Application Note

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A High Performance and Cost-Effective GC/MS Solution for Measuring Aromatics in Gasoline Using ASTM Method D5769

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Abstract

This application note describes an Agilent 8860/5977 gas chromatography/mass spectrometry (GC/MS) system for the analysis of benzene, toluene, and total aromatics in motor gasoline using ASTM method D5769. A modified stainless-steel detector source was employed to lower costs while providing the high performance required by the ASTM method. Before running samples, the 8860/5977 system was verified by passing all performance and QC tests required by the D5769 method. Gasoline samples run with this system showed excellent precision and agreement with other laboratory results.

Introduction

ASTM method D5769 uses GC/MS to measure the total aromatic content in gasoline.[1] The U.S. Environmental Protection Agency (EPA) has designated D5769 as the official gasoline total aromatics method for regulatory compliance.[2] The EPA also allows ASTM D1319 as an alternative method for the same total aromatics measurement. D1319 is a simple technique using a fluorescence-indicating dye on a silica gel column to separate and detect the total aromatics in gasoline. This method is commonly used for routine aromatics analysis, but the results must be correlated to the primary D5769 method. Recently, supplies of the dye have been disrupted with no alternative replacement. This event prompted many laboratories to transition their gasoline analysis operations from D1319 to D5769 and begin investment into GC/MS systems. To ease the higher cost of transition to the more complex GC/MS analysis, this application note presents a cost-effective GC/MS instrument platform that delivers the necessary performance to meet D5769 analysis requirements.

An operational challenge often encountered with the D5769 method is achieving calibration linearity for each target compound as measured by their coefficients of determination. GC/MS systems are designed to measure compounds at low concentrations, typically in the parts-per-million (ppm) to parts-per-billion (ppb) range. Individual aromatic compounds in gasoline are present at single- or double-digit percent levels; greater than 10^5 times higher than levels usually measured using GC/MS. This application note demonstrates an effective way to improve detection linearity for higher concentrations by making a simple modification to the mass spectrometer source. Once the detector linearity requirements and method performance tests were met, the 8860/5977 GC/MS system was used to measure the benzene, toluene, and total aromatic contents in two Tier III-reformulated gasoline samples from an inter-laboratory cross-check program (ILCP). The results obtained from these samples were evaluated for precision and agreement with the reported ILCP results.

Experimental

A 8860/5977 GC/MS system was configured to meet the D5769 method requirements (Table 1). The stainless-steel source on the mass spectrometer (MSD) was modified by replacing the standard 3 mm draw-out plate with a 9 mm draw-out plate. Larger aperture draw-out plates have previously been shown to improve linear response for higher concentration components in gasoline samples.[3,4] The D5769-specified operating parameters are listed in Tables 2 and 3, and were used to acquire all data.

Table 1. GC/MS hardware configuration.

G7082BW	5977B MSD bundle with 8860 GC
	Stainless steel MSD source
	Split/splitless inlet
G3440-20022	9-mm draw-out plate for MSD source
G4567A	7650A auto injector (ALS)

Table 2. D5769 GC operating conditions.

Auto Injector (ALS)	
Syringe	5 µL (p/n G4513-80206)
Injection Volume	0.1 µL
Wash Solvent	isooctane
Split/Splitless Inlet	
Carrier Gas	Helium
Mode	Split, 350:1
Temperature	250 °C
Liner	Split (p/n 5190-2295)
Column	
Type	DB-1, 60 m × 0.25 mm, 1.00 µm (p/n 122-1063)
Flow Rate	1.8 mL/min constant flow (35 cm/s)
Initial Temperature	60 °C
Initial Hold Time	0 min
Ramp Rate 1	3 °C/min
Temperature 1	120 °C
Hold Time 1	0 min
Ramp Rate 2	10 °C/min
Temperature 2	250 °C
Hold Time 2	2 min
Total Run Time	35 min

Table 3. D5769 MS operating conditions.

GC/MS Interface	
Type	Direct
Temperature	280 °C
Agilent 5977 MSD	
Ionization Voltage	70 eV
Source Temperature	230 °C
Quad Temperature	150 °C
Scan Range	45 to 300 amu
Scan Rate	3 scans/s
Tuning Algorithm	Atune

Calibration standards and performance check standards were obtained from Accustandard, Inc. The quality control check sample and reformulated gasoline samples were obtained from Spectrum Quality Standards. The Tier III-reformulated gasolines were commercial samples obtained from an interlaboratory cross-check program (ILCP) used to help laboratories meet the EPA Tier III §80.47 Performance-based Analytical Test Method Approach. Ten replicates of each gasoline sample were prepared with each replicate run once on the 8860/5977 system.

