



A Honeywell Company

Impurities in, and Purity of, High Purity *p*-Xylene by GC

UOP Method 720-08

Scope

This method is for determining trace hydrocarbon impurities in high purity *p*-xylene. The lower limit of detection for any single component is 0.002 mass-%. The method can also be used for determining the total purity of the *p*-xylene. Mixed xylene isomers and/or diethylbenzenes in other process streams should be determined using UOP Method 744, "Aromatics in Hydrocarbons by Gas Chromatography."

References

- ASTM Practice D4307, "Preparation of Liquid Blends for Use as Analytical Standards,"
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 to be analyzed is injected into a gas chromatograph (GC) that is equipped with a fused silica capillary column, a capillary injection port, 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 1* 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

Bottle, 120-mL, clear, round, glass, with TFE lined closure, VWR, Cat. No. 16151-286

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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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 Carbowax 20M, Supelco, Cat. No. 2-4085 (Supelcowax 10). See *Note 2*.

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 0.002 mass-% *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/Freezer, 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 *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, total hydrocarbons less than 2.0 ppm as methane (zero gas)

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

p-Diethylbenzene, 99.9% minimum purity, Chemsampco, Cat. No. 1135.72-1. See *Note 3*.

Ethylbenzene, 99.9% minimum purity, Chemsampco, Cat. No. 2379.03-1

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-Nonane, 99.9% minimum purity, Chemsampco, Cat. No. 6780.00-1

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

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

m-Xylene, 99.9% minimum purity, Chemsampco, Cat. No. 1240.12-1

o-Xylene, 99.9% minimum purity, Chemsampco, Cat. No. 1240.02-1

p-Xylene, 99% minimum purity, Chemsampco, Cat. No. 1240.21. See *Purification of p-Xylene*.

Calibration

Purification of *p*-Xylene

p-Xylene containing no other measurable C₈ aromatic impurities must be prepared to be used in a calibration blend. Prepare the purified *p*-xylene as follows.

1. Cool approximately 500 mL of commercial *p*-xylene in an explosion-proof freezer at $-10 \pm 5^{\circ}\text{C}$ until approximately 1/2 to 3/4 of the *p*-xylene crystallizes.
 - This requires about 5 hours.
2. Remove the *p*-xylene from the freezer and decant and discard the liquid portion.
3. Allow the frozen *p*-xylene to thaw, and then repeat the above crystallization step on the remaining *p*-xylene several times until no ethylbenzene, *m*- and *o*-xylene are detected in the *p*-xylene, as indicated by gas chromatographic analysis (refer to *Chromatographic Technique*). See Note 3.
 - Typically 4 or 5 recrystallizations are required.

Preparation of Calibration Blend

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

1. Prepare a stock solution as described in ASTM Method D4307 to contain approximately 1.5 mass-% each of *n*-nonane, ethylbenzene, *m*-xylene, *o*-xylene, and *p*-diethylbenzene in the purified *p*-xylene (see *Purification of p-Xylene*). Thoroughly mix the solution by shaking. Record all weights to the nearest 0.1 mg.
 - 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 purified *p*-xylene. 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*-nonane, ethylbenzene, *m*-xylene, *o*-xylene, and *p*-diethylbenzene in the calibration blend to the nearest 0.0001 mass-% using Equation 1. Using the above percentages, the resulting calibration blend should contain approximately 0.023 mass-% of each added component.

$$M = \frac{100 AB}{CD} \quad (1)$$

where:

- A** = mass of *n*-nonane, ethylbenzene, *m*-xylene, *o*-xylene, or *p*-diethylbenzene in the stock solution, g
B = mass of base blend in the calibration blend, g
C = total mass of the stock solution, g
D = total mass of the calibration blend, g

M = concentration of *n*-nonane, ethylbenzene, *m*-xylene, *o*-xylene, or *p*-diethylbenzene in the calibration blend, mass-%

100 = factor to convert to percent

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% 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 external standard 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*-nonane, ethylbenzene, *m*-xylene, *o*-xylene, and *p*-diethylbenzene, to three significant figures, using Equation 2.

