



Test Method for Benzene, Toluene, Xylene, (BTX) Concentrates Analysis by Capillary Column Gas Chromatography¹

This standard is issued under the fixed designation D 6563; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method covers the determination of the total nonaromatic hydrocarbons, benzene, toluene, ethylbenzene, xylenes, and C₉ + aromatic hydrocarbons in BTX concentrates by capillary column gas chromatography. This test method is applicable to materials with a final boiling point below 215°C.

1.2 Individual components can be determined from 0.01 to 90 %.

1.3 The following applies to all specified limits in this standard: for purpose of determining conformance with this standard, an observed value or a calculated value shall be rounded off “to the nearest unit” in the right-hand digit used in expressing the specification limit, in accordance with the rounding-off method of Practice E 29.

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* For a specific precautionary statement, see Section 9.

2. Referenced Documents

2.1 ASTM Standards:

D 3437 Practice for sampling and Handling Liquid Cyclic Products²

E 29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications³

E 355 Practice for Gas Chromatography Terms and Relationships³

E 691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method³

E 1510 Practice for Installing Fused Silica Open Tubular Capillary Columns in Gas Chromatographs³

2.2 Other Documents:

OSHA Regulations, 29 CFR, paragraphs 1910.1000 and 1910.1200⁴

3. Terminology

3.1 Definitions of Terms Specific to This Standard:

3.1.1 *extracted reformat*—An aromatic concentrate obtained by solvent extraction of reformat.

3.1.2 *reformat*—The product of a catalytic process that increases the concentration of aromatic hydrocarbons.

3.1.3 *pyrolysis gasoline*—Depentanized by-product recovered from ethylene manufacture.

3.1.4 *synthetic blend*—Blend of reagent hydrocarbons that simulate a process product.

3.1.5 *hydrogenated pyrolysis gasoline*—Pyrolysis gasoline that has been treated with hydrogen to reduce the olefins content.

3.1.6 *crude ethylbenzene*—Product produced from the reaction of impure fluid cat cracking, (FCC) ethylene and benzene.

3.1.6.1 *Discussion*—It typically contains greater than 40 % of ethylbenzene and benzene.

3.1.7 *light blending aromatics feedstock*—Light aromatics fraction (with high amounts of benzene and toluene) typically recovered from the isomerization of a *p*-xylene or *m*-xylene depleted C₈ aromatics stream.

4. Summary of Test Method

4.1 The specimen to be analyzed is injected into a gas chromatograph equipped with a flame ionization detector (FID) and a capillary column. The peak area of each component is measured and adjusted using effective carbon number (ECN) response factors. The concentration of each component is calculated based on its relative percentages of total adjusted peak area and normalized to 100.00. Results can be reported as either volume or weight percent.

4.2 Volumetric results can be derived by dividing each component’s weight percent by its relative density and re-normalizing to 100 %.

5. Significance and Use

5.1 This test method was primarily developed to determine

¹ This test method is under the jurisdiction of ASTM Committee D16 on Aromatic Hydrocarbons and Related Chemicals and is the direct responsibility of Subcommittee D16.01 on Benzene, Toluene, Xylenes, Cyclohexane, and Their Derivatives.

Current edition approved June 10, 2000. Published August 2000.

² *Annual Book of ASTM Standards*, Vol 06.04.

³ *Annual Book of ASTM Standards*, Vol 14.02.

⁴ Available from the Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20402.

benzene, toluene, and xylenes in chemical intermediate and solvent streams such as reformat, BTX extracts, pyrolysis gasoline, hydrogenated pyrolysis gasoline, crude benzene, crude ethylbenzene, commercial toluene, and light blending aromatic feedstocks. This test method may not detect all components and there may be unknown components that would be assigned inappropriate response factors and thus, the results may not be absolute.

6. Interferences

6.1 Nonaromatic hydrocarbons may interfere with the determination of benzene and toluene when certain columns are used.

6.2 Styrene may be present in some samples. It will elute with C₉+ aromatics.

7. Apparatus

7.1 *Gas Chromatograph*—Any gas chromatograph having a flame ionization detector and a splitter injector suitable for use with a fused silica capillary column may be used, provided the system has sufficient sensitivity to obtain a minimum peak height response of 0.1 mV for 0.01 % of any component of interest in the sample being analyzed or in the system blend when operated at the stated conditions. Background noise should not exceed 0.01 mV. Largest component of interest should not exceed 90 % full scale of the electronic integration device.

