

TRACE IMPURITIES IN MIXED XYLENES BY GAS CHROMATOGRAPHY

UOP Method 931-94

SCOPE

This method is for determining trace impurities in high-purity mixed xylenes by gas chromatography. 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 range of detection for any single component is 5 to 500 mass-ppm. Impurities at concentrations above 500 mass-ppm should be determined by UOP Method 744.

OUTLINE OF METHOD

The sample is injected into a gas chromatograph that is equipped with a fused silica capillary column, internally coated with Carbowax 20M, and a flame ionization detector. The mass-ppm 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

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 0.5 μ m with cross-linked Carbowax 20M, Supelco, Cat. No. 204085M

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 5 mass-ppm benzene when operated at the recommended conditions

Gas treatment system, Tri-Cycle Module RTC-2, R&D Separations

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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UOP Methods are available through ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken PA 19428-2959, United States. The 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.

Integrator, electronic, for obtaining peak areas. This device must integrate areas at a sufficiently fast rate so that narrow peaks typically resulting from a capillary column can be accurately measured.

Pipet, Pasteur, disposable, 146-mm, Fisher Scientific, Cat. No. 13-678-20A

Pipet bulb, 1-mL, Fisher Scientific, Cat. No. 13-678-9A

Recorder, 1-mV full scale, 1-sec or less full-scale response

Regulator, air, two-stage, high purity, Matheson Gas Products, Model 3122-590

Regulator, hydrogen, two-stage, high purity, Matheson Gas Products, Model 3122-350, 2 required

Regulator, nitrogen, two-stage, high purity, Matheson Gas Products, Model 3122-580

Sample injector, any syringe or injector capable of introducing a 1.0- μ L volume of sample, such as a Hamilton 701-NWG syringe, Alltech Associates, Cat. No. 80307

Vial, 14.8-mL, with a screw cap, Fisher Scientific, Cat. No. 03-339-21J

REAGENTS AND MATERIALS

All reagents shall conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, when such specifications are available, unless otherwise specified.

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

Air, zero gas, total hydrocarbons less than 2.0 ppm as methane

Benzene, 99.9% minimum purity, Wiley Organics, Cat. No. 160.84

1-Ethyl-2-methylbenzene (1-methyl-2-ethylbenzene), 99% minimum purity, Wiley Organics, Cat. No. 2900.00

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

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

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

Toluene, 99.9% minimum purity, Wiley Organics, Cat. No. 3830.00

n-Undecane, 99.9% minimum purity, Wiley Organics, Cat. No. 9480.00-1

PROCEDURE

Chromatographic Technique

1. Install the gas treatment system in the supply line between the hydrogen carrier gas source and the carrier gas inlets on the gas chromatograph.
 - Column life is significantly reduced if a gas treatment system is not used.
2. Install the fused silica capillary column in the gas chromatograph.
 - **CAUTION:** Hydrogen carrier gas leakage into a confined volume of the column oven can cause a violent explosion. It is, therefore, mandatory to test for leaks each time a connection is made and periodically thereafter.
3. Establish the recommended operating conditions as given in Table 1.
 - Other conditions may be used provided they produce the required sensitivity and chromatographic separations equivalent to those shown in the Typical Chromatogram (see Figure).
4. Program the column oven to 210°C 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. 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.
7. 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.
8. Cap the vial and mix well by inverting several times.
9. Inject a 1.0- μ L volume of the sample-internal standard mixture into the gas chromatograph and start the recorder, integrator and column temperature programming sequence.
10. Identify the components of interest by comparing the chromatogram obtained to the Typical Chromatogram (see Figure). The numbered peaks are identified in Table 2. Compounds eluting after indane are grouped and reported as the composite C₁₀ plus aromatics.

Table 1

Carrier Gas	hydrogen
Carrier gas velocity at 210°C	27.1 cm/sec
Column head pressure	68 kPa gauge (10 psig)
Injection port temperature	230°C
Split flow	60 mL/min
Column temperature program	
Initial temperature	50°
Initial time	5 min
Programming rate 1	8°C/min
Intermediate temperature 1	100°C
Programming rate 2	2°C/min
Intermediate temperature 2	120°C
Programming rate 3	20°C/min
Final temperature	210°C
Final time	20 min
Detector	flame ionization
Detector temperature	240°C
Hydrogen flow rate*	30 mL/min
Air flow rate	275 mL/min
Makeup nitrogen flow rate*	30 mL/min
Chart speed	10 mm/min
Sample size	1.0 µL