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

where:

L = absolute response factor for *n*-nonane, ethylbenzene, *m*-xylene, *o*-xylene, or *p*-diethylbenzene

M = concentration of *n*-nonane, ethylbenzene, *m*-xylene, *o*-xylene, or *p*-diethylbenzene in the calibration blend, mass-%

P = average peak area for *n*-nonane, ethylbenzene, *m*-xylene, *o*-xylene, or *p*-diethylbenzene in the calibration blend

Use the absolute response factor for *n*-nonane to calculate the concentration of the non-aromatics, benzene, and toluene composite. Use the absolute response factor for ethylbenzene, *m*-xylene, and *o*-xylene to calculate the concentration of each of these components. Use the absolute response factor for *p*-diethylbenzene to calculate the concentration of the composite of all peaks eluting after *m*-xylene, excluding *o*-xylene.

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).

Table 1
Recommended Operating Conditions

Carrier gas	hydrogen
Mode	constant pressure
Head pressure	35 kPa gauge (5 psig)
Linear velocity @ 70°C	17 cm/sec
Equivalent flow @ 70°C	0.86 mL/min
Split flow	150 mL/min
Injection port temperature	230°C
Column temperature program	
Initial temperature	70°C
Initial hold time^a	29 min
Programming rate	10°C/min
Final hold temperature	240°C
Final hold time	0 min
Detector	flame ionization
Detector temperature	240°C
Hydrogen flow rate^b	30 mL/min
Air flow rate^b	350 mL/min
Makeup gas	nitrogen
Makeup gas flow rate^b	30 mL/min
Sample size	0.5 µL, repeatable

^aAdjust the initial time so that the programming rate does not begin until after the *m*-xylene elutes.

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

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.
7. Inject nominally 0.5 µL of sample into the gas chromatograph and start the integrator and the column oven programming sequence.
 - When using an autosampler or autoinjector, the injection sequence of a GC is typically automated, performing the injection, and starting the data system and column temperature 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 *m*-xylene peak must be measured by performing a tangent skim on the tail of the *p*-xylene peak. See Note 2.

- Non-aromatics are determined as a composite group that includes all components eluting before ethylbenzene. The composite also includes benzene and toluene, if present. See *Note 4*.
- C₉+ aromatics are determined as a composite group that includes all components eluting after *m*-xylene excluding *o*-xylene.

Calculations

Obtain peak areas for each individual component or group of components and calculate the composition of the sample to the nearest mass-% using Equation 3:

$$\text{Component, mass-\%} = LS \quad (3)$$

where:

L = absolute response factor, previously defined, Equation 2

S = peak area of individual component or group of components

Calculate the concentration of *p*-xylene in the sample by subtracting the sum of all the measured components from 100%.

Report each measured component or group of components to the nearest 0.001 mass-%. Report the concentration of *p*-xylene to the nearest 0.01 mass-%.

Notes

1. 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 *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 validated, 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.

2. The column must be capable of separating the *p*- and *m*-xylene in a sample so that the distance from the baseline to the valley between the peaks is not more than 20% of the *m*-xylene peak height when the *m*-xylene is at a concentration of 0.005 mass-%.
3. *p*-Xylene from some sources may retain *p*-diethylbenzene after purification. If so, select a different C₁₀ aromatic for use in blend preparation under *Calibration*.
4. 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. Prepare the calibration blend to include the addition of benzene and/or toluene to the other components, determine calibration factors for benzene and/or toluene, and report the benzene and/or toluene separately from the non-aromatics composite.

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 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, 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	0.009	0.0005	0.002	0.0006	0.002
Ethylbenzene	0.036	0.0007	0.003	0.0009	0.005
<i>p</i>-Xylene	99.878	0.0008	0.003	0.0022	0.014
<i>m</i>-Xylene	0.051	0.0005	0.002	0.0010	0.004
<i>o</i>-Xylene	0.018	0.0005	0.002	0.0007	0.004
C₉+ Aromatics	0.010	0.0008	0.003	0.0009	0.003

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. Neither the elapsed time nor labor requirement includes the time required for the purification of *p*-xylene.

