



**PROCEDURE FOR THE DETERMINATION OF BENZENE, TOLUENE,
ETHYLBENZENE, P/M-XYLENE, O-XYLENE, C9 AND HEAVIER AROMATICS AND
TOTAL AROMATICS IN GASOLINE BY GAS CHROMATOGRAPHY**

SOP MV-FUELS-121
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Fuels Analysis and Methods Evaluation Section
Chemical Analysis and Emissions Research Branch
Mobile Source Laboratory Division

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1 Introduction

- 1.1 This document describes an automated method of analyzing benzene, toluene, ethylbenzene, the xylenes, aromatic hydrocarbons with nine or more carbons (C9 and heavier aromatics), and total aromatics in gasoline by gas chromatography.
- 1.2 This test method requires two separate analyses in order to determine the total aromatic content of gasoline. The first analysis is used to quantitate benzene and toluene. The second analysis is used to quantitate ethylbenzene, p/m-xylene, o-xylene, and the C9 and heavier aromatics. The results of both analyses are summed to determine the total aromatic content.
- 1.3 This test method covers the following concentration ranges, in liquid volume percent, for the aromatics listed above: benzene, 0.1 to 5%; toluene, 1 to 15%; individual C8 aromatics (ethylbenzene, o-xylene, m-xylene, p-xylene), 0.5 to 10%; total C9 and heavier aromatics, 5 to 30%; and total aromatics, 10 to 80%.
- 1.4 Nonaromatic hydrocarbons having a boiling point higher than that of n-dodecane may cause interferences with the determination of C9 and heavier aromatics. There are no other known interferences.
- 1.5 This procedure is based on American Society for Testing and Materials (ASTM) D5580-02(2007).

2 Method

- 2.1 Gasoline samples are collected and brought to the laboratory where an internal standard, 2-hexanone, is added volumetrically to the samples prior to analysis.
- 2.2 A two-column gas chromatographic system equipped with a column switching valve is used. Two analyses are performed. The first analysis is used to speciate benzene and toluene. The second analysis is used to speciate the C8 aromatics and to determine the C9 and heavier aromatics.
- 2.3 For the first analysis, an autosampler injects a known volume of sample onto a packed precolumn containing a polar liquid phase (1,2,3,-tris-2-cyanoethoxypropane (TCEP). The C9 and lighter nonaromatics are vented to a second detector as they elute from the precolumn. The precolumn is backflushed immediately before the elution of benzene, and the remaining portion of the sample is directed onto a second capillary column containing a nonpolar liquid phase. Benzene, toluene, and 2-hexanone elute and are detected by a flame ionization detector (FID). Immediately after the elution of the 2-hexanone, the flow through the second nonpolar column is reversed to backflush the remainder

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of the sample (C8 and heavier aromatics plus C10 and heavier nonaromatics) from the column to the FID.

- 2.4 The analysis is repeated in order to quantitate the C8 and heavier aromatics allowing the C12 and lighter nonaromatics, benzene, and toluene to elute from the polar TCEP precolumn to vent. The precolumn is backflushed immediately prior to the elution of ethylbenzene and the remaining aromatic portion is directed into the second nonpolar column. 2-Hexanone and the C8 aromatic components elute in the order of their boiling points and are detected by an FID. Immediately after o-xylene has eluted, the flow through the WCOT column is reversed to backflush the C9 and heavier aromatics to the flame ionization detector.
- 2.5 The data system identifies the aromatic compound associated with each chromatographic peak. The FID response, proportional to the concentration of each component, is used to calculate the amount of aromatics that are present by comparison with the internal standard.

3 Instrumentation

3.1 Gas chromatograph compliant with all apparatus specifications in ASTM D5580-02(2007).

3.2 Columns

3.2.1 The polar TCEP and the nonpolar capillary columns are connected to the gas chromatograph as shown in FIG. 1 from ASTM D5580-02(2007).

