Application Note

Analysis of Total Aromatic Content in Motor Gasoline by ASTM D5769 Using an Agilent 8850/5977C GC/MSD System

Author

Scott J. Hoy
Agilent Technologies, Inc.

Abstract

This application note demonstrates the quantification of benzene, toluene, and total aromatics in motor gasoline according to ASTM D5769 with a run time of nine minutes using an Agilent 8850 Gas Chromatograph (GC) System coupled to an Agilent 5977C GC/MSD. System performance was evaluated using several gravimetric standards and a reformulated gasoline (RFG) sample from an interlaboratory cross-check program (ILCP). The detector source was configured with an optional 9 mm extraction lens, resulting in excellent linearity for 24 individual aromatic species, including toluene, which had an R^2 of 0.99996. All performance requirements of D5769 were met with excellent precision across replicate analyses.

Introduction

ASTM D5769[1] determines the total aromatic concentration of gasoline by enhancing the separating power of gas chromatography with the selectivity of mass spectrometry (MS). The combination of GC and MS produces a detector signal that is both proportional to the concentration of the compound being measured and contains information on the masses of the different structural fragment ions that are characteristic of that compound. This allows the GC/MS system to selectively filter ("extract") the aromatic species from other compound classes in the sample by only looking at the fragment ions that are characteristic of aromatic compounds. While many other gasoline aromatics methods require multiple GC columns and valves to isolate the aromatic species, ASTM D5769 uses a simple flow path comprised of one inlet, one column, and one detector.

This application note demonstrates the rapid quantification of total aromatics in gasoline by ASTM D5769 using an 8850 GC with a 5977C GC/MSD and hydrogen carrier gas. The 8850 GC is a high-performance single-channel GC with the ideal feature set to provide fast and repeatable separations for ASTM D5769 in a footprint that is half the width of the Agilent 8890 GC System and other standard size GCs. When paired with the 5977C GC/MSD, the total system footprint is 2/3 the width of standard benchtop GC/MS systems. The compact 8850/5977C GC/MSD provides the sensitivity and selectivity required to quantify trace-level aromatic compounds in gasoline, and the linear dynamic range to measure bulk components like toluene in the same sample. In addition to the standard 3 mm extraction lens, the 5977C GC/MSD EI Extractor ion source offers two optional extraction lenses, either 6 mm or 9 mm in diameter, enabling method-specific optimization to improve analytical performance. This application note demonstrates that the larger 9 mm extraction lens provides increased linearity when measuring higher concentration components, and this benefit was previously demonstrated using an Agilent 8860 GC system coupled to a 5977B GC/MSD.[2]

Experimental

An 8850 GC and 5977C GC/MSD were configured according to "Condition 3" in ASTM D5769-22 except for the changes listed here. Notably, the standard 3 mm extraction lens in the 5977C GC/MSD ion source was replaced with a 9 mm extraction lens to extend measurement linearity for bulk compounds. The 8850 GC was configured for hydrogen carrier gas and outfitted with the Agilent Hydrogen Leak Detector Series 2. The column was an Agilent J&W DB-1 40 m × 0.18 mm, 0.4 µm (part number 121-1043E), and the injection volume was increased to 0.3 µL. The GC and GC/MSD configuration, consumables, and method parameters are listed in Table 1.

The calibration and performance-check standards were purchased from Accustandard (part number M-GRA-K2-SET, Accustandard, Inc.). To evaluate the system, a Tier III-reformulated gasoline sample from an interlaboratory cross-check program (ILCP) was analyzed and compared to the accepted ILCP reference results.

Table 1. GC and GC/MSD configuration, consumables, and method parameters (continued on the next page).

Parameter	Value
8850 GC	
Sampler	7650A Automated Liquid Sampler (ALS)
Inlet	Split/splitless
Column	Agilent J&W DB-1, 40 m × 0.18 mm, 0.4 µm (p/n 121-1043E)
Carrier Gas	Hydrogen
Hydrogen Leak Sensor	Hydrogen Sensor Module Series 2 for 8850 GC (p/n G3982A)
5977C GC/MSD	
Source	Extractor
Extractor Lens	9 mm (G3870-20449)
Acquisition Mode	Scan
Consumables	
Inlet Septum	Advanced Green, non-stick (p/n 5183-4759)
Inlet Liner	Deactivated, low pressure drop split liner w/ glass wool (p/n 5183-4647)
ALS Syringe	Blue Line, 5 µL, fixed needle, 23-26s/42/cone (p/n 4513-80206)
Carrier Gas Filter	Agilent Gas Clean purifier kit for carrier gas, 1/8 in (p/n CP17976)
Method Parameters	
Runtime	9 min

Table 1. GC and GC/MSD configuration, consumables, and method parameters (continued from the previous page).