Suggested Suppliers

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

Chemsampco, 40 Enterprise Ave., Trenton, NJ 08638 (609-656-2440) www.chemsampco.com

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

Supelco, 595 North Harrison Road, Bellefonte, PA 16823 (814-359-3441) www.sigma-aldrich.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

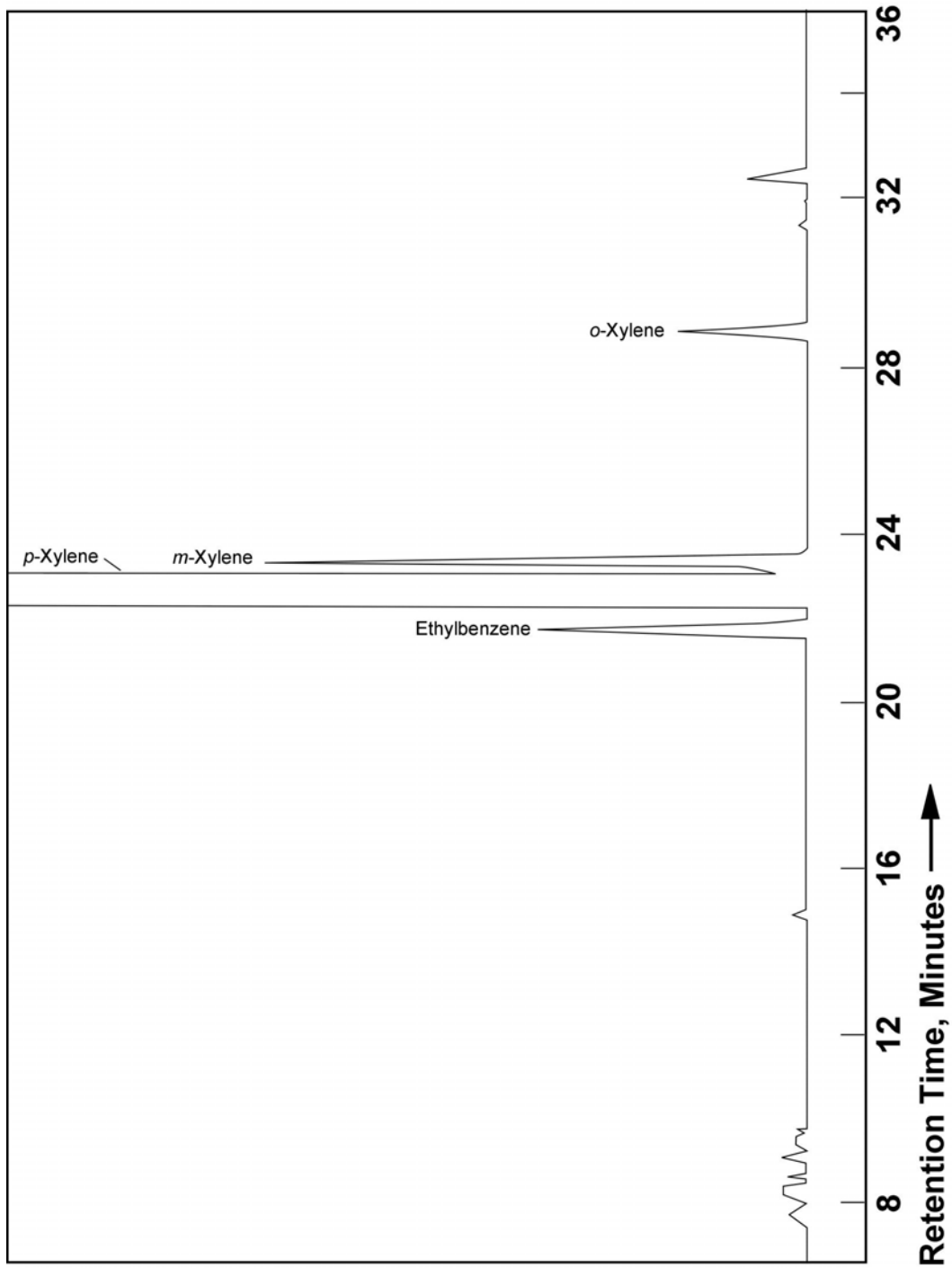


Figure 1
Typical Chromatogram, High-Purity *p*-Xylene

UOP Method 720

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 *p*-xylene. 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 *p*-xylene 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 *p*-xylene 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.

Undecane, 99% minimum purity, VWR, Cat. No. AA31807-18

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 as described in ASTM Method D4307, whose composition is similar to the samples to be analyzed. Add the internal standard and analyze the blend as a sample

to verify instrument calibration. 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-%

Undecane (Internal Standard)	1.000
Non-aromatics	1.003
Benzene*	0.916
Toluene*	0.926
Ethylbenzene	0.934
<i>m</i>-Xylene	0.934
<i>o</i>-Xylene	0.923
C₉+ Aromatics	0.945

*Use the response factors for benzene and toluene only if they are clearly separated from the non-aromatic components. See *Note 4* in the body of the method.