7.2 *Column*—Capillary columns have found to be satisfactory. For example, a 60 m by 0.25 mm inside diameter fused silica capillary, internally coated to a 0.25- μ m thickness with a bonded (cross-linked) polyethylene glycol can be used (see Table 1 for parameters). Other columns may be used after it has been established that such a column is capable of separating all major impurities under operating conditions appropriate for the column.

7.3 *Recorder/Electronic Integration*—Electronic integration with tangent capabilities is recommended.

8. Reagents

8.1 *Carrier Gas*—Helium with a minimum purity of 99.99 mol %.

TABLE 1 Instrument Parameters

Column	Size of 60 m by 0.25 mm ID μ m-bonded polyethylene glycol-fused silica capillary, internally coated to a 0.25- μ m thickness
Carrier gas	helium
Flow, linear velocity at 70°C, cm/s	20
Split ratio	200:1
Detector gas	
Hydrogen flow rate, mL/min	30
Air flow rate, mL/min	300
Make-up flow rate, mL/min	30
Sample size, μ L	0.5
Temperatures	
Injector, °C	250
Detector, °C	300
Column	
Initial, °C	70
Hold, min	10
Rate, °C/min	5
Final, °C	200
Hold, min	24

8.2 *Detector Gas*—Hydrogen with a minimum purity of 99.99 mol %.

8.3 *Flame Support Gas*—Air, hydrocarbon free, with a minimum purity of 99.99 mol %.

9. Hazards

9.1 Consult current OSHA regulations, supplier's Material Safety Data Sheets, and local regulations for all material used in this test method.

10. Sampling

10.1 Sample material in accordance with Practice D 3437.

11. Preparation of Apparatus

11.1 *Chromatograph*—Follow manufacturer's instructions for mounting and conditioning the column in the chromatograph and adjusting the instrument to the conditions as described in Table 1 to give the desired separation. Allow sufficient time for the instrument to reach equilibrium as indicated by a stable recorder/electronic baseline. See Practices E 355 and E 1510 for additional information on gas chromatography practices and terminology.

12. Procedure

12.1 Bring the sample to ambient room temperature.

12.2 Inject an appropriate amount of sample into the chromatograph that meets the criteria outlined in 7.1. See Practices E 355 and E 1510 for additional information on gas chromatography practices and terminology.

12.3 Sample chromatograms are illustrated in Figs. 1-3.

12.4 Measure the area of all peaks. The nonaromatics fraction includes all peaks up to ethylbenzene (except for the peaks assigned to benzene and toluene). Sum together all the nonaromatic peaks as a total area. The C₉+ aromatics fraction includes cumene and all peaks eluting after *o*-xylene. Sum together all the C₉+ aromatic peaks as a total area.

13. Calculation

13.1 Calculate the weight percent concentration of each component as follows:

$$C_i = \frac{A_i \times ECN_i}{\sum_{i=1}^n (A_i \times ECN_i)} \quad (1)$$

where:

C_i = concentration of component in weight percent,

A_i = area of component, *i* peak,

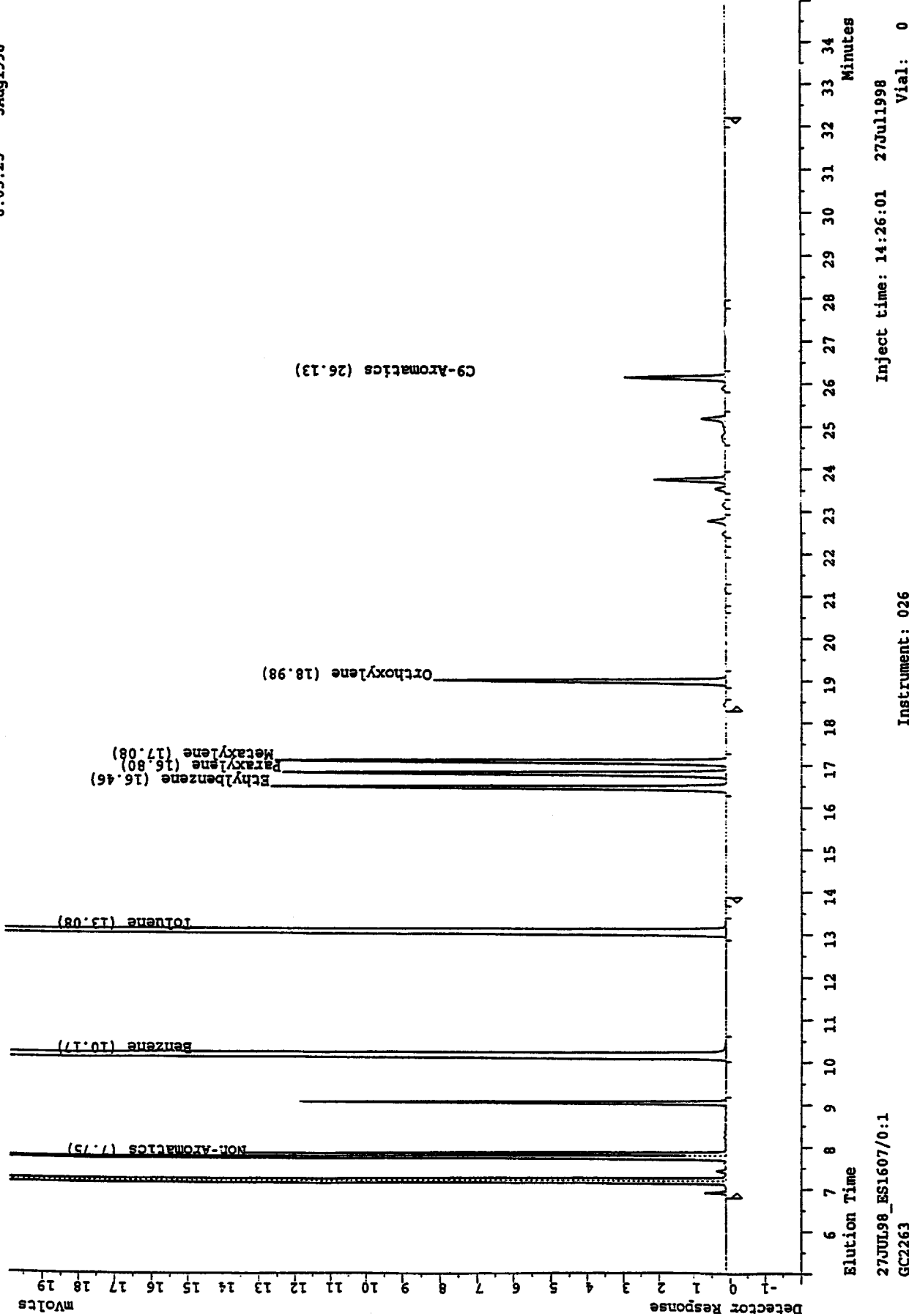
ECN_i = effective carbon response factor for component, and

$\sum_{i=1}^n (A_i \times ECN_i)$ = the summation of all response corrected areas in the chromatogram.