Parameter	Value
Inlet, Flow Rate, and ALS	
Temperature	250 °C
Flow Rate	1 mL/min constant flow
Septum Purge	3 mL/min
Injection Volume	0.3 µL
Mode	Split, 700:1
Gas Saver	On, 20 mL/min after 2 minutes
Oven Program	
Initial Temperature	35 °C
Initial Hold	1 min
Ramp Rate	25 °C/min
Final Temperature	210 °C
Final Hold	1 min
5977C MSD	
Transfer Line Temperature	250 °C
Solvent Delay	2 min
Ionization Voltage	70 eV
Source Temperature	250 °C
Quad Temperature	150 °C
Scan Range	40 – 200 amu
Scan Rate	8 scans/sec
Tuning Algorithm	atune
Gain Factor	0.3
Trace Ion Detection (TID)	Enabled

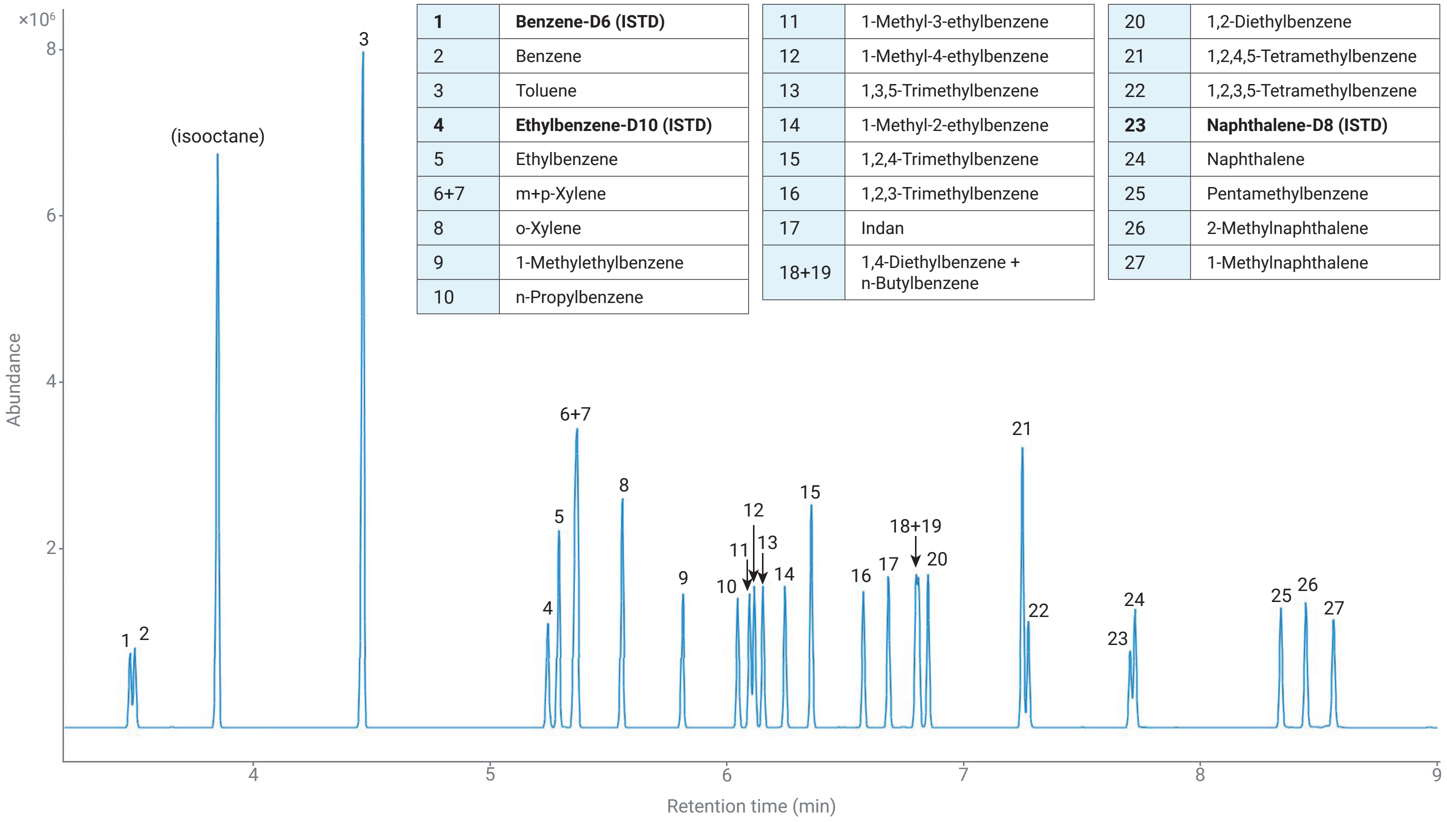
Results and discussion

The separation was evaluated using the aromatic checkout standard which contains 24 individual aromatic species and three deuterated internal standards (benzene-d6, ethylbenzene-d10, naphthalene-d8) in a matrix of 2,2,4-trimethylpentane (isooctane). The checkout standard separation and peak identities are shown in Figure 1. The coelutions of m-xylene with p-xylene and 1,4-diethylbenzene with n-butylbenzene are allowed by the method and the composite peaks are reported as a single compound. Table 2 shows the concentration and %RSD obtained for each component of the aromatic checkout standard across ten consecutive replicates.

Table 2. Aromatic checkout standard results for n = 10 consecutive replicates.

Peak	Component	Average (% mass)	%RSD
2	Benzene	1.99	0.37
3	Toluene	15.17	1.04
5	Ethylbenzene	3.54	0.49
6+7	p-Xylene/m-Xylene	8.51	0.42
8	o-Xylene	4.37	0.48
9	Isopropylbenzene	2.11	1.12