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 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 integrator and the column oven programming sequence.
3. Identify the components in the resultant chromatogram and determine the areas of the impurity and undecane peaks.
 - A chromatogram is shown in Figure A1.
 - The area of the *m*-xylene peak must be measured by performing a tangent skim on the tail of the *p*-xylene peak.
 - Non-aromatics are determined as a composite group that includes all components eluting before ethylbenzene except the undecane internal standard. The composite also includes benzene and toluene, if present. See *Note 4* in the body of the method.
 - C₉+ aromatics are determined as a composite group that includes all components eluting after *m*-xylene excluding *o*-xylene.

Calculations

Calculate the concentration of each impurity or group of impurities in the *p*-xylene sample to the nearest 0.001 mass-% using Equation A1:

$$\text{Impurity, mass-\%} = 100 \frac{DFG}{BH} \quad (\text{A1})$$

where:

- B** = peak area of the undecane
- D** = peak area of component of interest
- F** = component response factor from Table A1
- G** = mass of undecane added to sample, g
- H** = mass of sample, g
- 100** = factor to convert to mass-%

Calculate the purity of the *p*-xylene by subtracting the sum of the impurity concentrations from 100%, and report to the nearest 0.01 mass-%.

Report each measured component or group of components to the nearest 0.001 mass-%. Report the concentration of *p*-xylene to the nearest 0.01 mass-%.

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 on one sample of *p*-xylene with two analysts in each of five laboratories. Each analyst carried out tests on two separate days, performing two tests each day. The total number of tests performed was 40. Using a stepwise analysis of variance procedure, the within-day and within laboratory estimated standard deviations (esd) were calculated and are listed in Table A2. Two tests performed by the same analyst on the same day should not differ by more than the repeatability allowable difference shown in Table A2 with 95% confidence. Two tests performed in one laboratory by different analysts on different days should not differ by more than the site precision allowable difference shown in Table A2 with 95% confidence.

Table A2
Repeatability, Site Precision, and Reproducibility, mass-%

<u>Component</u>	<u>Mean</u>	<u>Repeatability</u>		<u>Site Precision</u>		<u>Reproducibility</u>	
		<u>Within-Day esd</u>	<u>Allowable Difference</u>	<u>Within-Lab esd</u>	<u>Allowable Difference</u>	<u>Between-Lab esd</u>	<u>Allowable Difference</u>
Ethylbenzene	0.025	0.0008	0.002	0.0017	0.005	0.0020	0.006
<i>p</i> -Xylene	99.920	0.0023	0.007	0.0059	0.018	0.0063	0.019
<i>m</i> -Xylene	0.036	0.0019	0.006	0.0025	0.007	0.0036	0.011
<i>o</i> -Xylene	0.018	0.0018	0.005	0.0020	0.005	0.0022	0.006

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

The between laboratory estimated standard deviations (esd) were calculated and are listed in Table A2. Two tests performed in different laboratories by different analysts on different days, should not differ by more than the allowable differences shown (95% probability).