Results and discussion

The highest-level calibration mix was run to establish identity and elution order for the target compounds and internal standard compounds. Figure 1 shows the resulting total ion chromatogram (TIC). There are two pairs of target compounds not completely resolved on this column: *m*-xylene/*p*-xylene and 1,4-dimethylbenzene/*n*-butylbenzene. The ASTM D5769 method allows each pair to be reported as a single compound.

The method requires a correlation of determination (R^2) of 0.99 or greater for each compound's linear regression calibration. This can be difficult to achieve using the standard 3 mm draw-out plate in the MS source, especially for toluene where the upper calibration standard has a concentration of 19% (v/v). In Figure 2, the profile for toluene's extracted ion chromatogram (EIC) shows evidence of detector saturation, with a peak height ion count exceeding 8.0×10^6. Ideally the maximum peak height should be less than 5×10^6 ion counts. The resulting

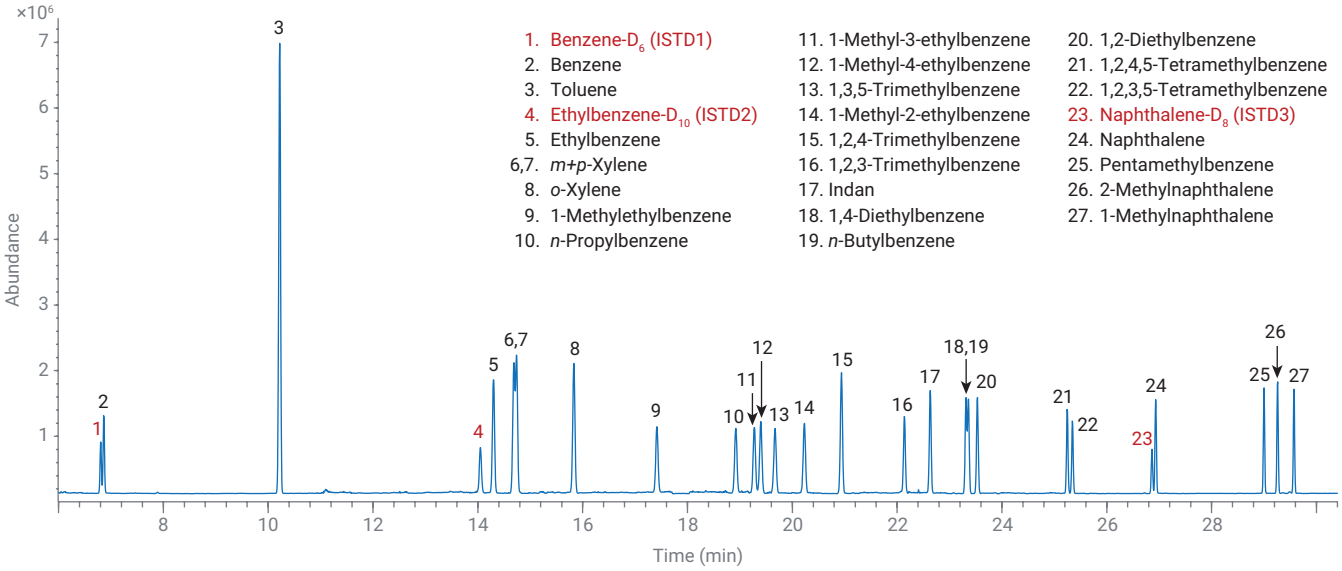

Figure 1. Total ion chromatogram (TIC) showing the elution order of aromatic compounds in the D5769 calibration mix. The three deuterated internal standards are shown in red text.

