Satisfying ASTM Method D5769: A Solution for Determination of High-Concentration Aromatic Compounds in Finished Gasolines

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Key Words: ASTM, Petroleum, Gasoline, Aromatics, Benchtop

1. Introduction

ASTM D5769 is a widely accepted standard method used in the petroleum industry for the determination of benzene, toluene, and total aromatics in finished gasolines by GC-MS. A common difficulty encountered with this method is the concern with saturation of the ion source, which leads to non-linearity in calibration curves, especially for the quantification of high-concentration aromatics, such as toluene. LECO's Pegasus® BT GC-TOFMS easily satisfies the method requirements for sensitivity, ion ratios, and calibration linearity, providing a solution for analysis of the aromatic compounds listed in ASTM D5769, without saturation of the ion source. Calibration curves were built for the standard method analytes, and then applied to samples with the addition of semi-quantification for similar analytes on a sample of 93-octane gasoline, as stipulated in the method.

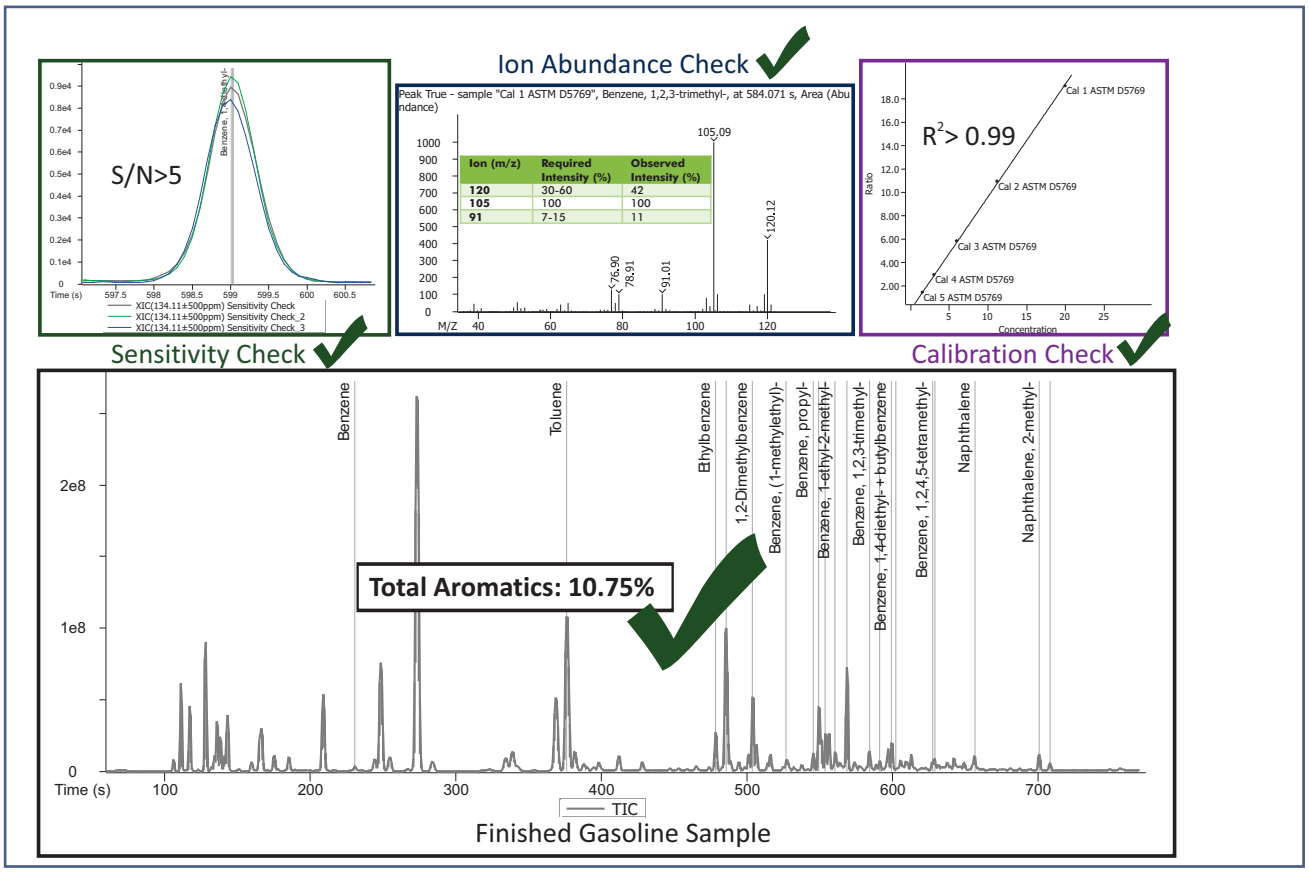

Figure 1. Total aromatics were determined for a commercially available sample of 93-octane gasoline. The chromatogram with peak markers automatically placed for calibrated analytes and deuterated internal standards is shown, along with the required method checks exceeded by the Pegasus BT.