*** Consult the manufacturer's instrument manual for suggested flow rates.**

Table 2

<u>Peak No.</u>	<u>Identification</u>
1	Non-aromatic region
2	Benzene
3	Toluene
4	<i>n</i> -Undecane
5	Ethylbenzene
6	<i>p</i> -Xylene
7	<i>m</i> -Xylene
8	Isopropylbenzene (Cumene)
9	<i>o</i> -Xylene
10	<i>n</i> -Propylbenzene
11	1-Methyl-4-ethylbenzene
12	1-Methyl-3-ethylbenzene
13	1,3,5-Trimethylbenzene
14	Styrene
15	1-Methyl-2-ethylbenzene
16	1,2,4-Trimethylbenzene
17	1-Methyl-2-isopropylbenzene
18	1-Methyl-3- <i>n</i> -propylbenzene
19	1,4-Diethylbenzene
20	1,3-Dimethyl-5-ethylbenzene
21	1,2-Diethylbenzene
22	1,2,3-Trimethylbenzene
23	1,4-Dimethyl-2-ethylbenzene
24	1,3-Dimethyl-4-ethylbenzene
25	1,2-Dimethyl-4-ethylbenzene
26	Indane

Calibration

Relative response factors are required to relate the peak areas for the trace impurity components to mass-%, since they do not all respond equally to a flame ionization detector.

1. Prepare a calibration blend as described in ASTM Method D 4307 to contain 2 mass-% each of benzene, toluene, 1-methyl-2-ethylbenzene and *n*-undecane (internal standard) in *n*-heptane.
 - The components are weighed to the nearest 0.1 mg.
 - Calibration should be performed when the instrument is set up and whenever operating conditions or the column is changed.
 - *n*-Heptane is substituted for mixed xylenes in the blend due to the common impurities between commercial mixed xylenes and the mixed xylenes to be analyzed by the method.
2. Analyze the calibration blend in duplicate as described in Steps 9 and 10 under *Chromatographic Technique*.

3. Average the individual impurity peak areas from the replicate runs.
 - The peak areas for each component of the two 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 further runs until the required repeatability is obtained on two consecutive runs.
4. Calculate the relative response factor for each of the impurity components to 3 decimal places using *n*-undecane (internal standard) as a reference as follows:

$$R = \frac{A B}{C D} \quad (1)$$

where:

A = concentration of the impurity in the calibration blend, mass-%
B = average peak area of the internal standard in the calibration blend
C = concentration of the internal standard in the calibration blend, mass-%
D = average peak area of the impurity in the calibration blend
R = response factor for the impurity relative to the internal standard

- The response factor for 1-methyl-2-ethylbenzene is used for all C₉ or C₁₀ aromatics. A response factor of 1.000 is used for non-aromatics.
5. Determine relative response factors each time the recommended operating conditions are established.

CALCULATIONS

Calculate the concentration of each impurity in the sample to the nearest mass-ppm using the following formula:

$$E = \frac{10^6 \text{ GHR}}{\text{ML}} \quad (2)$$

where:

E = concentration of impurity, mass-ppm
G = peak area of impurity in sample
H = mass of internal standard added to sample, g
L = peak area of internal standard in sample
M = mass of sample prior to addition of internal standard, g
R = relative response factor, previously defined, Eq. 1
10⁶ = factor to convert to mass-ppm

PRECISION

Repeatability

Based on two tests performed by each of two analysts on each of two different days (8 tests), the within-laboratory estimated standard deviations (esd) were calculated for components at specific concentrations and are listed in Table 3. Two tests performed in one laboratory by different analysts on different days should not differ by more than the allowable differences in Table 3 at the concentrations listed (95% probability).

Table 3

Component	Concentration, mass-ppm	Within-lab esd, mass-ppm	Allowable Difference, mass-ppm
Toluene	284	2.7	9
1-Methyl-4-ethylbenzene	25	0.5	2
1-Methyl-3-ethylbenzene	53	0.5	2
1-Methyl-2-ethylbenzene	12	0.5	2
1,3,5-Trimethylbenzene	29	0.4	2

Reproducibility

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

TIME FOR ANALYSIS

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

REFERENCES

ASTM D 4307, www.astm.org

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

UOP Method 744, "Aromatics in Hydrocarbons by Gas Chromatography"

SUGGESTED SUPPLIERS

Aldrich Chemical Co., Inc., 940 W. St. Paul Ave., Milwaukee, WI 53201 (414-273-3850)

Alltech Associates, 2051 Waukegan Rd., Deerfield, IL 60015 (708-948-8600)