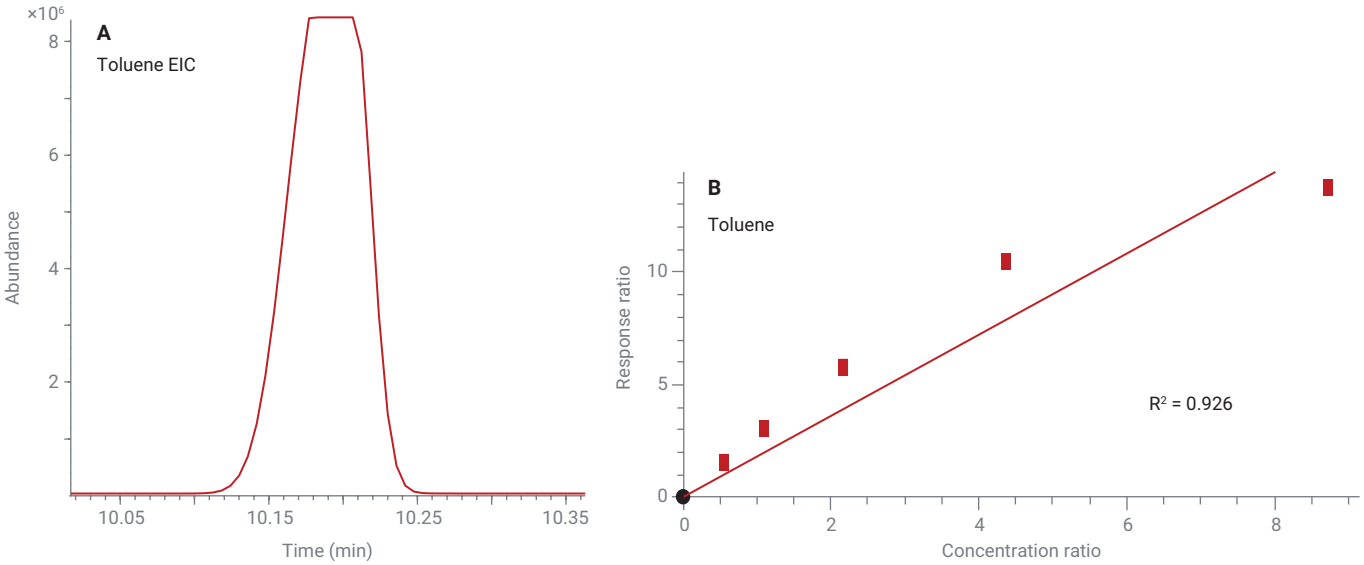

Figure 2. Detector saturation was observed for toluene at the 19 % (v/v) calibration level. The resulting linear calibration curve failed the ASTM required coefficient of determination (R^2) of 0.99 or greater.

calibration curve exhibits a nonlinear response over the five-point calibration range, with a failed R^2 of 0.93.

The detector linearity problem was solved by replacing the standard 3 mm id draw-out plate with a 9 mm id draw-out plate. In Figure 3, the toluene EIC does not show any detector saturation and the height is well below 5 × 10^6 ion counts.

The linear calibration curve for toluene now has an R^2 of 0.99999. Table 4 shows the R^2 values for all calibrated compounds greatly exceeding the ASTM requirement for acceptable calibration.

After successful calibration, several other required performance measures were met before running the samples. First, a signal-to-noise (S/N) test was performed by running a 0.01% (m/m) of 1,4-dimethylbenzene in isooctane. The ASTM D5769 method requires a minimum S/N of five for this test. The 8860/5977 GC/MS system delivered a S/N of 16.2, as shown in Figure 4, showing no detrimental effect on method sensitivity with the 9 mm draw-out plate installed in the MS source.