13.2 Calculate the volume percent concentration of each component as follows:

$$V = \frac{100 C/D}{\sum(C/D)} \quad (2)$$

8:05:25 3Aug1998



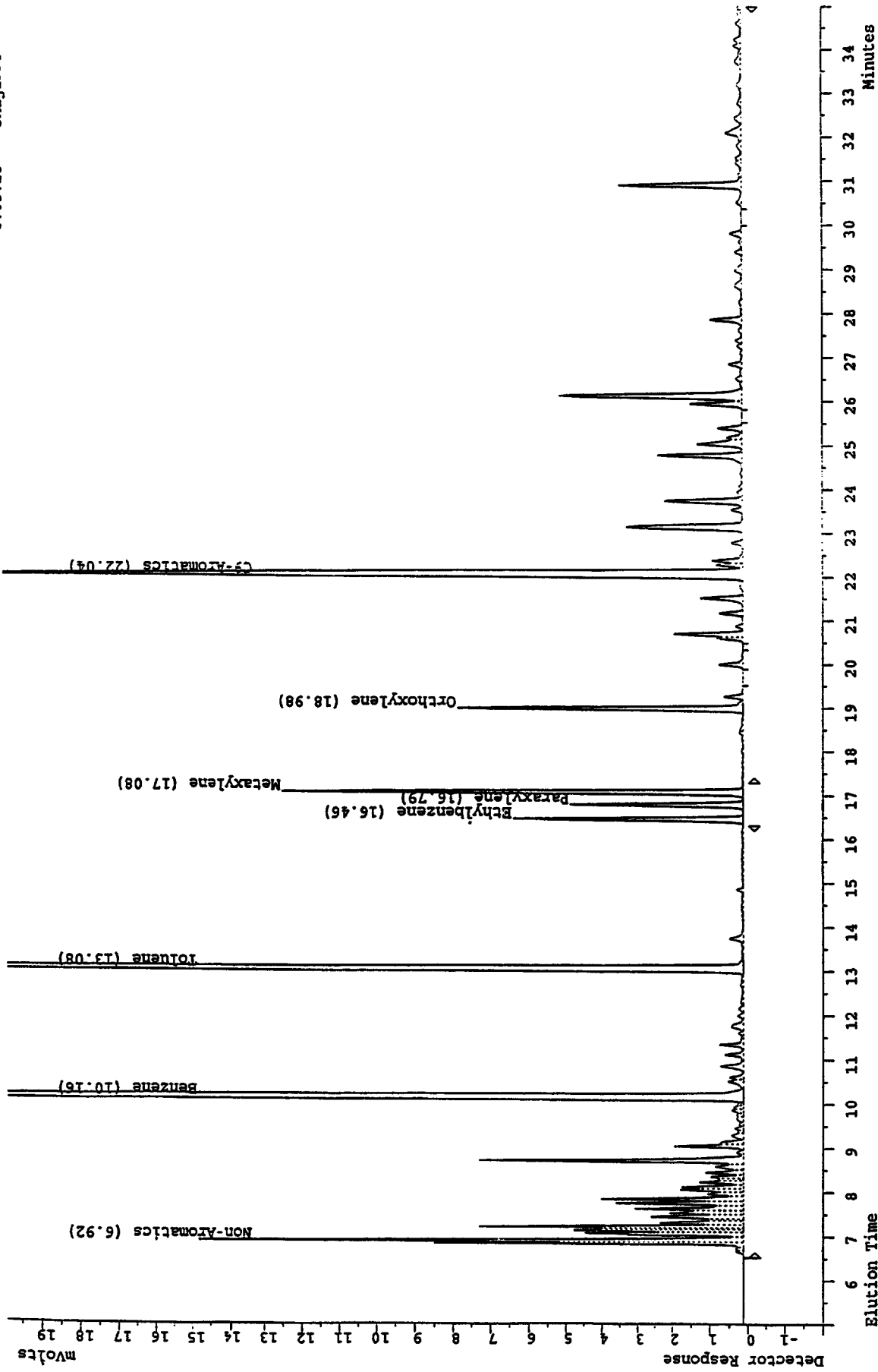
27JUL98_ES1607/0:1
GC2263

Inject time: 14:26:01 27Jul1998

Instrument: 026
FIG. 1 Synthetic Blend

Vial: 0

8:05:28 3Aug1998

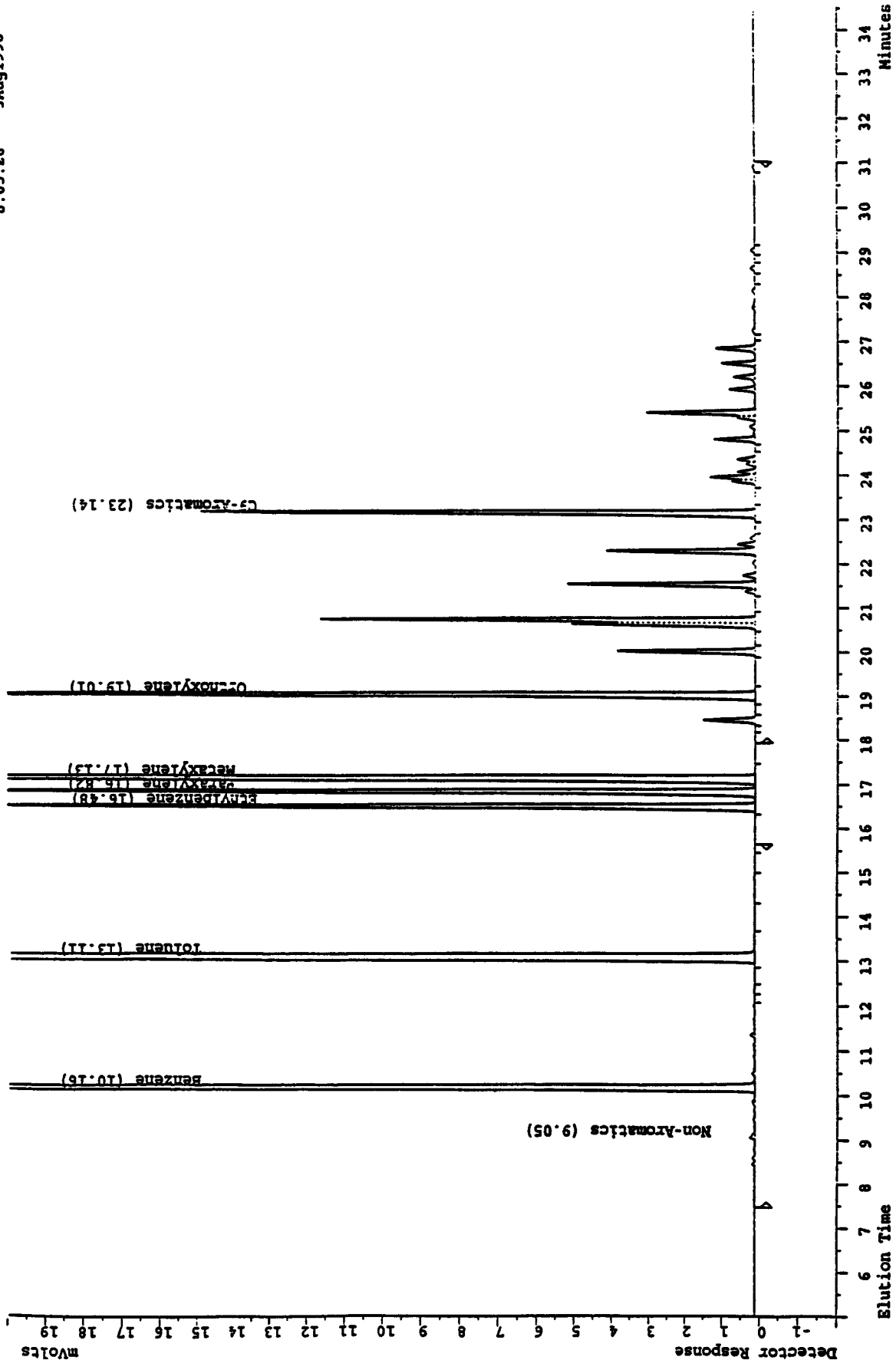


27JUL98_ES1609/0:1
GC2263

Inject time: 16:45:35 27Jul1998
Vial: 0

Instrument: 026
FIG. 2 Pyrolysis Gasoline

8:05:26 3Aug1998



27JUL98_ES1608/0:1
GC2263

Instrument: 026
FIG. 3 Extracted Reformate

Inject time: 15:35:51 27Jul1998
Vial: 0

where:

V = calculated vol % concentration of component,
 C = calculated wt % concentration of component
 from 12.1,

D = relative density of component, and

$\Sigma(C/D)$ = sum of the quotients C/D .

13.3 Use the following effective carbon number (ECN) response factors for the calculations:

Component	ECN Response Factor ^{A,B}	Relative Density ^C at 60°F
Non Aromatics	1.0000	0.7200 (average)
Benzene	0.9100	0.8829
Toluene	0.9200	0.8743
Ethylbenzene	0.9275	0.8744
<i>p</i> -Xylene	0.9275	0.8666
<i>m</i> -Xylene	0.9275	0.8694
<i>o</i> -Xylene	0.9275	0.8849
C ₉ + aromatics	0.9333	0.8752 (average)

^AScanlon, J., T., and Willis, D., E., "Calculation of Flame Ionization Detector Relative Response Factors Using the Effective Carbon Number Concept" *Journal of Chromatographic Science*, Vol 35, August, 1985, pp. 333-339.

^BResponse Factors are relative to *n*-heptane.

^CDS # 4A *Physical Constants of Hydrocarbons C₁ through C₁₀*, ASTM, 1971.