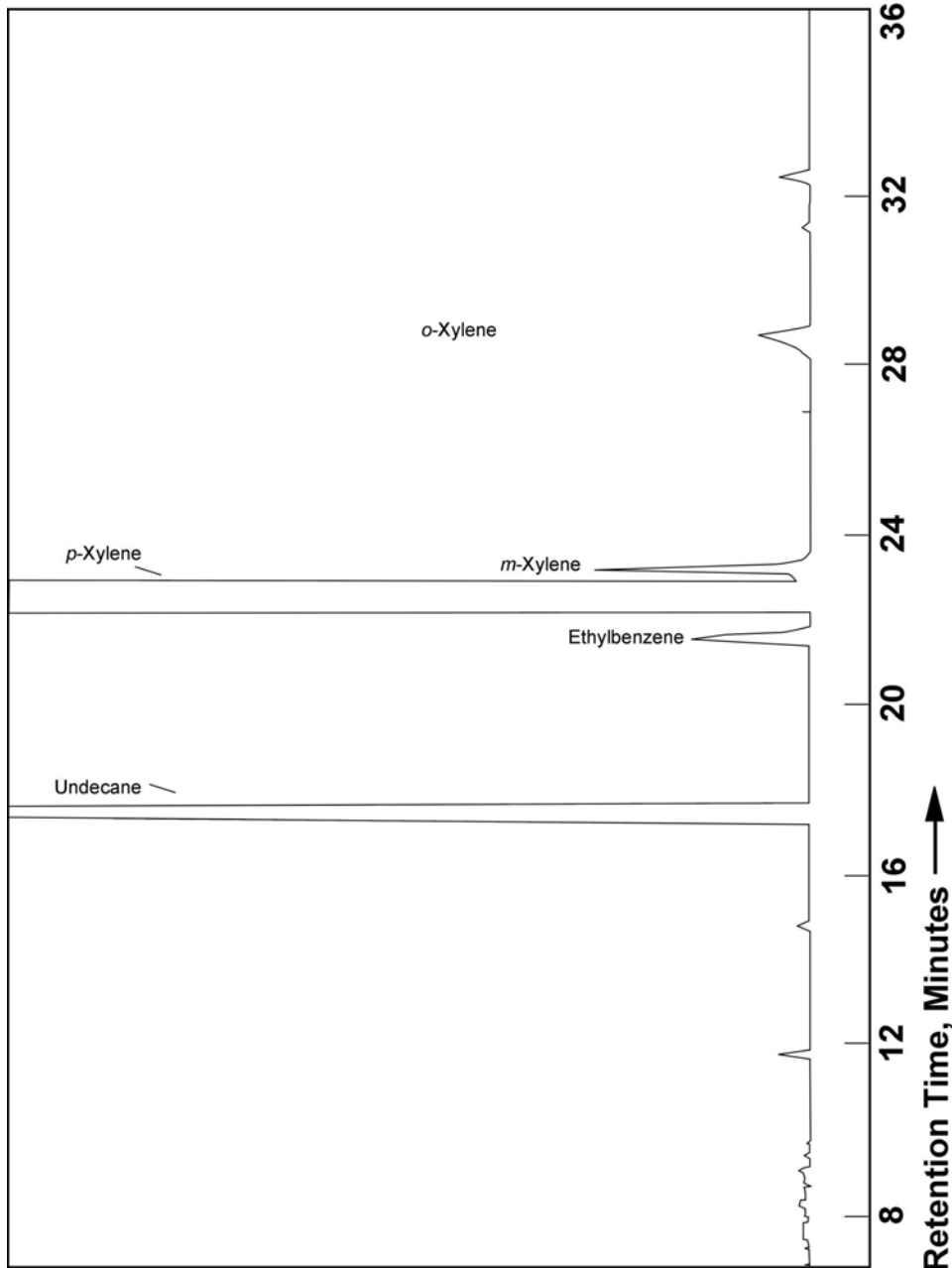


Figure A1

Typical Chromatogram, High-Purity *p*-Xylene, with Internal Standard

UOP Method 720

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 *p*-xylene. 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 (*p*-xylene).

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 *p*-xylene is analyzed, stop. Do not use the total normalization technique.
3. Visually inspect the top of the *p*-xylene 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-%

Non-aromatics	1.074
Benzene*	0.981
Toluene*	0.992
Ethylbenzene	1.000
<i>p</i>-Xylene	1.000
<i>m</i>-Xylene	1.000
<i>o</i>-Xylene	1.000
C₉+ Aromatics	1.011

*Use the response factors for benzene and toluene only if they are clearly separated from the non-aromatic components. See Note 4 in the body of the method.

Calculations

Obtain peak areas for each individual component or group of components and calculate the composition of the sample to the nearest 0.001 mass-% using Equation B1:

$$\text{Component, mass-\%} = 100 \frac{\text{PR}}{\text{T}} \quad (\text{B1})$$

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

100 = factor to convert to mass-%

Report each measured component or group of components to the nearest 0.001 mass-%. Report the concentration of *p*-xylene to the nearest 0.01 mass-%.

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-%

<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	0.041	0.0005	0.002	0.0008	0.005
Toluene	0.006	0.0005	0.002	0.0005	0.002
Ethylbenzene	0.185	0.0004	0.001	0.0004	0.001
<i>p</i>-Xylene	99.364	0.0026	0.010	0.0027	0.011
<i>m</i>-Xylene	0.268	0.0026	0.010	0.0033	0.013
<i>o</i>-Xylene	0.086	0.0000	0.000	0.0000	0.000
C₉+ Aromatics	0.053	0.0015	0.006	0.0015	0.006

Reproducibility

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