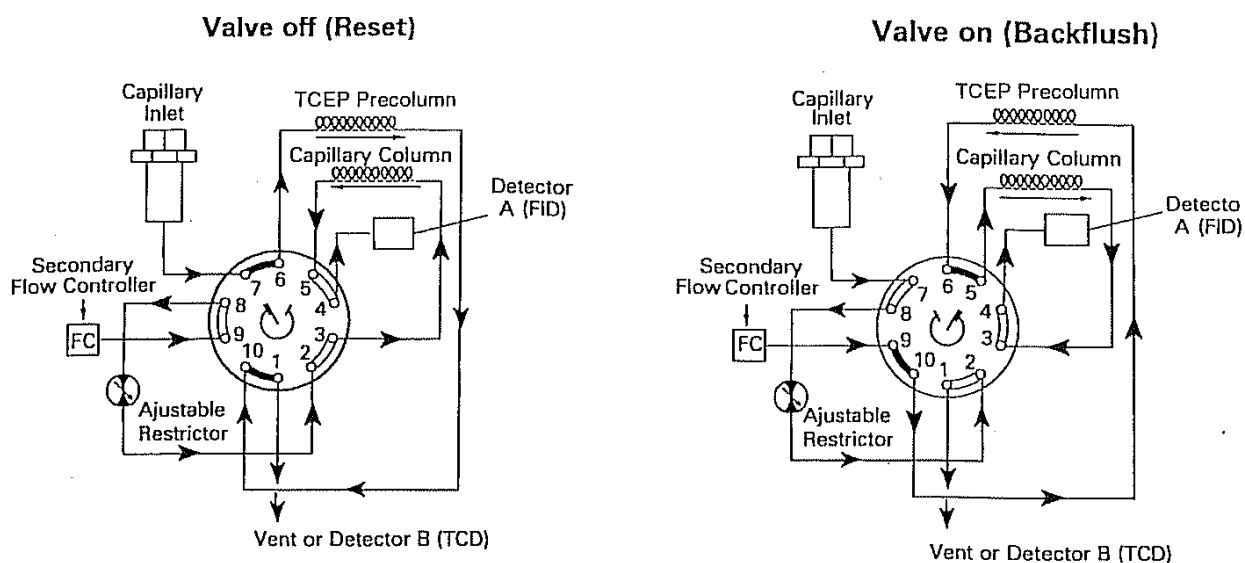


FIG. 1 Valve Diagram, Aromatics in Gasoline

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- 3.2.2 Polar precolumn: any column with chromatographic efficiency and selectivity equivalent or better than: 560 mm by 1.6 mm outside diameter by 0.38 mm inside diameter stainless steel tube packed with 0.14 to 0.15 g of 20% 1,2,3,-tris-2-cyanoethoxypropane (TCEP) on 80/100 mesh chromasorb P(AW).
- 3.2.3 Nonpolar analytical column: 30 m long by 0.53 mm inside diameter fused silica wall-coated open tubing (WCOT) column with a 5.0 micrometer film thickness of cross-linked methyl siloxane (J&W DB-1 or equivalent).
- 3.3 Liquid autosampler
- 3.4 Digital data acquisition system
- 4 Reagents
 - 4.1 Benzene, toluene, ethylbenzene, o-xylene, p/m-xylene, 1,2,4-trimethylbenzene, 2,2,4-trimethylpentane (isooctane), n-dodecane, American Chemical Society (ACS) reagent grade or equivalent
 - 4.2 2-Hexanone, 98% or higher
 - 4.3 Air, Zero grade
 - 4.4 Nitrogen, 99.998%
 - 4.5 Helium, 99.995%
 - 4.6 Hydrogen, 99.995%
 - 4.7 D5580 calibration standards
 - 4.7.1 Calibration standards set that meets the specifics required by D5580. A set contains five mixes and each includes benzene, toluene, ethylbenzene, o-xylene, and 1,2,4-trimethylbenzene at predetermined concentrations in wt%. To make a set of five-level calibration standards, each mix is prepared as follows: Tare a capped 10 mL volumetric flask on an analytical balance and then transfer an aliquot of 1.0 mL 2-Hexanone to the flask with an electronic pipettor, record the weight to the nearest 0.1 mg, tare the flask again, then break an ampule and pipette the content to the flask to the mark; weigh and record the weight to 0.1 mg. Repeat the same procedure for rest of the ampules. The weight of each compound at each level is calculated as the following:

$$wt_i (g) = (wt\%)_i \times \text{Sample wt (g)}$$

$wt_i (g)$ is divided by 100 before being entered to method calibration table since $wt\%$ is reported. Actual calculations may be done in an Excel file "D5580 Calibration Stds". Store the calibration standards in a refrigerator at 0 to 5 °C when not in use.