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2. Experimental

High-split, low-volume injections into the GC were utilized combined with full mass range acquisition with LECO's *Pegasus* BT GC-TOFMS, a benchtop time-of-flight mass spectrometer. ChromaTOF®'s Target Analyte Find feature was used to automatically identify analytes of interest and quantify both calibrated and uncalibrated analytes using Quantitation and Semi-Quantitation data processing tools.

Table 1. GC-TOFMS (*Pegasus* BT) Conditions

Gas Chromatograph	**Agilent 7890 with Agilent 7693 Liquid Autosampler**
Injection	0.1 µl injection, split 1200:1 @ 260°C
Carrier Gas	He @ 1.0 mL/min, Constant Flow
Column	Rxi-1ms, 30 m x 0.25 mm i.d. x 1.00 µm coating (Restek, Bellefonte, PA, USA)
Oven Program	55°C (1 min), to 70°C @ 20°C/min (4 min), to 220°C @ 30°C/min (5 min)
Transfer Line	280 °C
Mass Spectrometer	**LECO *Pegasus* BT**
Ion Source Temperature	250°C
Mass Range	35-550 m/z
Acquisition Rate	10 spectra/s

3. Results and Discussion

In order to meet the requirements for using ASTM D5769 to characterize a sample, three fundamental mass spectrometer criteria must be met: sensitivity of 0.01 mass % for 1,4-diethylbenzene, achieving specified ion abundance ratios for key masses of 1,2,3-trimethylbenzene, and calibration linearity for all analytes.

The first requirement is stated in Section 6.2.3 of the method and stipulates that the signal-to-noise (S/N) ratio of 0.01 mass % 1,4-diethylbenzene at mass 134 must be consistently greater than 5. As can be seen in Figure 2 and Table 2, repeat analysis shows that the instrument easily surpasses the required S/N of 5, with an average Peak S/N of over 100.

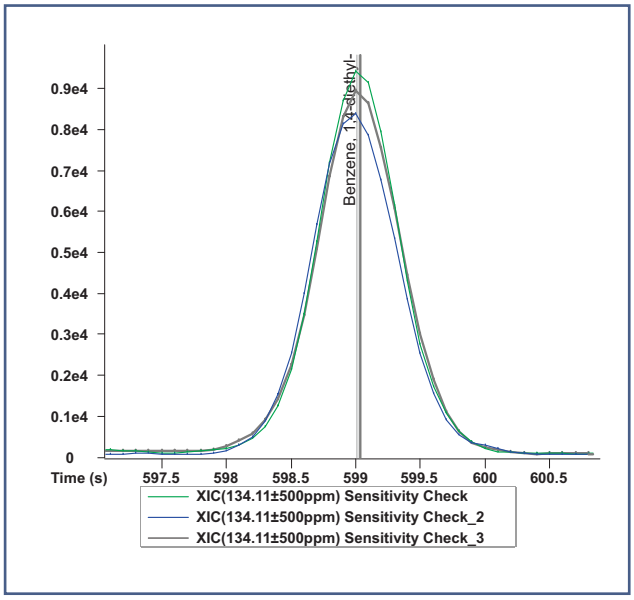

Figure 2. This chromatogram shows replicates of 0.01 mass % 1,4-Diethylbenzene acquired for the sensitivity check.

Table 2. S/N Results for Replicates of 0.01 mass % 1,4-Diethylbenzene

Name	Quant Masses	Quant S/N
1,4-Diethylbenzene	XIC (134.11 ±500 ppm)	141
1,4-Diethylbenzene	XIC (134.11 ±500 ppm)	151
1,4-Diethylbenzene	XIC (134.11±500 ppm)	132

The second requirement stated in Section 9.2.5 of the method specifies expected ion ratios for 3 mass % 1,2,3-Trimethylbenzene. This criterion is satisfied with values shown in Figure 3 and Table 3.