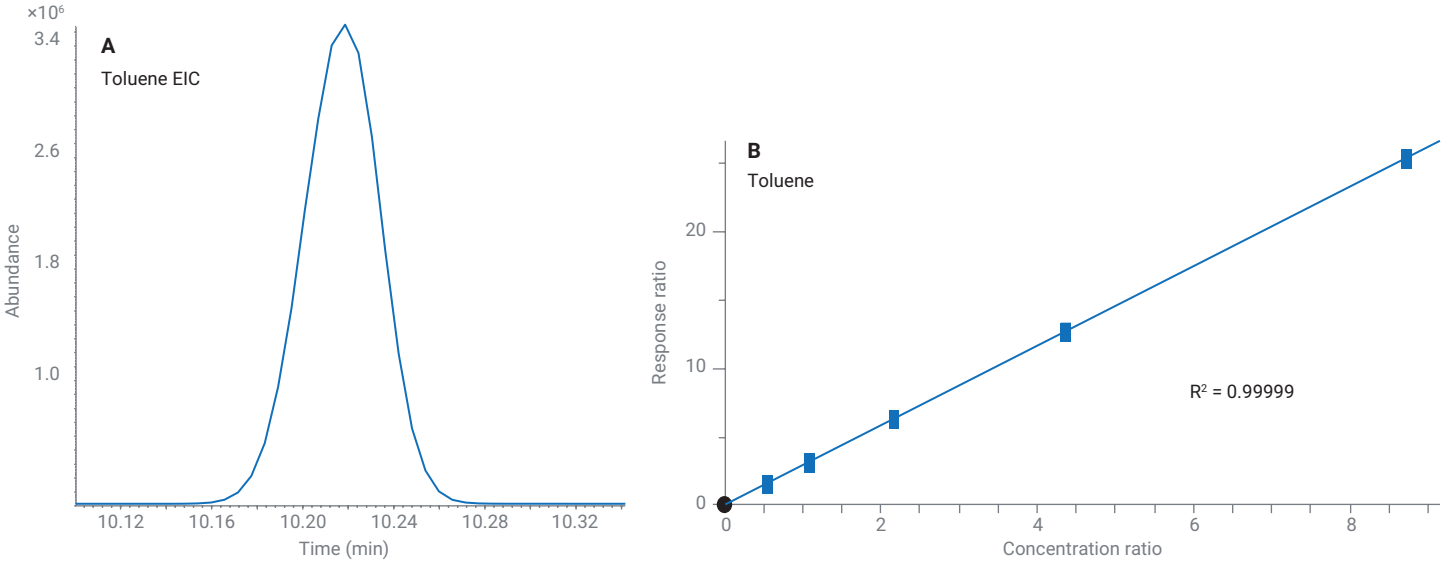

Figure 3. Improved peak shape and response for toluene was obtained using a 9 mm draw-out plate in the MS source (A). The resulting linear calibration now has an ideal R^2 of 0.99999 (B).

Table 4. Coefficients of determination.

Peak	Compound	R^2
2	Benzene	0.99992
3	Toluene	0.99999
5	Ethylbenzene	0.99990
6,7	*m,p*-Xylene	0.99996
8	*o*-Xylene	0.99999
9	1-Methylethylbenzene	0.99986
10	*n*-Propylbenzene	0.99997
11	1-Methyl-3-ethylbenzene	0.99996
12	1-Methyl-4-ethylbenzene	0.99993
13	1,3,5-Trimethylbenzene	0.99999
14	1-Methyl-2-ethylbenzene	0.99993
15	1,2,4-Trimethylbenzene	0.99998
16	1,2,3-Trimethylbenzene	0.99994
17	Indan	0.99999
18	1,4-Diethylbenzene	0.99996
19	*n*-Butylbenzene	0.99940
20	1,2-Diethylbenzene	0.99999
21	1,2,4,5-Tetramethylbenzene	0.99993
22	1,2,3,5-Tetramethylbenzene	0.99997
24	Naphthalene	0.99991
25	Pentamethylbenzene	0.99954
26	2-Methylnaphthalene	0.99988
27	1-Methylnaphthalene	0.99996

Two other performance tests, one for chromatographic resolution and another for mass spectral response, were also run using procedures described in the D5769 method. The 8860/5977 system passed the chromatographic resolution performance test as shown in Figure 5. The mass spectral response test using 1,2,3-trimethylbezene was also passed as shown in Table 5.