4.7.2 Calibration standards may be prepared as follows: Prepare multi-component calibration standards containing benzene, toluene, ethylbenzene, o-xylene, and 1,2,4-trimethylbenzene at the concentrations given below. O-Xylene is used to represent the xylenes and 1,2,4-trimethylbenzene is used for the C9 and heavier aromatics. For benzene, concentrations of 0.1, 0.5, 1.0, 2.0, and 5.0 volume % can be used. For toluene, the concentrations are 1.0, 2.5, 5.0, 10.0, and 15.0 volume %. For the other components, the concentrations are 0.5, 1.0, 2.5, 5.0, and 10.0 volume %. The samples are prepared using an analytical balance and that mass percentages are used with the data acquisition software. Prepare standards by transferring a fixed volume of aromatic component using pipettes to a 100 mL volumetric flask. Cap and record the tare weight of the flask to 0.1 mg. Remove the cap and add the aromatic components to the flask starting with the least volatile (1,2,4-trimethylbenzene), capping and weighing the flask after each addition. Do not exceed 50 volume % for all aromatics added. Similarly, add 10 mL of 2-hexanone and record its mass to the nearest 0.1 mg. Dilute each standard to the mark with isooctane. Store the calibration standards in a refrigerator at 0 to 5 °C when not in use.

5 Preparation of Instrument

5.1 The operating conditions are set to those listed in Table 1. The column temperature is set to 60 °C.

5.2 Flow Rate Adjustments

5.2.1 Attach a flow measuring device to detector B (the detector on the precolumn). With the valve in the RESET or forward flow position, adjust the pressure of the capillary injection port to give a 10.0 mL/min flow.

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- 5.2.2 Attach a flow measuring device to the split injector vent and adjust the flow controller to give a flow of 100 mL/min. Recheck the column vent flow set in 5.3.1 and adjust if necessary. The split ratio should be approximately 11:1.
- 5.2.3 Switch the valve to the BACKFLUSH position and adjust the variable restrictor to give the same precolumn vent flow set in Section 5.2.1. This is necessary to minimize flow changes when the valve is switched.
- 5.2.4 Switch the valve to the RESET position and adjust the auxiliary flow controller to give a flow of 10 mL/min at the detector A (analytical column) exit.
- 5.2.5 Set the nitrogen makeup flow to 20 mL/min, the hydrogen flow to 30 mL/min, and the air flow to 300 mL/min. These flows may be adjusted as necessary.

5.3 Valve Timing

- 5.3.1 Set the valve to RESET and injects a blend containing benzene, ethylbenzene, o-xylene, and 2-hexanone in isooctane. Alternatively, the calibration mixture described in 4.7 can be used instead. Determine the retention time at which benzene and ethylbenzene start to elute as measured by detector B. Subtract 0.05 minutes from these times and call them T1 and T2 respectively. See FIG. 2 from D5580-02(2007).

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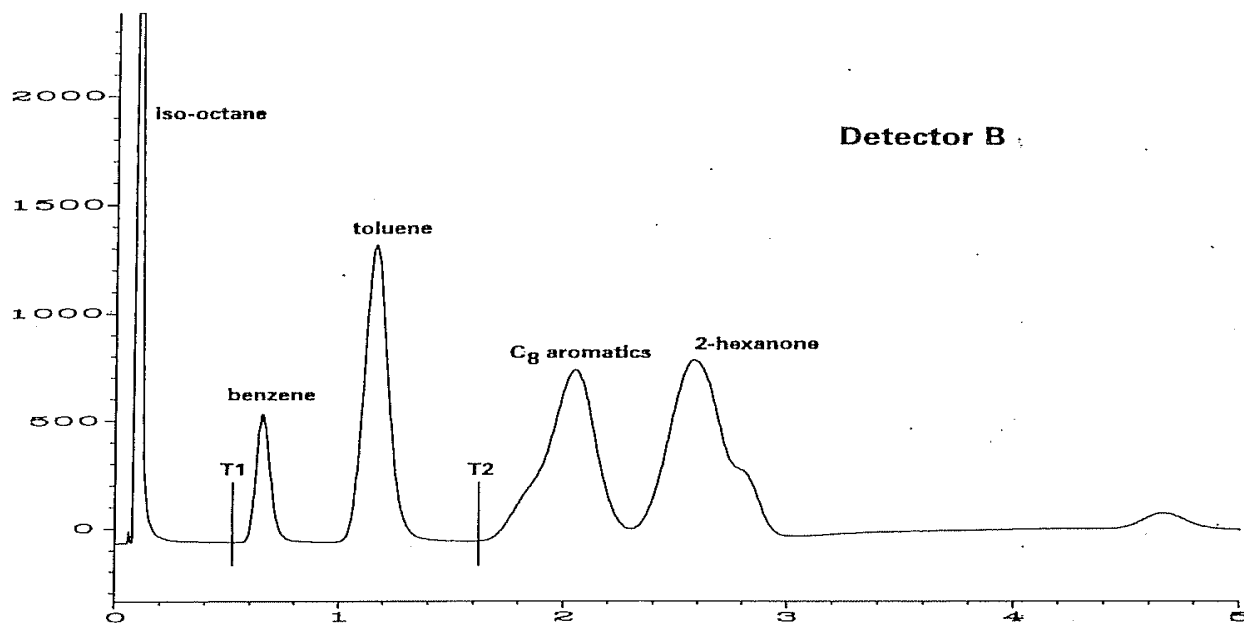