10	n-Propylbenzene	2.15	1.14
11	1-Methyl-3-ethylbenzene	2.10	0.88
12	1-Methyl-4-ethylbenzene	2.13	0.85
13	1,3,5-Trimethylbenzene	2.14	0.81
14	1-Methyl-2-ethylbenzene	2.20	0.89
15	1,2,4-Trimethylbenzene	3.43	0.87
16	1,2,3-Trimethylbenzene	2.18	0.85
17	Indan	2.46	0.60
18+19	n-Butylbenzene/1,4-DEB	3.62	1.58
20	1,2-Diethylbenzene	1.86	1.35
21	1,2,4,5-Tetramethylbenzene	3.49	1.24
22	1,2,3,5-Tetramethylbenzene	1.22	1.08
24	Naphthalene	1.48	0.29
25	Pentamethylbenzene	1.42	1.72
26	2-Methylnaphthalene	1.47	0.92
27	1-Methylnaphthalene	1.45	0.96

ASTM D5769-22 requires measuring individual aromatic species at concentrations from 500 to 149,000 ppm with linear calibrations of $R^2 > 0.99$ for each. This is challenging for GC/MS due to its high sensitivity which makes it more appropriate for measuring parts-per-million (ppm) or lower concentrations. The optional 9 mm extraction lens made it easier to achieve calibration linearity at the higher concentration levels. To further attenuate the MSD signal, the voltage applied to the electron multiplier (EM) was reduced by decreasing the Gain Factor from 1.0 to 0.3. In practice, the highest-level calibration standard is run and the gain value set such that the maximum abundance of the extracted ion chromatogram (EIC) of the primary ion of the highest-responding component is approximately 1 million counts. This approach resulted in a linear calibration of toluene with an R^2 of 0.99996 up to a concentration of 16.3% (Figure 2). A summary of the resulting R^2 values for all calibrated compounds is shown in Table 3.

