ASTM METHOD D5769:
AN EASY SOLUTION FOR DETERMINATION OF HIGH CONCENTRATION AROMATIC COMPOUNDS IN FINISHED GASOLINES

ASTM D5769 is a widely accepted standard method used in the petroleum industry for 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 nonlinearity in calibration curves, especially for the quantification of the high-concentration aromatics, such as toluene.

LECO's Pegasus® BT easily satisfies the regular method requirements for sensitivity, ion ratios, and calibration linearity. The Pegasus BT also provides a solution for analysis of the aromatic compounds 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. The Pegasus BT is a time-of-flight (TOFMS) mass spectrometer that measures all the masses all the time without spectral skewing, allowing for separation of chromatographically overlapped analytes using mathematical algorithms in a process called deconvolution. Deconvolution leads to more reliable mass spectra from sample to sample and project to project, because proper masses are assigned to the appropriate analytes based on spectral profiles during acquisition. Additionally, the open-style source design on the Pegasus BT allows neutrals to be pumped away, eliminating interactions of analytes within the source housing to dramatically reduce source saturation and peak tailing. Maintaining the ability to generate EI spectra consistent with commercially available MS libraries, the ion source stays clean and performs consistently for long periods of time.

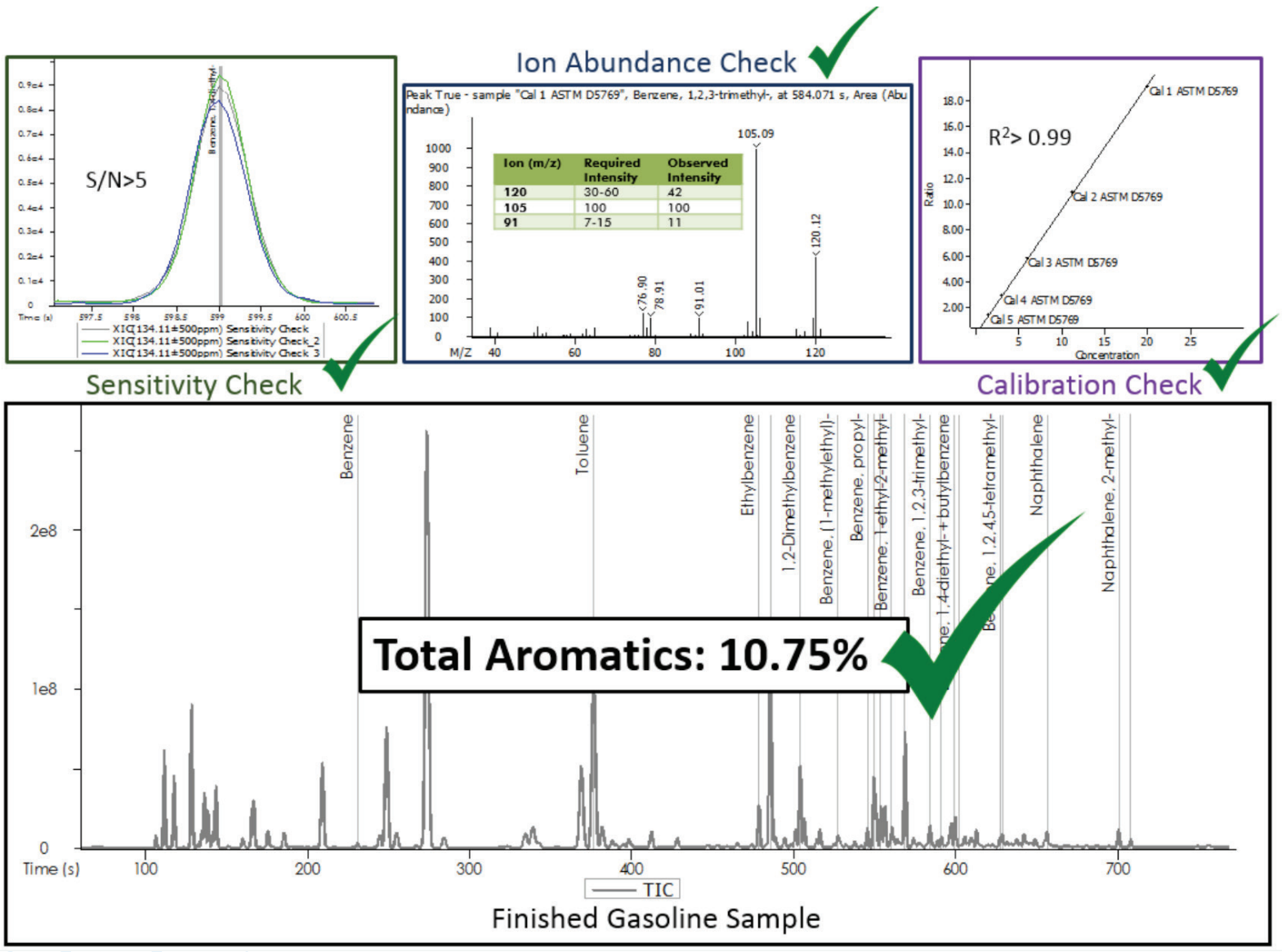

Figure 1. Total aromatics were determined for a commercially available sample of 93-octane gasoline. The chromatogram with peak markers automatically placed for calibrated analytes and deuterated internal standards is shown, along with the required method checks exceeded by the Pegasus BT TOFMS.

Gas Chromatograph	Agilent 7890 with Agilent 7693 Liquid Autosampler
Injection	0.1µL 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

Table 1. GC-TOFMS (Pegasus BT) Conditions

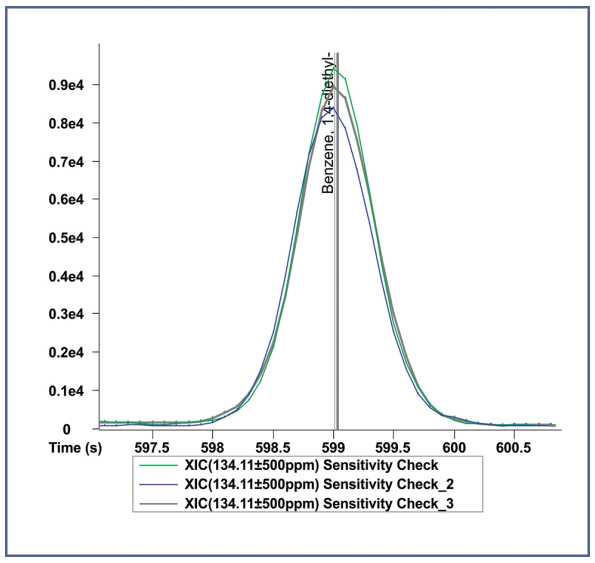

Figure 2. This chromatogram shows replicates of 0.01 mass % 1,4-Diethylbenzene acquired for the sensitivity check.

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

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

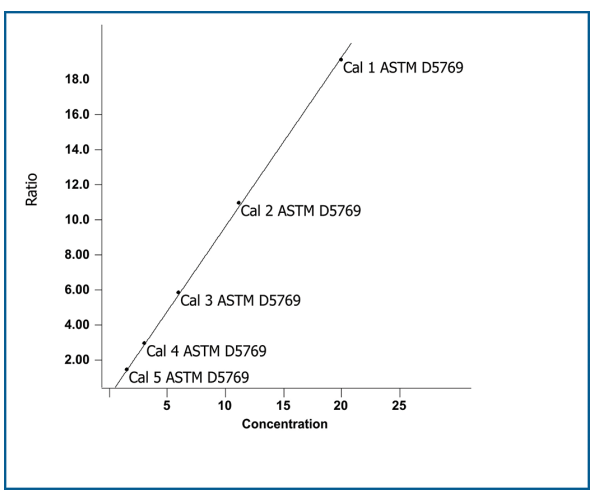

Figure 4. Linear calibration curve generated for toluene, with R^2 value of 0.9998.

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

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

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**

Table 4: R^2 Values for Calibrated Analytes

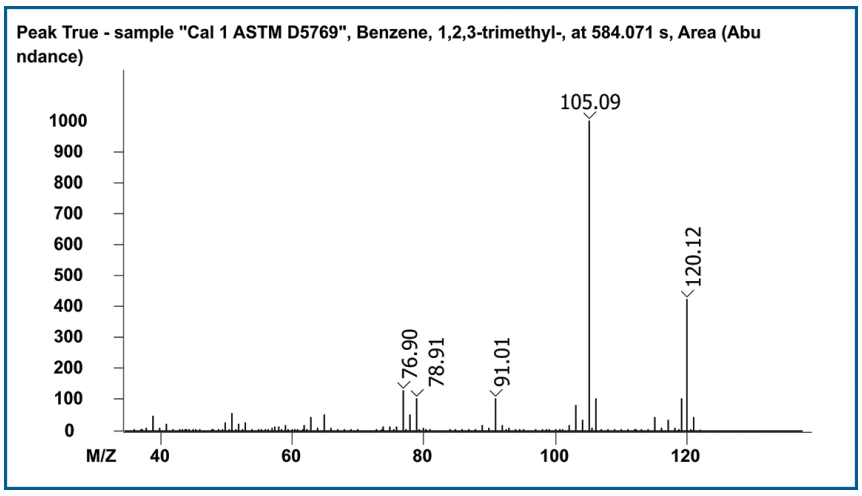

Figure 3. Deconvoluted mass spectrum for the peak 1,2,3-Trimethylbenzene at 3 mass % level.