14. Report

14.1 Report the following information:

14.1.1 All component concentrations to the nearest 0.01 wt (or vol) %.

14.1.2 For concentrations less than 0.01 wt (or vol) %, report as <0.01 wt (or vol) %.

15. Precision and Bias⁵

15.1 *Precision*—The following criteria should be used to judge the acceptability of results obtained by this test method (95 % confidence level). The precision criteria was derived from an interlaboratory study using data submitted by fourteen laboratories. Each interlaboratory study participant was provided two gravimetrically prepared BTX known samples and three unknown samples of varying concentrations. Each sample was run twice on two days by two different operators. Results of the interlaboratory study were calculated and analyzed using Practice E 691.

15.2 *Intermediate Precision, (formerly Repeatability)*—Results in the same laboratory should not be considered suspect unless they differ by more than \pm the amount shown in Table 2, Table 3, Table 4, Table 5, or Table 6. On the basis of

⁵ Supporting data are available from ASTM International Headquarters. Request RR:D16-1025.

TABLE 2 Interlaboratory Precision and Reproducibility for Synthetic Blend Sample

NOTE 1—This data was calculated after removal of outliers using Practice E 691.

Component	Concentration Weight %	Intermediate Precision	Reproducibility
Nonaromatics	22.447	0.296	1.746
Benzene	42.891	0.781	1.887
Toluene	19.961	0.212	0.715
Ethylbenzene	3.061	0.055	0.191
Total xylenes	7.921	0.195	0.512
C ₉ + aromatics	4.192	0.169	1.009

TABLE 3 Interlaboratory Precision and Reproducibility for Pyrolysis Gasoline Sample

NOTE 1—This data was calculated after removal of outliers using Practice E 691.

Component	Concentration Weight %	Intermediate Precision	Reproducibility
Nonaromatics	17.918	0.237	1.394
Benzene	36.580	0.666	1.610
Toluene	17.117	0.181	0.613
Ethylbenzene	1.519	0.027	0.095
Total xylenes	6.271	0.154	0.406
C ₉ + aromatics	20.419	0.823	4.917

TABLE 4 Interlaboratory Precision and Reproducibility for Extracted Reformate Sample

NOTE 1—This data was calculated after removal of outliers using Practice E 691.

Component	Concentration Weight %	Intermediate Precision	Reproducibility
Nonaromatics	0.264	0.003	0.021
Benzene	21.015	0.382	0.925
Toluene	34.516	0.366	1.236
Ethylbenzene	5.473	0.098	0.342
Total xylenes	24.173	0.595	1.564
C ₉ + aromatics	14.744	0.594	3.550

TABLE 5 Interlaboratory Precision and Reproducibility for Hydrogenated Pyrolysis Gasoline

NOTE 1—This data was calculated after removal of outliers using Practice E 691.

Component	Concentration Weight %	Intermediate Precision	Reproducibility
Nonaromatics	27.871	0.368	2.168
Benzene	61.111	1.112	2.689
Toluene	10.966	0.116	0.391
Ethylbenzene	trace
Total xylenes	trace
C ₉ + aromatics	trace

TABLE 6 Interlaboratory Precision and Reproducibility for Standard Sample

NOTE 1—This data was calculated after removal of outliers using Practice E 691.

Component	Concentration Weight %	Intermediate Precision	Reproducibility
Nonaromatics	4.538	0.060	0.353
Benzene	50.0655	0.911	2.203
Toluene	30.039	0.318	1.075
Ethylbenzene	5.067	0.091	0.316
Total xylenes	5.069	0.125	0.328
C ₉ + aromatics	5.308	0.214	1.278

test error alone, the difference between two results obtained in the same laboratory on the same material will be expected to exceed this value only 5 % of the time.

15.3 *Reproducibility*—Results submitted by each of two laboratories should not be considered suspect unless they differ by more than \pm the amount shown in Table 2, Table 3, Table 4, Table 5, or Table 6. On the basis of test error alone, the

difference between two results obtained in different laboratories on the same material will be expected to exceed this value only 5 % of the time.

15.4 *Bias*—Since there was no accepted reference material available at the time of the interlaboratory study, no statement on bias can be made at this time.

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16. Keywords

16.1 BTX concentrates; BTX extracts; capillary gas chromatography; commercial toluene; crude benzene; crude ethylbenzene; hydrogenated pyrolysis gas; light blending aromatic feedstock; pyrolysis gas