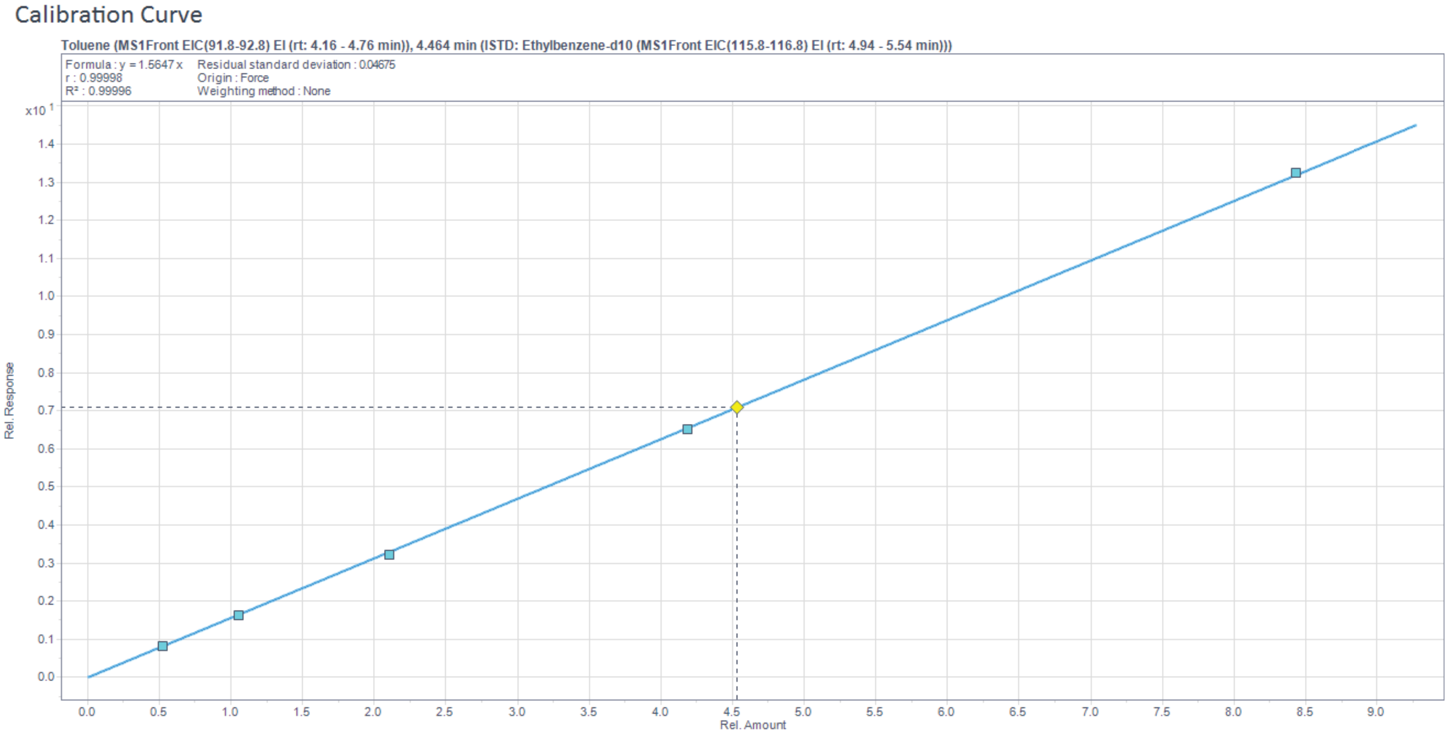


1	**Benzene-D6 (ISTD)**
2	Benzene
3	Toluene
4	**Ethylbenzene-D10 (ISTD)**
5	Ethylbenzene
6+7	m+p-Xylene
8	o-Xylene
9	1-Methylethylbenzene
10	n-Propylbenzene

11	1-Methyl-3-ethylbenzene
12	1-Methyl-4-ethylbenzene
13	1,3,5-Trimethylbenzene
14	1-Methyl-2-ethylbenzene
15	1,2,4-Trimethylbenzene
16	1,2,3-Trimethylbenzene
17	Indan
18+19	1,4-Diethylbenzene + n-Butylbenzene

20	1,2-Diethylbenzene
21	1,2,4,5-Tetramethylbenzene
22	1,2,3,5-Tetramethylbenzene
23	**Naphthalene-D8 (ISTD)**
24	Naphthalene
25	Pentamethylbenzene
26	2-Methylnaphthalene
27	1-Methylnaphthalene

Figure 1. Chromatogram of the aromatic checkout standard showing the 24 aromatic species and three deuterated internal standards.



Calibration Curve

Toluene (MS1Front EIC(91.8-92.8) EI (rt: 4.16 - 4.76 min)), 4.464 min (ISTD: Ethylbenzene-d10 (MS1Front EIC(115.8-116.8) EI (rt: 4.94 - 5.54 min)))

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Formula : y = 1.5647 x    Residual standard deviation : 0.04675
r : 0.99998               Origin : Force
R² : 0.99996              Weighting method : None
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Figure 2. Calibration model for toluene with an $R^2 = 0.99996$.