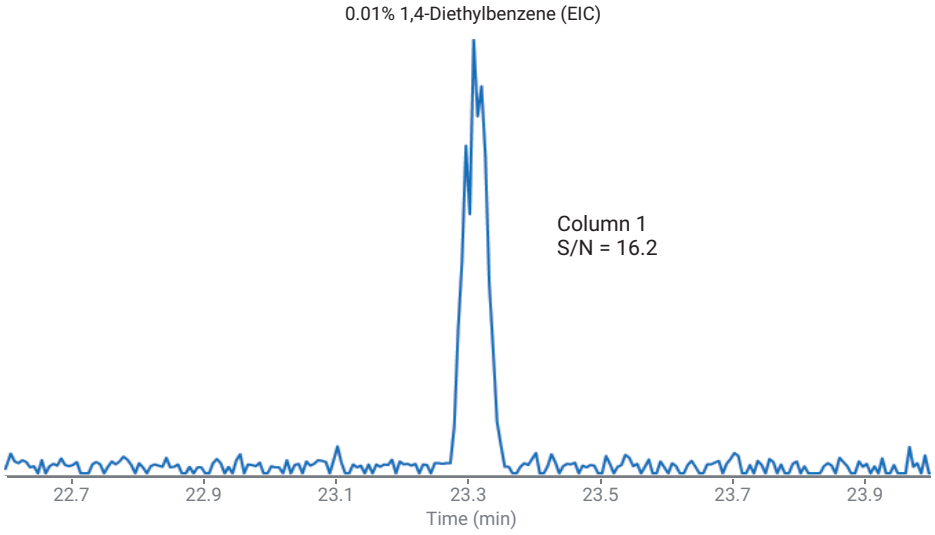

Figure 4. A signal-to-noise ratio of 16.2 exceeds the D5769 minimum required value of 5.

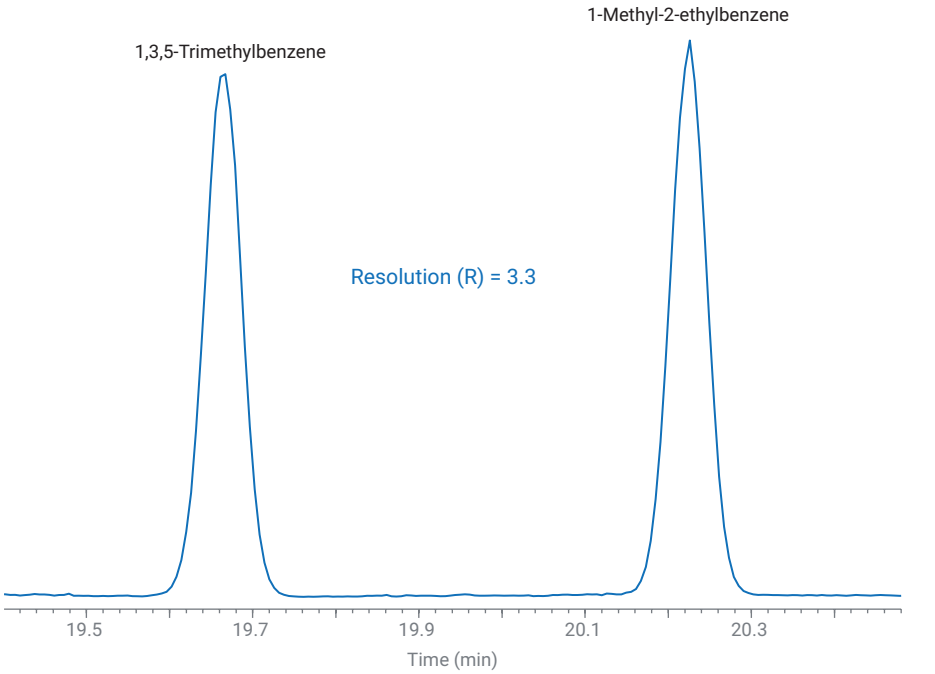

Figure 5. A resolution of 3.3 was measured for these two test compounds, exceeding the ASTM D5769 requirement of R = 2.

Table 5. Mass spectral response for 1,2,3-trimethylbenzene.

Ion (*m/z*)	Relative Intensity	
	Specification	Experimental
120	30 to 60	40
105	100	100
91	7 to 15	9

Before samples can be run, the D5769 method requires the analysis of a quality control test mix (Spectrum Quality Standards) containing certified amounts of eight aromatic compounds in a mixed saturated hydrocarbon matrix. Each aromatic compound must be within ±5% (m/m) of the reference value, except 1,2,4,5-tetramethylbenzene and naphthalene, which must be within ±10% (m/m). Table 6 lists the results obtained for the quality control test mix using the 8860/5977 GC/MS system. Each aromatic compound was quantified within the limits imposed by the D5769 method.

After successfully passing the performance tests and QC check, 10 replicates of two gasoline samples were run. Figure 6 shows representative TICs for each sample. Calculations were performed according to the ASTM D5769 method and the results reported for benzene, toluene, and total aromatics. Tables 7 and 8 list the results for each sample. The overall method precision was excellent, with low RSDs for each of the three reported values: benzene, toluene, and total aromatics.