FIG. 2 Determination of Precolumn Backflush Times, T1 and T2

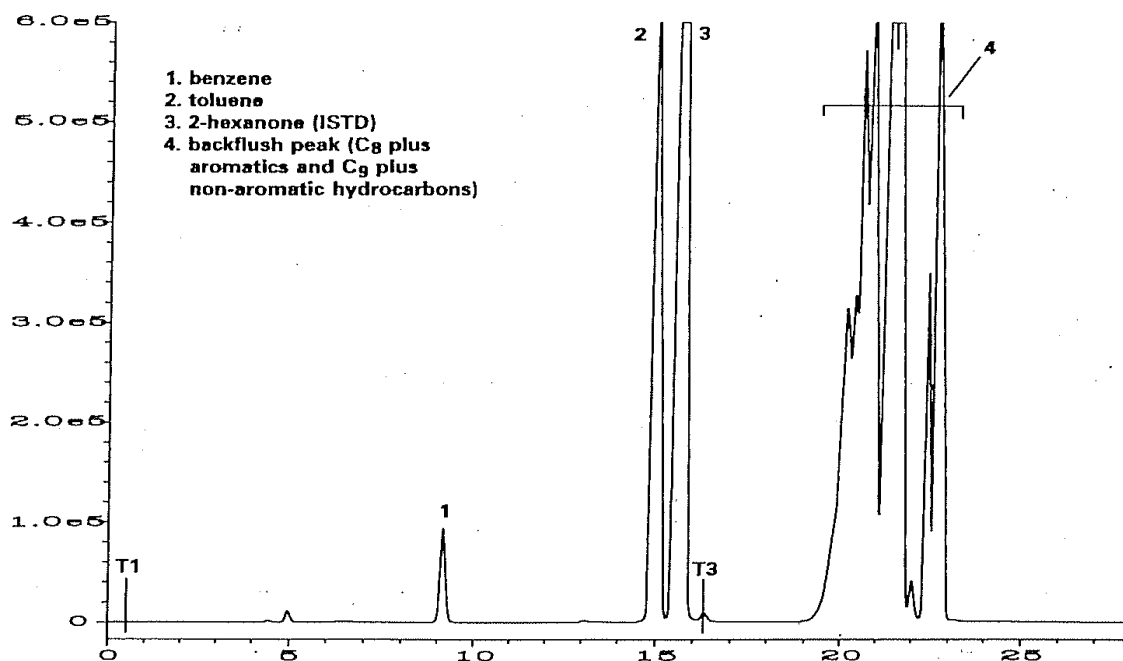


FIG. 4 Aromatics in Gasoline, Analysis No. 1

5.3.2 Re-inject the blend and turn the valve to BACKFLUSH at time T1. When the 2-hexanone peak on detector A returns to the baseline, switch the valve back to RESET. Call this time T3. See FIG. 4.

5.3.3 Re-inject the blend and turn the valve to BACKFLUSH at time T2. When the o-xylene peak on detector A returns to the baseline, switch the valve back to RESET. Call this time T4.

