



A Honeywell Company

Trace Non-Aromatic Hydrocarbons in High-Purity Aromatics by GC

UOP Method 543-11

Scope

This method is primarily for determining total non-aromatic hydrocarbons below the 1 mass-% level in individual or mixed aromatic hydrocarbon samples. For the purpose of this method, total non-aromatics are defined as the composite of those components eluting before benzene. The applicability is limited to samples containing compounds having a maximum of 11 carbon atoms. The method may also be used to determine mass-ppm concentrations of benzene in specific sample types containing predominantly C₇ and higher boiling aromatics, or benzene and toluene in specific sample types containing predominantly C₈ and/or higher boiling aromatics. The lower limit of quantitation for any single component is 1 mg/kg (mass-ppm).

References

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

ASTM D4307, "Preparation of Liquid Blends for Use as Analytical Standards," 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 (GC) that is equipped with a fused silica capillary column internally coated with 1,2,3-tris(2-cyanoethoxy)propane (TCEP), 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.

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

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Chromatographic column, 60 m of 0.25-mm ID fused silica capillary, internally coated to a film thickness of 0.4- μ m with TCEP, Restek Cat. No. 10999

Freezer, explosion-proof, -23 to -5°C, Lab-Line Model 3552, VWR Scientific, Cat. No. 55700-158

Gas chromatograph, capable of temperature ramping, equipped with electronic pressure control, 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 of *n*-undecane 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 the use of a capillary column can be accurately measured. Agilent Technologies, ChemStation.

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 1.0- 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, zero-gas, total hydrocarbons less than 2 ppm as methane, local supply

Benzene, 99.9% purity, Sigma-Aldrich, Cat. No. 270709. CAUTION: Benzene is a known carcinogen. All operations involving its use must be performed in a properly ventilated area, while wearing appropriate personal protective equipment.

n-Dodecane, 99+% purity, Sigma-Aldrich, Cat. No. 297879

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

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

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, 99.5% purity, Sigma-Aldrich, Cat. No. 244511

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

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

p-Xylene, 99+% purity, Sigma-Aldrich, Cat. No. 317195

Preparation of Apparatus

The analyst is expected to be familiar with general laboratory practices, the technique of gas chromatography, and the equipment being used.

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 column in the gas chromatograph according to the column and gas chromatograph manufacturers' instructions.
 - CAUTION: Hydrogen gas leakage into the confined volume of the column oven can cause violent explosion. It is, therefore, 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 Chromatograms (Figures 1-2).

Table 1
Recommended Operating Conditions

Carrier gas	hydrogen
Head pressure	138 kPa gauge (20 psig)
Linear velocity @ 120°C	40 cm/sec
Equivalent flow @ 120°C	1.6 mL/min
Split flow	50 mL/min
Injection port temperature	175°C
Column temperature program	
Initial temperature	120°C (isothermal)
Detector	flame ionization
Detector temperature	200°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	1.0 µL, repeatable

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

4. Program the column oven to 130°C and maintain this temperature until a stable baseline has been obtained at the required sensitivity.
5. Cool the column oven to a stabilized 120°C.
6. Prepare a resolution test mixture containing approximately 1 mass-% each of *n*-undecane and *n*-dodecane in benzene.

- This qualitative mixture is analyzed to determine whether column separation is satisfactory. Since TCEP is not a bonded stationary phase, deterioration is expected to occur relatively sooner than for bonded phases. Therefore, column resolution should be checked on a weekly basis when samples are being analyzed. The lifetime of the column can be extended by keeping the column at 50 °C when not in use.
7. Analyze the resolution test mixture as described in *Procedure*.
 8. Determine if the column has adequate resolution for this analysis by comparing the resolution test mixture chromatogram with Figure 3.
 - Replace the column if the valley between the n-dodecane peak and the benzene peak exceeds 20% of the height of the n-dodecane peak.

Calibration

It is difficult to obtain light aromatic compounds for the preparation of a calibration blend that are free of non-aromatic impurities. For this reason, the calibration blend is prepared in p-xylene, which can be further purified by crystallization.

Purification Procedure for p-Xylene

To prepare approximately 100 mL of high purity p-xylene to be used in calibration blends, proceed 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 one-half to three-quarters 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 non-aromatics, benzene, or toluene are detected as indicated by the gas chromatographic analysis (refer to *Procedure*).

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 mass-% each of n-undecane, benzene and toluene in purified p-xylene. Thoroughly mix the solution by shaking. Record all weights to the nearest 0.0001 g.
 - 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 mass-% of the stock solution in p-xylene. 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-undecane, benzene and toluene in the calibration blend to the nearest mg/kg using Equation 1. Using the above dilutions, the resulting calibration blend should contain approximately 100 mg/kg of each added component.

