A Solution for Determination of High-Concentration Aromatic Compounds in Finished Gasolines Satisfying ASTM D5769 Using a New Benchtop GC-TOFMS

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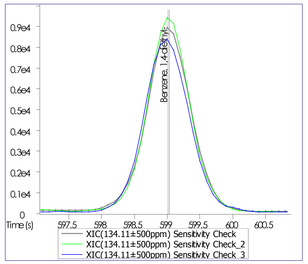
Introduction

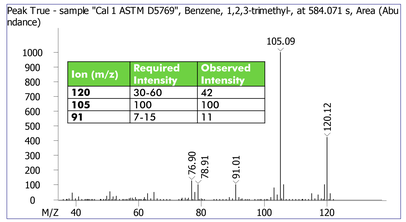
ASTM D5769 is a widely accepted standard method used in the petroleum industry for determination of benzene, toluene, and total aromatics in finished gasolines by GC-MS. A common difficulty encountered with this method is the concern with saturation of the ion source, which leads to nonlinearity in calibration curves, especially for the quantification of the high-concentration aromatics, such as toluene. LECO's Pegasus® BT 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.



Name	Quant S/N
1,4-Diethylbenzene	141
1,4-Diethylbenzene	151
1,4-Diethylbenzene	132

Figure 1: Triplicate injections of 0.01 mass % 1,4-diethylbenzene are shown. According to Section 6.2.3 of the method, the signal-to-noise (S/N) ratio of 0.01 mass % 1,4-diethylbenzene at mass 134 must be consistently greater than 5. Repeat analyses showed an average S/N greater than 100, easily surpassing method requirements.

Figure 2: The deconvoluted Peak True spectrum of 1,2,3-Trimethylbenzene is shown along with a table of relevant ion ratio intensity values as stipulated in Section 9.2.5 of the method.



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

Methods

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

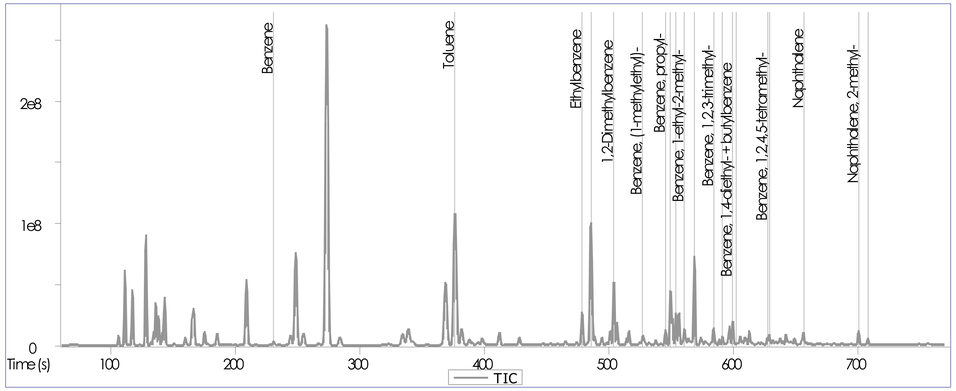
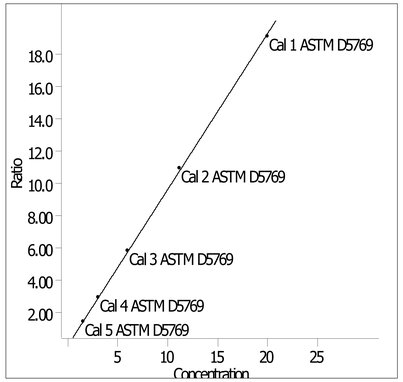


Figure 3: A total ion chromatogram (TIC) of 93-octane commercial gasoline is shown above with peak markers automatically placed for the 23 calibrated analytes. The table below reports concentration values for both calibrated and uncalibrated analytes of interest in volume % as specified in the method.

LECO Pegasus BT

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**



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: The calibration curve for toluene illustrates the excellent linearity that is shown in the table of R^2 values for each calibrated analyte.

Results

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. After all method criteria were successfully completed, a sample of commercially available 93-octane gasoline was analyzed. Automatic Peak Find with deconvolution provided all the necessary information to determine total aromatics.

Criteria	Result
Sensitivity	PASS
Ion Abundance Ratios	PASS
Calibration Linearity	PASS

Conclusions

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 in Figure 3. 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%.

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