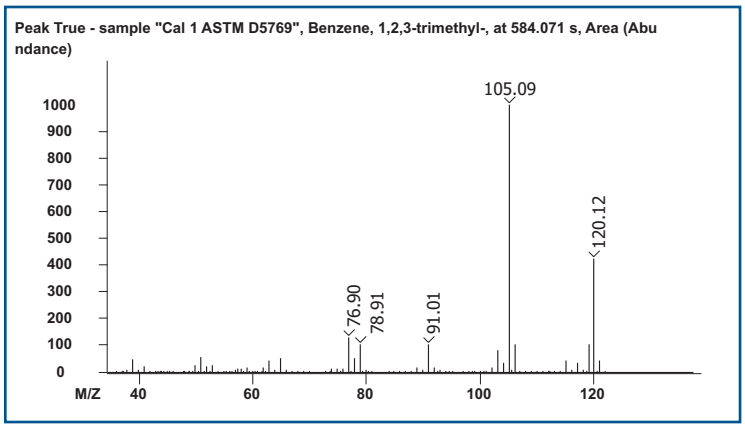

Figure 3. Deconvoluted mass spectrum for the peak 1,2,3-Trimethylbenzene at 3 mass % level.

Table 3. Ion Ratio Results for 3 mass % 1,2,3-Trimethylbenzene

Ion (m/z)	Required Intensity (%)	Observed Intensity (%)
120	30-60	42
105	100	100
91	7-15	11

Linear calibration curves for all analytes are also required, with linear least-squares R^2 values greater than 0.99 according to Section 9.3.3. Table 4 shows that the linear least-squares R^2 values of each analyte exceed the criteria, with the average value at 0.99987. Figure 4 illustrates the excellent linearity achieved for a known problem compound, toluene, with concentrations ranging from less than 2 mass % to over 20 mass %. The open-style source of the LECO *Pegasus* BT avoids rollover due to saturation from these high-concentration aromatics, easily yielding linear calibration curves for a wide dynamic range.

Table 4: R^2 Values for Calibrated Analytes

Analyte	R^2
Benzene	0.99994
Toluene	0.99980
Ethylbenzene	0.99998
Benzene, 1,3-dimethyl- + 1,4-dimethyl	0.99998
1,2-Dimethylbenzene	0.99998
Benzene, (1-methylethyl)-	1.00000
Benzene, propyl-	1.00000
Benzene, 1-ethyl-3-methyl-	0.99950
Benzene, 1-ethyl-4-methyl-	0.99980
1,3,5-Trimethylbenzene	0.99996
Benzene, 1-ethyl-2-methyl-	0.99998
Benzene, 1,2,4-trimethyl-	1.00000
Benzene, 1,2,3-trimethyl-	0.99996
Indane	0.99988
Benzene, 1,4-diethyl- + butylbenzene	0.99994
Benzene, 1,2-diethyl-	0.99992
Benzene, 1,2,4,5-tetramethyl-	0.99992
Benzene, 1,2,3,5-tetramethyl-	0.99986
Naphthalene	0.99992
Naphthalene, 2-methyl-	0.99950
Naphthalene, 1-methyl-	0.99954
Average Value	**0.99987**

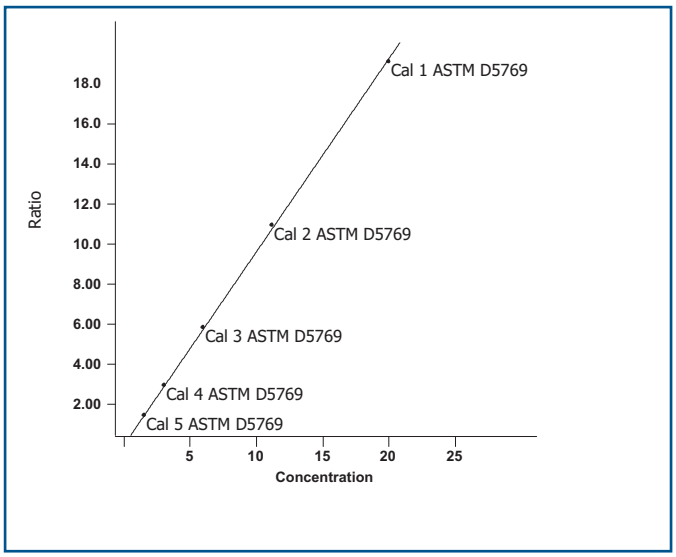

Figure 4. Linear calibration curve generated for toluene, with R^2 value of 0.9998.