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

where:

- A** = mass of n-undecane, benzene or toluene 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
- M** = concentration of n-undecane, benzene, or toluene 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 for each measured component 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-undecane, benzene, and toluene, to three significant figures, using Equation 2.

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

where:

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

Procedure

1. Fill an autosampler vial with an aliquot of the resolution test mixture, calibration blend, or sample and place in the autosampler (or autoinjector) tray.
2. Inject a repeatable volume, nominally 1.0 μ L, of the resolution test mixture into the gas chromatograph and start the data system.
 - 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.
3. Identify the components in the resultant chromatogram and determine the areas of the impurity peaks.
 - Typical chromatograms are shown in Figures 1-2.
 - Total non-aromatics are defined as all components eluting before benzene. Sum the peak areas for all such components for use in Equation 3, Calculations.
4. Obtain the density, at 25°C, of the sample(s) using ASTM Method D4052, or if it is a pure compound, from Table 2.

Calculations

Calculate the total non-aromatics, benzene or toluene concentrations using Equation 3. Use the n-undecane absolute response factor for calculating the sum of the total non-aromatics. Report to the nearest mg/kg, not to exceed 3 significant figures.

$$\text{Total non-aromatics, benzene, or toluene in the sample, mg/kg} = \frac{\text{ERG}}{\text{F}} \quad (3)$$

where:

E = peak area of non-aromatics, benzene or toluene in the sample, units consistent with **P** in Equation 2

F = density of the sample (from ASTM D4052, "Density, Relative Density, and API Gravity of Liquids by Digital Density Meter," or Table 2^b), g/mL

G = density of p-xylene (from ASTM D4052 or Table 2^b), g/mL

R = absolute response factor for n-undecane, benzene or toluene, from Equation 2

^bIf the sample is essentially a pure compound, e.g., benzene, Table 2 may be used. If the sample is a mixture of aromatics, determine the density of the sample using ASTM D4052, and for consistency, also determine the density of the p-xylene calibration blend using ASTM D4052.

Table 2	
<u>Density @ 25°C, g/mL</u>	
Benzene	0.874
Toluene	0.862
p-Xylene	0.857

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 three samples of benzene and one sample of xylene by two analysts, with each analyst performing analyses on two separate days, performing three analyses each day for a total of 48 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.

Table 3
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 in benzene	1.6	0.03	0.1	0.06	0.4
Non-aromatics in benzene	11.1	0.06	0.2	0.28	1.7
Non-aromatics in xylene	19.6	0.13	0.4	0.36	2.2
Non-aromatics in benzene	47.2	0.16	0.5	1.31	8.0
Benzene in xylene	5.4	0.04	0.1	0.09	0.6
Toluene in xylene	2.8	0.03	0.1	0.03	0.1

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 and labor requirement for one analysis are the same, 0.5 hour. This does not include the p-xylene purification procedure.

Suggested Suppliers

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

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

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

Sigma-Aldrich, 1000 West Saint Paul Avenue, 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 Parkway, West Chester, PA 19380, YSA (610-431-1700)
www.vwr.com