Table 3. R^2 values for each calibrated aromatic compound.

Peak No.	Component	R^2
2	Benzene	0.99998
3	Toluene	0.99996
5	Ethylbenzene	0.99998
6+7	p-Xylene / m-Xylene	0.99999
8	o-Xylene	1.00000
9	Isopropylbenzene	0.99998
10	n-Propylbenzene	0.99997
11	1-Methyl-3-ethylbenzene	0.99997
12	1-Methyl-4-ethylbenzene	0.99993
13	1,3,5-Trimethylbenzene	0.99996
14	1-Methyl-2-ethylbenzene	0.99996
15	1,2,4-Trimethylbenzene	0.99999
16	1,2,3-Trimethylbenzene	0.99996
17	Indan	0.99990
18+19	n-Butylbenzene/1,4-Diethylbenzene	0.99992
20	1,2-Diethylbenzene	0.99994
21	1,2,4,5-Tetramethylbenzene	0.99997
22	1,2,3,5-Tetramethylbenzene	0.99992
24	Naphthalene	0.99996
25	Pentamethylbenzene	0.99990
26	2-Methylnaphthalene	0.99996
27	1-Methylnaphthalene	0.99998

Maintaining control of ASTM D5769 is a balance between reducing the MS sensitivity for high-concentration components while still achieving enough sensitivity to measure 1,4-diethylbenzene at 100 ppm. Figure 3 shows the chromatographic peak and resulting signal-to-noise ratios for 1,4-diethylbenzene at 100 ppm using gain factors of 0.3, 0.2, and 0.1. As can be seen, the signal intensity decreases proportionally with gain factor, while the signal-to-noise ratio remains consistent and approximately ten times higher than the method requirement of 5. The EM Gain Factor parameter is a normalization of the EM voltage model established during tuning of the MSD and provides a simple way to set the desired amplification ("gain") of the detector signal regardless of the EM age or voltage. This parameter also enables users to unify the response of multiple GC/MS systems running D5769 by setting a common gain factor to facilitate system health monitoring. For example, monitoring the decrease in signal height of a QC sample over time across several systems against a common minimum signal threshold can provide early indication that a specific system will soon need maintenance despite still being in-control.