4. Conclusion

The *Pegasus* BT GC-TOFMS easily met all requirements necessary to properly analyze a finished gasoline sample for total aromatics. All 23 calibrated analytes are labeled in the chromatogram below.

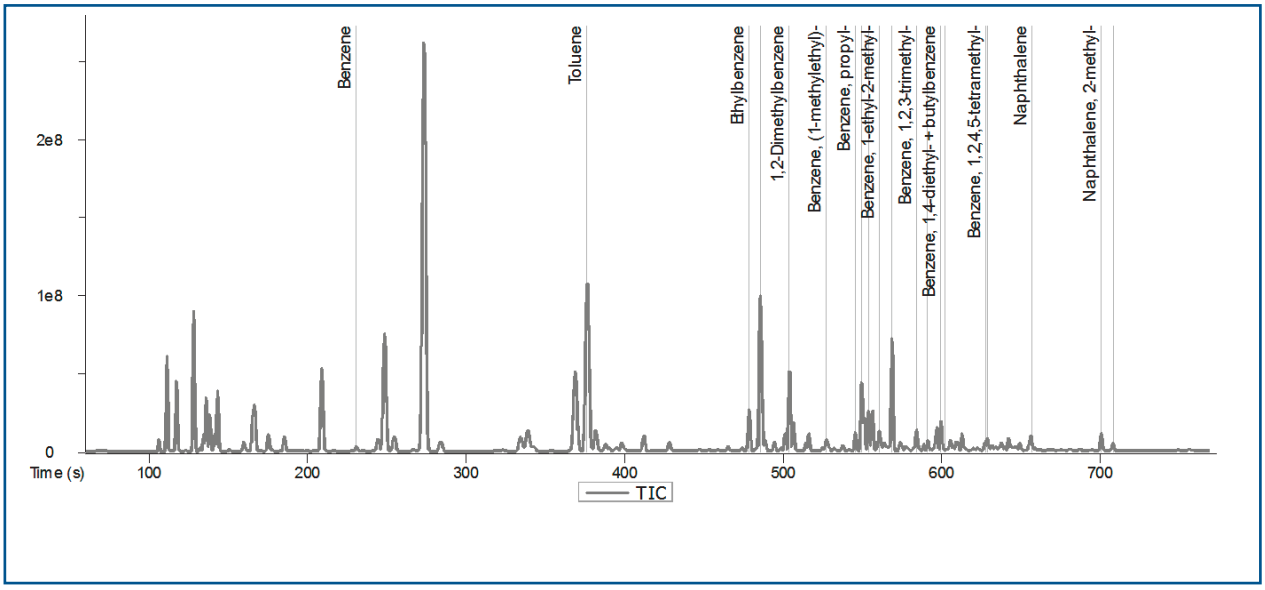

Figure 5. A chromatogram of 93-octane commercial gasoline is shown with peak markers automatically placed for the 23 calibrated analytes.

Results for the commercial 93 octane gasoline fell within the expected ranges of 0.09 to 4% for benzene at 0.2%, 1.0 to 13% for toluene, at 1.44%, and 9 to 42% for total aromatics determined at 10.75%, as can be seen in Table 5.

Table 5: Results for Aromatic Determination of 93 Octane Gasoline

Analyte	Volume %
Benzene	0.20
Toluene	1.44
Ethylbenzene	0.20
Benzene, 1,3-dimethyl- + 1,4-dimethyl	0.64
1,2-Dimethylbenzene	0.31
Benzene, (1-methylethyl)-	0.09
Benzene, propyl-	0.09
Benzene, 1-ethyl-3-methyl-	0.11
Benzene, 1-ethyl-4-methyl-	0.22
1,3,5-Trimethylbenzene	0.11
Benzene, 1-ethyl-2-methyl-	0.16
Benzene, 1,2,4-trimethyl-	0.11
Benzene, 1,2,3-trimethyl-	0.25
Indane	0.13
Benzene, 1,4-diethyl- + butylbenzene	0.31
Benzene, 1,2-diethyl-	0.16
Benzene, 1,2,4,5-tetramethyl-	0.08
Benzene, 1,2,3,5-tetramethyl-	0.11
Naphthalene	1.98
Naphthalene, 2-methyl-	0.36
Naphthalene, 1-methyl-	0.18
Uncalibrated Indans	2.82
Uncalibrated C10-Benzenes	0.51
Uncalibrated C11-Benzenes	0.19
Uncalibration C12-Benzene	0.01
Total Aromatics	**10.75**

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