2. Experimental

High split, low volume injections into the GC were utilized combined with full mass range acquisition with LECO's Pegasus BT TOFMS, a benchtop time-of-flight mass spectrometer. LECO's ChromaTOF® brand software'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.

3. Results and Discussion

Three fundamental criteria must be met in order to satisfy the requirements for ASTM D5769. They are the following: mass spectrometer sensitivity for 0.01 mass % for 1,4-diethylbenzene, achieving specified ion abundance ratios for key ions of 1,2,3-trimethylbenzene, and calibration linearity for all analytes.

The first requirement stated in Section 6.2.3 of the method 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 injections show that the instrument easily surpasses the required S/N of 5, with an average Peak S/N of well over 100.

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**

Table 5: Results for Aromatic Determination of 93 Octane Gasoline

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

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.

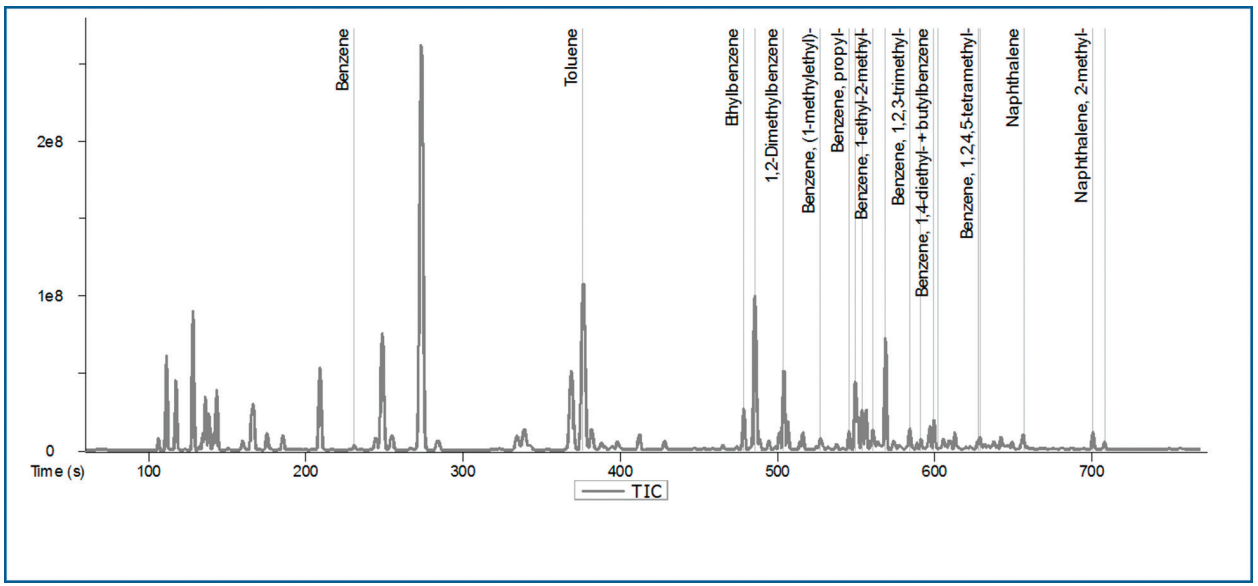

Figure 5. A chromatogram of 93-octane commercial gasoline is shown with peak markers automatically placed for the 23 calibrated analytes.

4. Conclusion

The Pegasus BT 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. Results for the commercial 93 octane gasoline fell within the expected ranges of 0.09-4% for benzene at 0.2%, 1.0-13% for toluene, at 1.44%, and 9-42% for total aromatics determined at 10.75%, as can be seen in Table 5. Consistent performance of the Pegasus BT with easy, automated data processing provides a clear solution for complete aromatics analysis.

Author Contact Details

Christina Kelly, Applications Chemist • LECO Corporation • Saint Joseph, MI USA • Tel: 269-985-5496 • Email: info@leco.com • **Web:www.leco.com**