Since both gasoline samples were used in an interlaboratory study (ILS), the average total aromatic results were published along with the standard deviations. For both samples, the 8860/5977 total aromatic results compare favorably with the ILS consensus results. Z-scores calculated for the 8860/5977 results were low, within one standard deviation of the average values reporting for the ILS. Again, this indicated exceptional agreement between the 8860/5977 results and the ILS results.

Table 6. Quality control test results.

	Percent (m/m)		
Component	Reference	Experimental	% Difference
Benzene	0.99	0.95	4.04%
Toluene	8.93	9.14	2.35%
m-Xylene	2.98	3.03	1.68%
o-Xylene	2.98	3.05	2.35%
Ethylbenzene	2.98	3.00	0.67%
1,2,4-Trimethylbenzene	2.98	3.07	3.02%
1,2,4,5-Tetramethylbenzene	1.99	2.08	4.52%
Naphthalene	1.00	0.97	3.00%

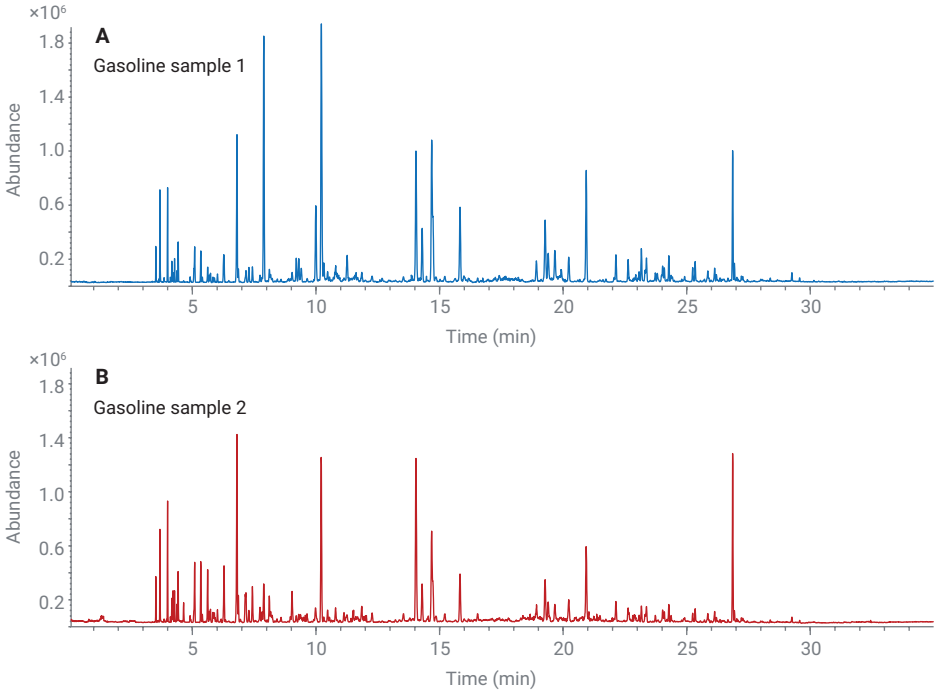

Figure 6. Total ion chromatograms (TICs) of two commercial reformulated gasoline samples used in an interlaboratory study (ILS).

Table 7. Sample 1 results.

	Average % (v/v)	Std. Dev.	RSD	Z-score
Benzene (8860/5977)	0.23	0.004	1.82%	
Toluene (8860/5977)	3.88	0.082	2.12%	
Total Aromatics (8860/5977)	19.65	0.255	1.30%	-0.51
Total Aromatics (ILS)	20.15	0.980	4.86%	

Table 8. Sample 2 results.

	Average % (v/v)	Std. Dev.	RSD	Z-score
Benzene (8860/5977)	0.47	0.007	1.48%	
Toluene (8860/5977)	3.26	0.042	1.30%	
Total Aromatics (8860/5977)	14.40	0.289	2.01%	-0.74
Total Aromatics (ILS)	14.82	0.570	3.85%	

Conclusion

The Agilent 8860/5977 GC/MS system was configured to run ASTM D5769 for the analysis of total aromatics in motor gasoline. This cost-effective system included a stainless-steel source modified to easily meet the D5769 calibration linearity requirements using the standard operating conditions published in the method. All D5769 performance and verification tests were also met. Replicate analysis of two reformulated gasoline samples showed outstanding precision and agreement with other laboratories analyzing these same samples.

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