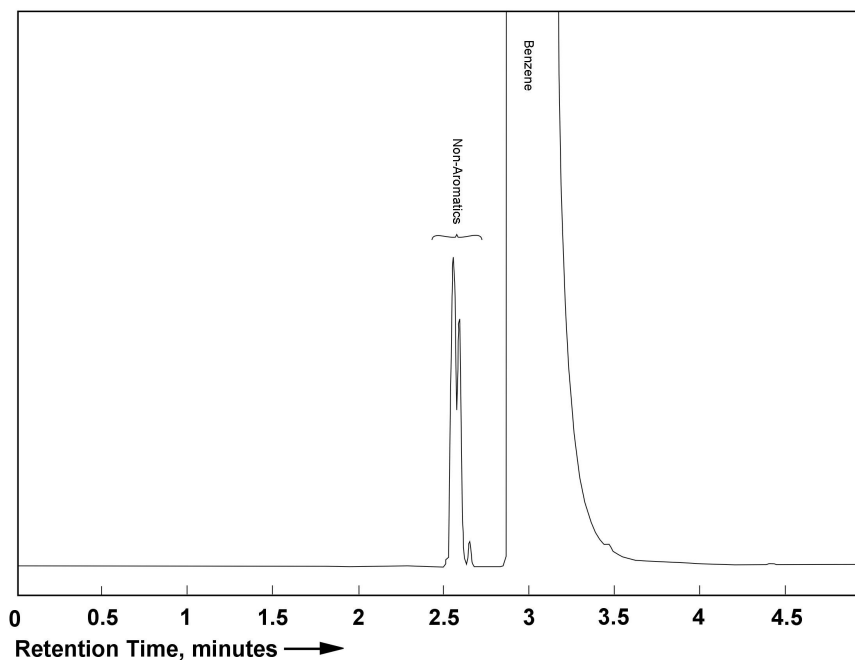


Figure 1
Typical Chromatogram
47 mass-ppm Non-Aromatics in Benzene

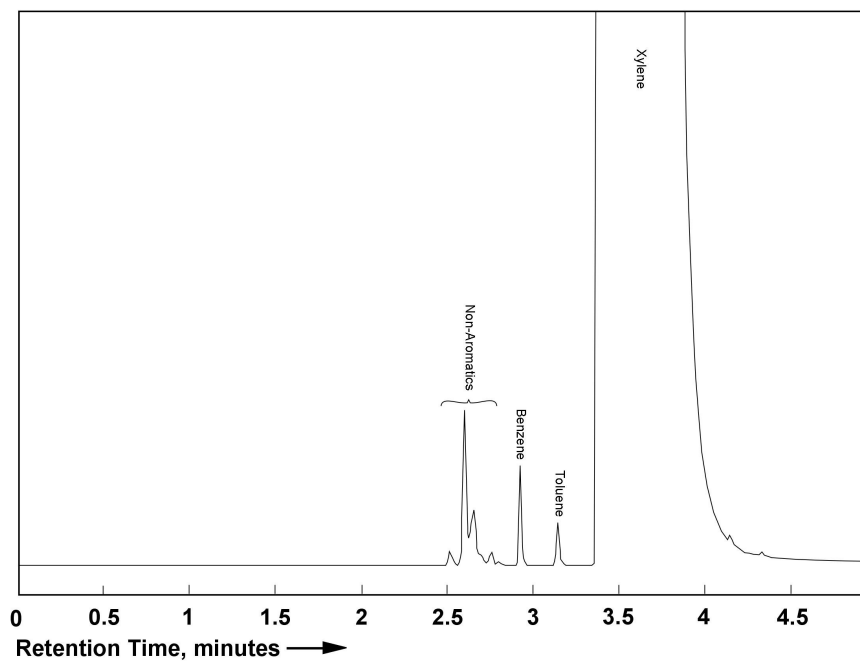


Figure 2

Typical Chromatogram

19 mass-ppm Non-Aromatics, 5 mass-ppm Benzene and 3 mass-ppm Toluene in Xylene

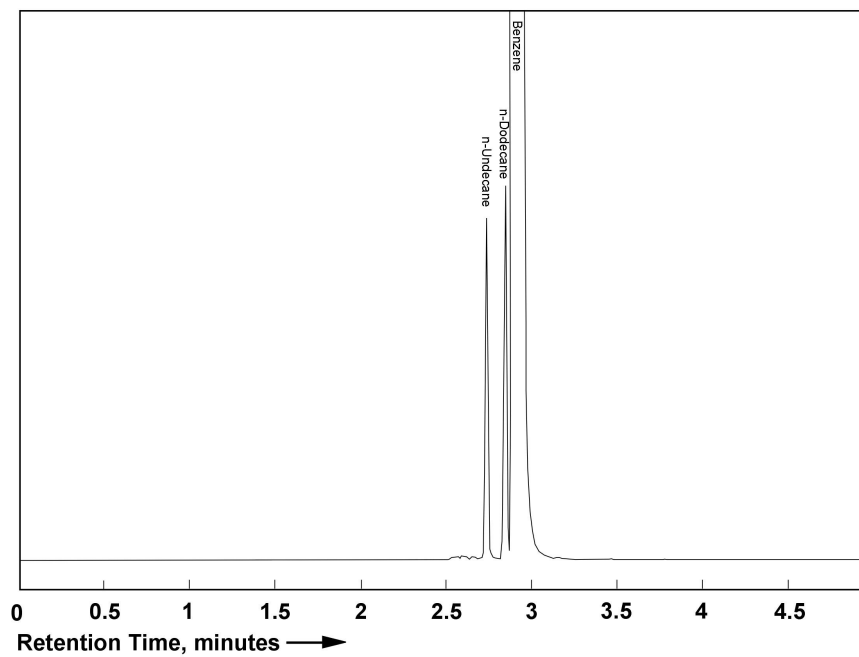


Figure 3

Typical Chromatogram
Resolution Test Mixture