5.4 Polar Precolumn Sensitivity Check

5.4.1 Prepare a blend containing approximately 2% n-dodecane in isooctane. Inject 1.0 µL of the mixture under as if it were a sample and actuate the valve at time T2 (BACKFLUSH) and time T4 (RESET). Verify by that n-dodecane fully elutes from the polar precolumn (detector B) before time T2. The detector B chromatography should show that the n-dedocane peak returned to the baseline. If not, part of the n-dodecane peak will be backflushed to the nonpolar WCOT column and be detected by detector A after time T4. The quantity of n-dodecane may be estimated by method described in section 9 and the acceptable amount should be less than 0.2% of the original n-dodecane concentration.

5.4.2 If the entire n-dodecane peak is not completely vented from the polar precolumn, recheck the instrument parameters and valve backflush times or replace the polar precolumn. If the valve and precolumn are contained in a separate heated zone it may be necessary to raise the temperature of the zone.

6 Calibration

6.1 Calibration must be performed whenever significant adjustments or repairs are performed on the instrument (e.g. column replacement) or when the instrument repeatedly fails its quality control criteria (see Section 10).

6.2 With the valve initially in the RESET position, chromatograph each of the calibration mixtures twice using the valve timing procedures described above. Use times T1 and T3 for the first analysis. Use times T2 and T4 for the second analysis.

6.3 The data acquisition software with automatically generate calibration curves and calculate an r2 value. If this value is less than 0.990, the calibration must be rerun or the instrument parameters and hardware checked.

6.4 Y-intercept test: For an optimum calibration, the absolute value of the y-intercept must be at a minimum. The y-intercept for each component's calibration can be tested using the equation below:

$$t_i = (b_i / m_i)(W_s / W_g)100\%$$

where b_i is the y-intercept for the aromatic component in question from the calibration equation, m_i is the slope of the calibration line, W_s is the mass in

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grams of internal standard added, and W_g is the mass in grams of the calibration mixture. For benzene, t_i must be less than 0.02 mass %. For the other components, t_i must be less than 0.2 mass %. If any of the t_i values exceeds the limit, the calibration must be rerun.

7 Procedure

7.1 Transfer 1 mL of 2-hexanone by an electronic pipettor into a tared and capped 10 mL volumetric flask. Record the net mass of internal standard to 0.1 mg. Re-tare the flask and fill to the mark with sample. Cap the flask and record the net mass of sample added to 0.1 mg. Mix thoroughly. Transfer an appropriate amount of the mixture to a glass autosampler vial.

7.1.1 Repeat step 7.1 for each sample.

7.2 A 1.0 μ L aliquot of each sample is injected via autosampler into the gas chromatograph under the same conditions used for the calibration samples. Each sample is chromatographed twice, once using T1 and T3 and once using T2 and T4 for valve timing.

7.3 A quality control (QC) standard is analyzed at the beginning of each set of samples.

7.4 Peak identifications provided by the data system are check and corrected, if necessary. See Figures 2 and 4 for sample chromatograms.

8 Safety

8.1 All chemical compounds used in this method are flammable. Aromatic compounds are toxic and benzene is a known carcinogen. Persons using this method must use a fume hood with adequate ventilation and wear protective gloves and eyewear while working with reagents and samples.

9 Calculations

9.1 The mass of each aromatic component in the sample is determined by the following equation:

$$W_i = ((A_i / A_s) - b_i) / m_i) W_s$$

where W_i is the mass of aromatic component i , A_i is the area of the peak corresponding to aromatic component i , A_s is the area of the 2-hexanone peak, W_s is the mass of 2-hexanone added, and m_i and b_i are the slope and intercept of the calibration curve for aromatic component i determined in Section 6.3.

- 9.2 The mass % of each aromatic component is determined by the following equation:

$$w_i = 100(W_i / W_g)$$

where w_i is the mass % of aromatic component i , W_i is the mass of aromatic component i determined in Section 9.1, and W_g is the mass of the gasoline sample. Total aromatic concentration is obtained by adding the mass % values of each aromatic component.

- 9.3 The volume % of each aromatic component is determined by the following equation:

$$v_i = w_i(D_f / D_i)$$

Where v_i is the volume % of aromatic component i , w_i is the mass % of aromatic component i determined in Section 9.2, D_f is the density of the gasoline, and D_i is the density of aromatic component i as given in table 2. Total aromatic volume % is obtained by adding the v_i values for all of the aromatic components.