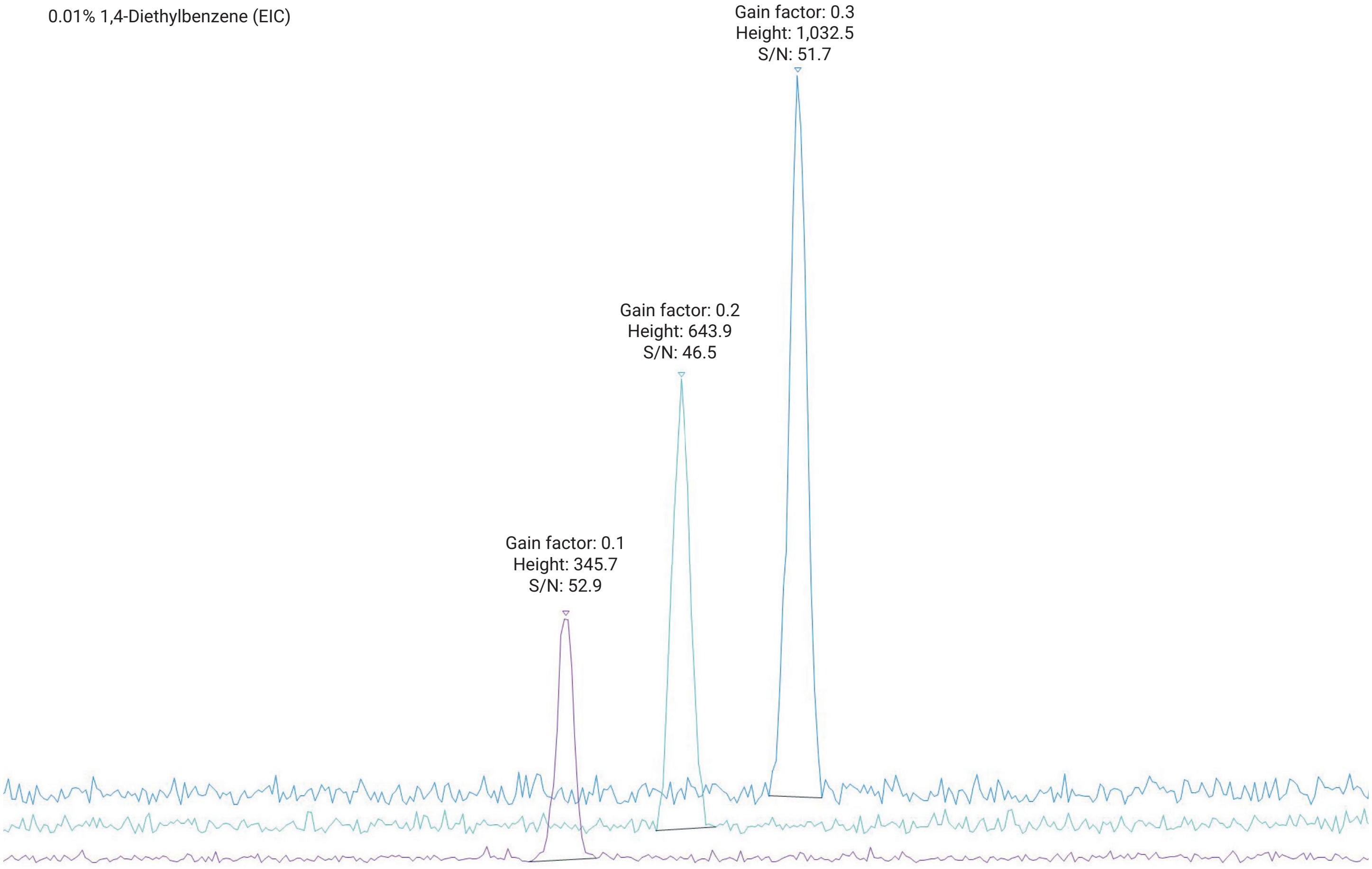

Figure 3. Staggered chromatograms showing the signal-to-noise ratios and peak heights for 100 ppm 1,4-diethylbenzene with gain factors of 0.3 (blue), 0.2 (green), and 0.1 (purple).

Method performance was evaluated using the multicomponent daily quality control standard (AccuStandard) for which the method requires ± 5% relative quantitative accuracy for each component except for 1,2,4,5-tetramethylbenzene and naphthalene which both require ± 10% relative quantitative accuracy. Table 4 shows the results from the quality control standard compared to the reference values. An additional performance check of the resolution (R) of 1,3,5-trimethylbenzene and 1-methyl-2-ethylbenzene resulted in R = 4.77 (Figure 4), exceeding the method requirement of R = 2. Finally, a reformulated gasoline (RFG) sample from an interlaboratory cross-check program was analyzed for total aromatic content and compared to the accepted reference value (ARV) established by the ILCP. Shown in Table 5, the RFG total aromatics result was 14.46% compared to the ARV of 14.82%, with a Z-score of −0.63, well-within one standard deviation of the results obtained by the ILCP participants. The chromatogram for the RFG sample is shown in Figure 5.

Table 4. Results obtained for replicate analysis (n = 10) of the quality control sample compared to the reference values.

Component	Reference (%m/m)	Experimental (%m/m)	% Difference	%RSD (n = 10)
Benzene	1.00	0.98	−1.90	0.72
Toluene	9.00	8.83	−1.85	0.69
Ethylbenzene	3.00	2.90	−3.32	0.65
p-Xylene/m-Xylene	2.98	2.90	−2.51	0.68
o-Xylene	2.98	2.92	−1.96	0.66
1,2,4-Trimethylbenzene	2.95	2.91	−1.11	1.04
1,2,4,5-Tetramethylbenzene	3.00	3.03	1.06	0.59

Table 5. RFG sample results.

