

IMPURITIES IN STYRENE BY GAS CHROMATOGRAPHY

UOP Method 913-92

SCOPE

This gas chromatographic method is for determining trace impurities in 99%+ purity styrene. Benzene and toluene are not separated from the non-aromatic impurities by this method but, if required, may be determined individually by UOP Method 543. Heavy non-aromatics may interfere with the determination of the C₈ aromatics and cumene. This method can also be used to calculate the total purity of styrene. The lower limit of detection for an individual impurity is 2 mass-ppm. Sample composition may change with time and, therefore, samples should be protected from air and analyzed soon after receipt.

OUTLINE OF METHOD

A sample is injected into a gas chromatograph equipped with a fused silica capillary column, internally coated with Carbowax 20M, and a flame ionization detector. The internal standard method of quantitation is used to calculate the concentration of each impurity. The styrene purity is obtained by subtracting the total impurities from 100 mass-%.

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 µm with cross-linked Carbowax 20M, Supelco, Cat. No. 2-4085M

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 3 times the background noise for 2 mass-ppm ethylbenzene when operated at the recommended conditions

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.

Oxygen remover, Oxy-Trap, Alltech Associates, Cat. No. 4001

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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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.

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 3104-590

Regulator, hydrogen, two-stage, high purity, Matheson Gas Products, Model 3104-350

Regulator, nitrogen, two-stage, high purity, Matheson Gas Products, Model 3104-580

Sample injector, any syringe or injector capable of introducing a 0.5- μ L volume of sample, such as a Hamilton 701-NWG syringe, Alltech Associates, Cat. No. 80307

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

REAGENTS AND MATERIALS

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

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

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

Cumene, 99% minimum purity, Aldrich Chemical, Cat. No. 18,579-5

Ethylbenzene, 99.9% minimum purity, Wiley Organics, Cat. No. 2379.03

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

n-Pentadecane, 99% minimum purity, Aldrich Chemical, Cat. No. P340-6

PROCEDURE

Chromatographic Technique

1. Install the oxygen remover in the supply line between the carrier gas source and the carrier gas inlets on the gas chromatograph.
 - Column life is significantly reduced if an oxygen remover 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.

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 the internal standard (*n*-pentadecane), 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 0.5- μ L volume of the sample and 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).

Table 1

Carrier gas	hydrogen
Carrier gas flow rate	2.4 mL/min
Column head pressure	70 kPa gauge (10 psig)
Injection port temperature	230°C
Split ratio	25:1
Column temperature program	
Initial temperature	50°C
Initial time	5 min
Programming rate 1	5°C/min
Intermediate temperature	100°C
Intermediate time	10 min
Programming rate 2	2°C/min
Intermediate temperature	120°C
Intermediate time	20 min
Programming rate 3	20°C/min
Final temperature	210°C
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	0.5 cm/min
Sample size	0.5 μL

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

Calibration

Relative response factors are required to relate the peak areas for each sample component to mass-%.

1. Prepare a calibration blend of approximately 10,000 mass-ppm (1.0 mass-%) each of ethylbenzene, cumene and *n*-pentadecane in *n*-heptane as described in ASTM Method D 4307.
 - Calibration should be performed when the instrument is set up and whenever operating conditions or the column is changed.
 - *n*-Heptane is substituted for styrene in the blend due to the common impurities between commercial styrene and the styrene to be analyzed by the method.
2. Chromatograph the calibration blend in duplicate as described under Steps 9 and 10, *Chromatographic Technique*.
3. Identify the peaks and average the peak areas from the duplicate runs.
4. Calculate the average relative response factors for the components of interest to 3 decimal places by using *n*-pentadecane as a reference and the following formula:

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

where:

- A** = component concentration in the blend, mass-ppm
- B** = peak area of *n*-pentadecane
- C** = *n*-pentadecane concentration in the blend, mass-ppm
- D** = peak area of component
- F** = relative response factor for component

5. Use the ethylbenzene relative response factor for all the C₈ aromatic components. Use the relative response factor for cumene for unidentified components. Use the *n*-pentadecane response factor for the non-aromatics-benzene-toluene group.

CALCULATIONS

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

$$\text{Component, mass-ppm} = \frac{10^6 EGF}{HS} \quad (2)$$

where:

- E** = peak area of component
- F** = previously defined, Eq. 1
- G** = mass of *n*-pentadecane added to sample, g
- H** = peak area of *n*-pentadecane
- S** = mass of sample before addition of *n*-pentadecane, g
- 10⁶** = factor to convert to mass-ppm

Calculate the mass-% purity of the styrene to two decimal places using the following formula:

$$\text{Styrene, mass-\%} = 100 - \left(\frac{\sum P_i}{10^4} \right) \quad (3)$$

where:

P_i = mass-ppm of component impurity i

10^4 = factor to convert to mass-%

100 = mass-%

PRECISION

Repeatability

Based on two tests performed by each of two analysts, on each of two days (8 tests) in one laboratory, the within-laboratory estimated standard deviations (esd) were calculated for the impurities listed in Table 2 and for styrene purity, Table 3. Two tests performed in one laboratory by different analysts on different days should not differ by more than the allowable difference values listed in Tables 2 and 3 at the concentrations listed (95% probability).

