	358.4	0.43	1.4	2.17	9.8

Reproducibility

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