10 Quality Control (QC)

- 10.1 A blank sample (isooctane) is analyzed after each new calibration set. If the blank chromatogram shows a peak in the region of any of the aromatic components, the blank is repeated or the instrument hardware is checked. All aromatic concentrations must be below the limit of detection before the analysis may proceed.
- 10.2 An ASTM cross check sample may be chosen as a QC standard for it contains all the compounds needed and its analytical report has consensus values for benzene and total aromatic content that are used as the "known" value for QC purposes. D5580 QC standard is also available commercially. The control is analyzed at the beginning of each set of samples.
- 10.3 The analyses of the control standard are recorded on quality control spreadsheet for both benzene and total aromatics. A result is considered to be out of control if its difference from the known value is greater than twice the value of the repeatability (see Sections 10.2 and 10.5). In this event, corrective action must be taken prior to analyzing samples. If any major repairs are performed on the instrument, it must be recalibrated.

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10.4 At least once per quarter, an appropriate National Institute of Standards and Technology (NIST) Standard Reference Material (SRM), such as SRM 2294, SRM 2296, or SRM 2297 must be analyzed for benzene and total aromatics. The values determined must agree with those provided by NIST within twice the value of the repeatability of the method (see Section 10.6), or corrective action must be taken.

10.5 For benzene measurements, the repeatability is given by the following equation:

$$r = 0.0265(X^{0.65})$$

where r is the repeatability and X is the measured benzene concentration in mass %. For total aromatics measurements, the repeatability is 0.46 mass %.

10.6 For benzene measurements, the reproducibility is given by the following equation:

$$R = 0.1087(X^{0.64})$$

where R is the reproducibility and X is the measured benzene concentration in mass %. For total aromatics measurements, the reproducibility is calculated by the following equation:

$$R = 0.2619(X^{0.5})$$

where R is the reproducibility and X is the measured concentration of total aromatics in mass%.

10.7 Limits of detection (LODs) are determined by the intercept test as discussed in section 6.4.

Table 1 Typical Chromatographic Operating Parameters

GC Parts	Temperatures
Injection Port	200 °C
FID Detector A	250 °C
FID Detector B	250 °C
Nonpolar column (oven)	
Initial	60 °C (6 minutes hold)
Ramp Rate	2 °C/min
Final	115 °C (Hold as necessary for elution)
Polar TCEP precolumn	80 °C (if a separate zone is available)
Valve	>115 °C (if a separate zone is available)
Flows and Conditions	
Carrier gas	helium
Flow to TCEP column	10 mL/min
Flow to nonpolar column	10 mL/min
Split flow	100 mL/min
Detector gases	as needed
Split ratio	11:1
Sample size	1 L

Table 2 Densities of Aromatic Components

Component	Density at 60 °F (g/mL)
Benzene	0.8845
Toluene	0.8719
Ethylbenzene	0.8717
p/m-Xylene	0.8679
o-Xylene	0.8848
C9 and heavier aromatics	0.8764

11 References

1. ASTM D5580-02 (2007), A Standard Test Method for Determination of Benzene, Toluene, Ethylbenzene, p/m-Xylene, o-xylene, C9 and Heavier Aromatics, and Total Aromatics in Finished Gasoline by Gas Chromatography.

12 Revision History

12.1 Revision 2.2 Effective Date: January 1, 2003

12.2 Revision 2.3 Effective Date: September 1, 2013

Significant changes:

3.1 – 3.4 Instrument, autosampler and data acquisition system all updated

3.2.1 Figure1 added

4.7.1 and 4.7.2 added to align the standard operating procedure (SOP) with actual lab practice

5.3.1 Figure 4 added

10.2 and 10.3 re-written to align the SOP with actual laboratory practice

12.3 Revision 2.4 Effective Date: September 1, 2014

Significant changes:

The equations for calculating reproducibility of benzene and total Updated aromatics

12.4 Revision 2.5 Effective Date: January 1, 2016

Significant changes:

Removed closing QC requirement to align SOP with ASTM method.

12.5 Version 3.0 Effective Date: May 1, 2017

Significant changes:

Updated Section 3.1 to a more current version of the ASTM method

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Removed brand-specific information in Sections 3 and 4.

Updated Section 10.4 to twice the value of repeatability

12.6 Version 3.1 Effective Date: December 1, 2019

SOP format updated for ADA compliance