Table 2

Impurity	Concentration, mass-ppm	Within Lab esd, mass-ppm	Allowable Difference, mass-ppm
Non-aromatics	482	29.4	98
1,3-Diethylbenzene	6	0.5	2
1,2-Diethylbenzene + α -Methylstyrene	175	7.7	30
Phenylacetylene	8	0.5	2

Table 3

Component	Concentration, mass-%	Within-Lab esd, mass-%	Allowable Difference, mass-%
Styrene	99.91	0.005	0.02

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.

REFERENCES

UOP Method 543, "Non-Aromatic Hydrocarbons in High Purity Aromatics by Gas Chromatography"
ASTM Method D 4307, www.astm.org

SUGGESTED SUPPLIERS

Aldrich Chemical Co., Inc., P.O. Box 355, Milwaukee, WI 53201 (414-273-3850)
Alltech Associates, Inc., 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)
Supelco, Inc., Supelco Park, Bellefonte, PA 16823-0048 (814-359-3441)
Wiley Organics, 1245 S. Sixth St., Coshocton, OH 43812 (614-622-0755)

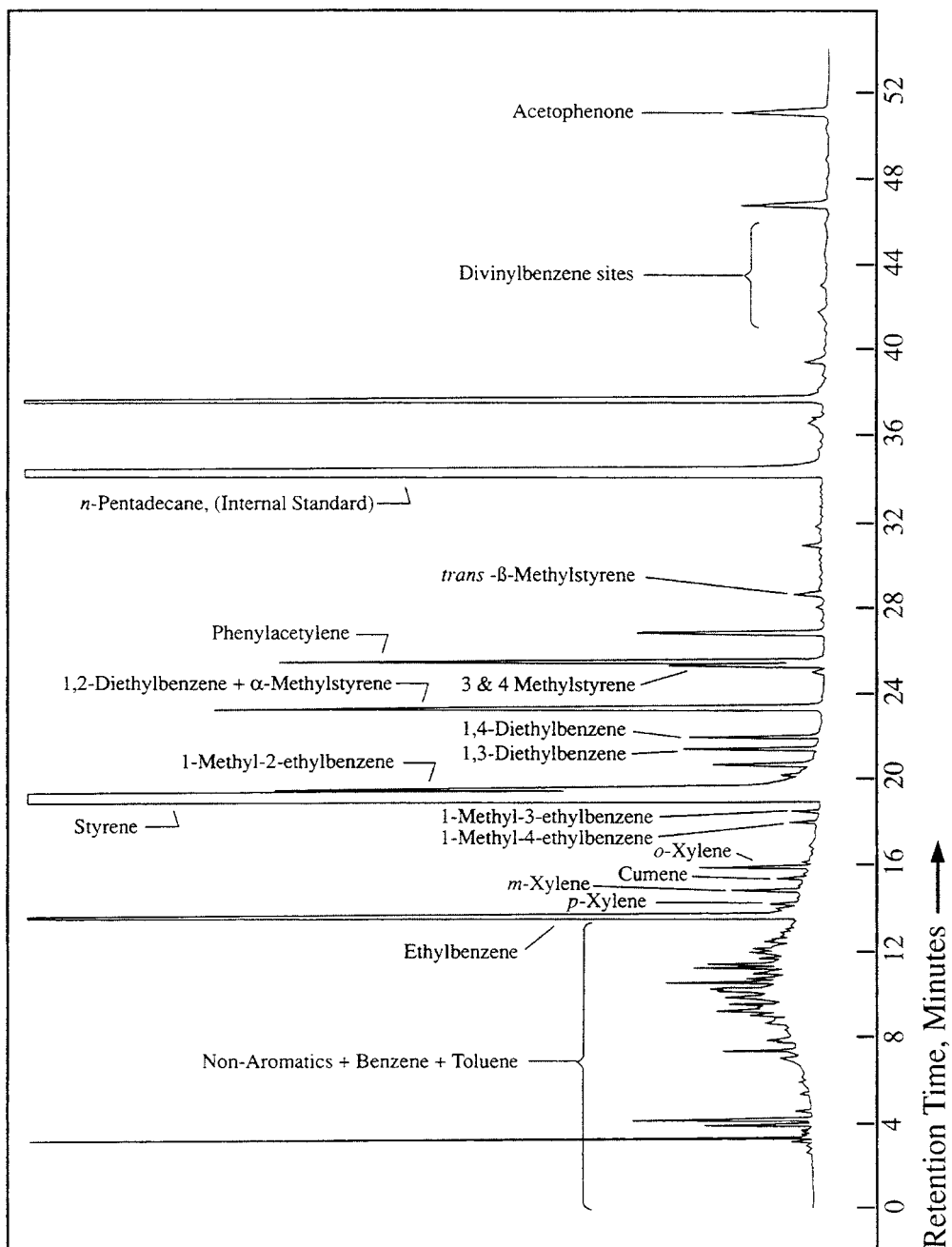


Figure
Typical Chromatogram