Component	Concentration (vol %)	ARV (vol %)
Benzene*	0.47	0.50
Toluene	2.74	N/A
Total Aromatics	14.46	14.82

* Benzene ARV is from method ASTM D3606

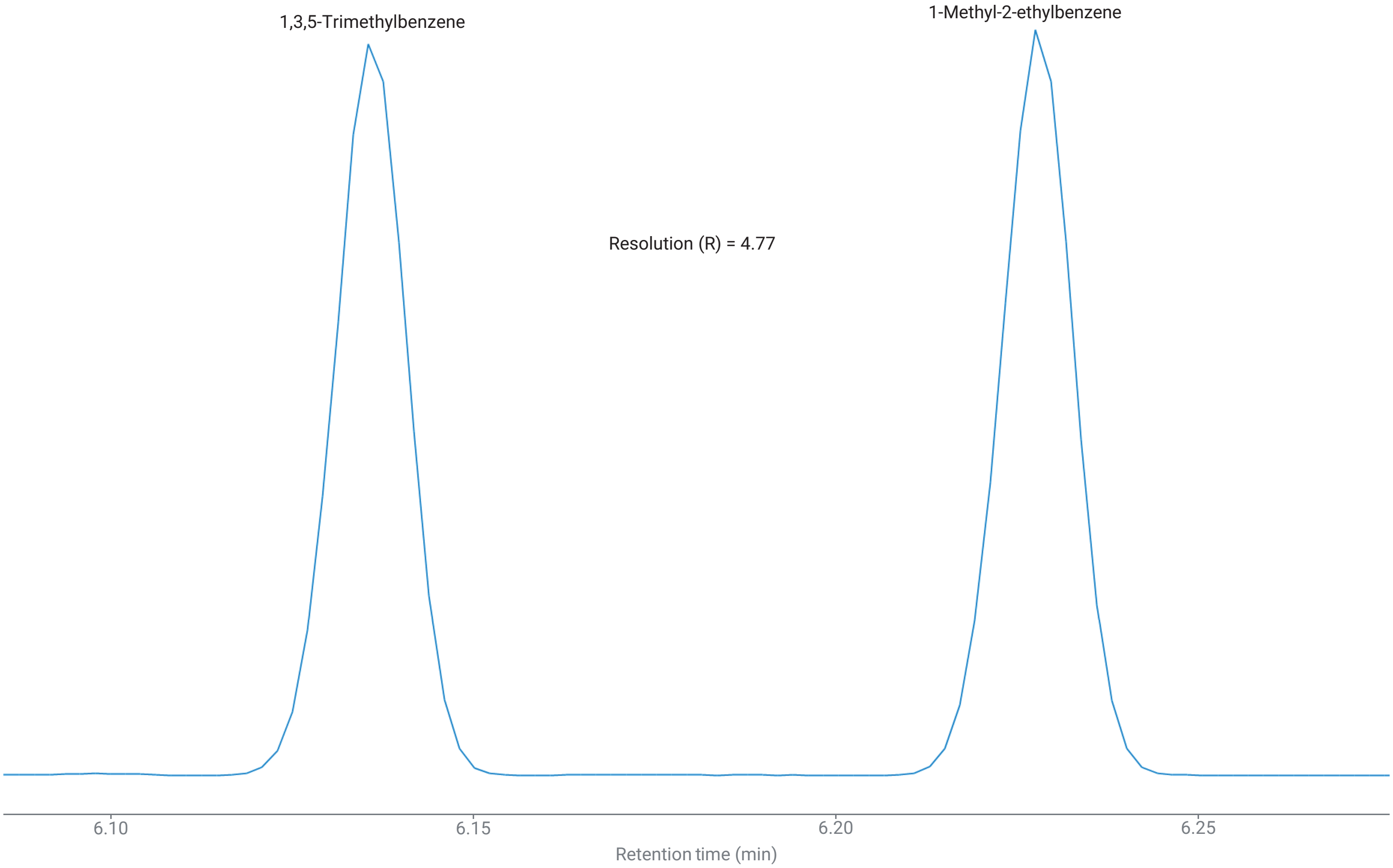

Figure 4. Separation of 1,3,5-trimethylbenzene and 1-methyl-2-ethylbenzene with a resolution (R) of 4.77, exceeding the method requirement of R = 2.