Fisher Scientific, 711 Forbes Ave., Pittsburgh, PA 15219 (412-562-8300)

Matheson Gas Products, Inc., P.O. Box 96, Joliet, IL 60434 (815-727-4848)

R&D Separations, Inc., 11358 Sunrise Gold Circle, Rancho Cordova, CA 95742 (916-635-2763)

Supelco, Inc., Supelco Park, Bellefonte, PA 16823 (814-359-3441)

Wiley Organics, 1245 South 6th St., Coshocton, OH 43812 (614-622-0755)

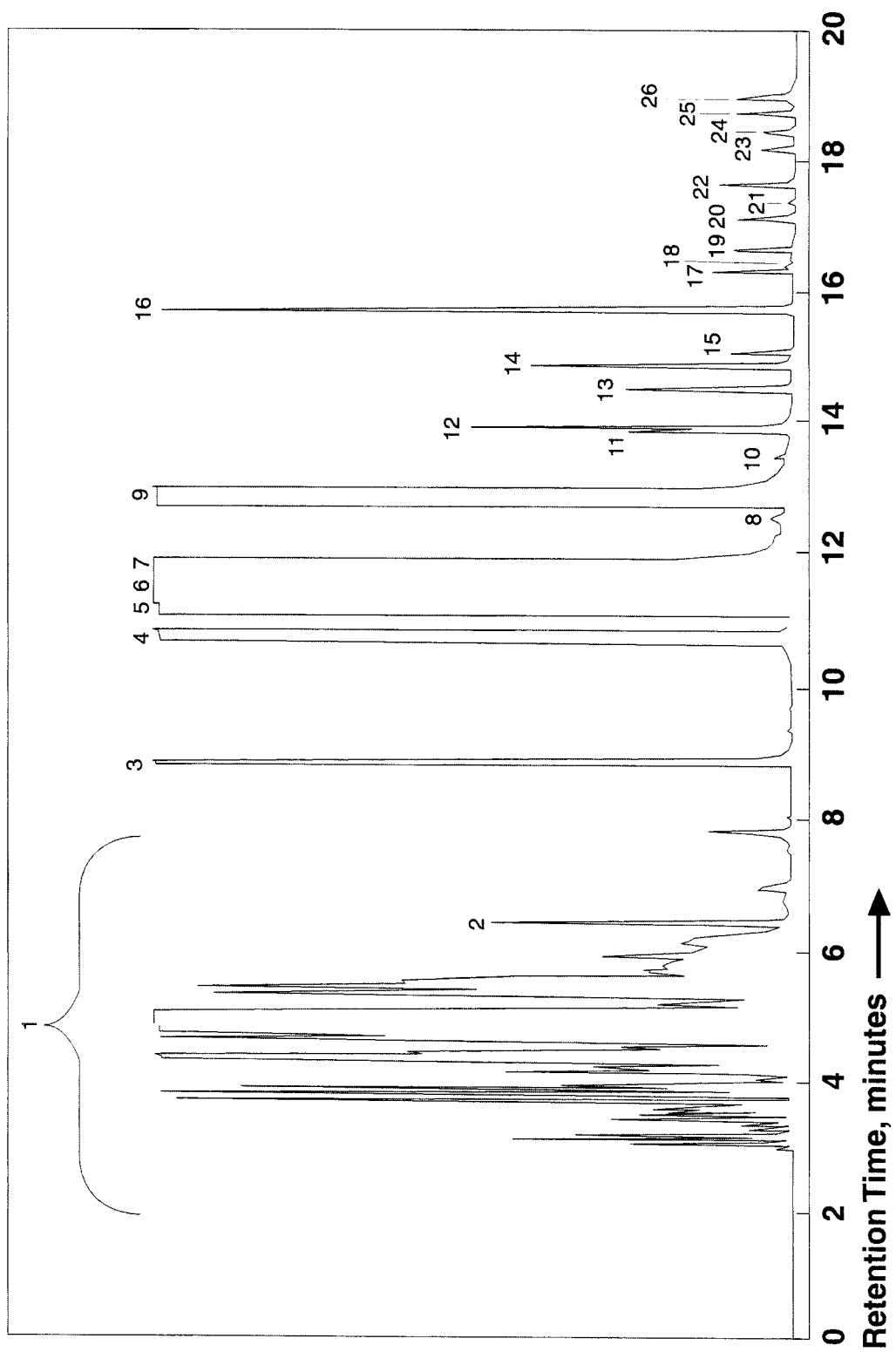


Figure
Typical Chromatogram