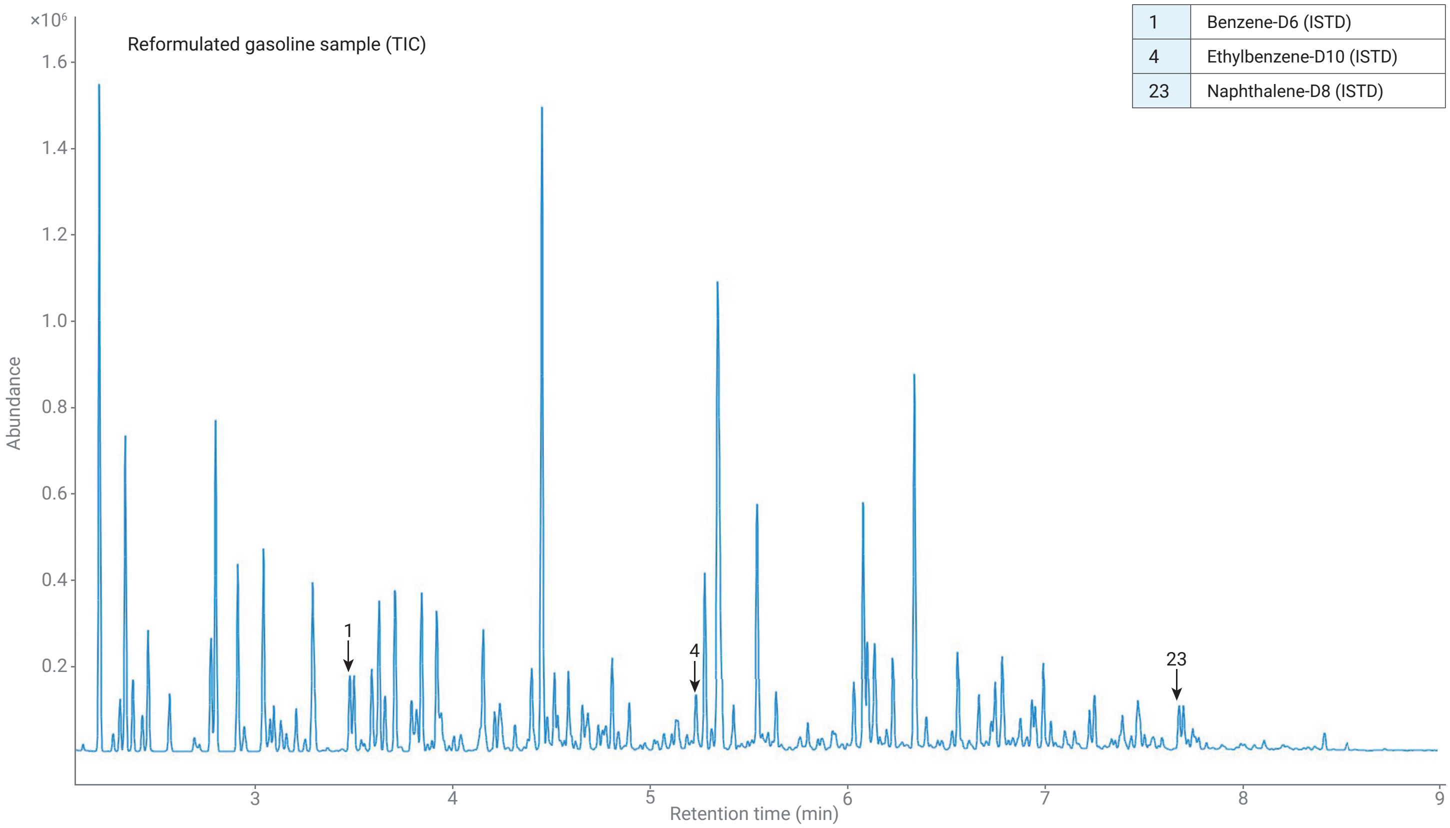

Figure 5. Total ion chromatogram (TIC) of the reformulated gasoline sample.

Conclusion

The Agilent 8850 GC combined with the Agilent 5977C GC/MSD successfully performed ASTM D5769 with a total runtime of nine minutes while meeting all method requirements. All measured aromatic species far exceeded method linearity requirements, including toluene which had an R^2 value of 0.99996, while maintaining enough sensitivity to measure 100 ppm of 1,4-diethylbenzene with a signal-to-noise of 52.

References

1. ASTM D5769-22, Standard Test Method for Determination of Benzene, Toluene, and Total Aromatics in Finished Gasolines by Gas Chromatography/Mass Spectrometry, ASTM International, West Conshohocken, PA, **2022** www.astm.org.
2. McCurry, J. D. A High Performance and Cost-Effective GC/MS Solution for Measuring Aromatics in Gasoline Using ASTM Method D5769, *Agilent Technologies application note*, publication number 5994-1967EN, May **2020**.

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