Application Note

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Fast GC/MS Analysis for Benzene and Total Aromatic Content of Motor Gasoline

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Abstract

This application note presents the performance of an Agilent Intuvo 9000 GC configured for ASTM D5769 conditions.[1] GC/MS calibration was performed according to ASTM D5769 specifications. The system produced excellent precision based on sequential injections of a calibration check standard. Additionally, the system provided an excellent linear working range for toluene.

Introduction

ASTM standard method D5769 is for the determination of benzene and total aromatics in motor gasoline. The aromatic hydrocarbon composition of motor gasoline has a direct effect on the operating characteristics of the gasoline engine. The determination of benzene, toluene, and aromatics is necessary to ensure compliance with fuel specifications and regulations.

Obtaining an excellent linear calibration for toluene can pose operating challenges. The GC split flow and column performance must provide repeatable performance. This application note describes the performance of the Intuvo 9000 GC and Agilent 5977B GC/MSD when using ASTM D5769.

Experimental

Instrument configuration and operating conditions

An Agilent Intuvo 9000 GC (G3950A) and a 5977B GC/MSD were configured according to ASTM D5769 conditions. This system included an Agilent HP-RFG Intuvo GC column 20 m × 0.10 mm, 0.40 µm HP-RFG (G3909-63014). The configuration and operating conditions conform to ASTM D5769, as shown in Tables 1 and 2. The column oven temperature profile provides an 11.3-minute run time.

Calibration standards

The mass-based multipoint calibration standards used follow the recommended standard ASTM D5769 specifications. The high-level calibration standard contained 20.01 weight percent toluene. The toluene calibration range used extended beyond the D5769 criteria to demonstrate the linear operating range capability of the GC/MS system. The internal standard mixture contained benzene-d_6, ethylbenzene-d_{10}, and naphthalene-d_8, as defined in D5769.

Sample preparation

The sample preparation consisted of weighing the sample and internal standard in a GC autosampler vial. The sample size used was approximately 0.8 and 0.04 g of the internal standard mixture.

Table 1. Gas chromatograph conditions.

Parameter	Value
Split/Splitless Inlet	250 °C
Injection Volume	0.1 µL
Inlet Liner	Focus liner, 4 mm (p/n 210-4004-5)
Septum Purge Flow	3 mL/min
Spit Ratio	4000:1 (Adjust to obtain signal/noise ratio of at least 5 at mass 134)
Total Flow	403 mL/min
Carrier Gas	Helium
Intuvo GC inlet to Column Transfer	Jumper Chip (p/n G4587-60575)
Column Head Pressure	21.91 psi
Average Velocity	14.05 cm/sec
Ramped Flow	0.1 mL/min (hold 0.1 minutes), 1 mL/min
Column	Agilent HP-RFG Intuvo, 20 m × 0.100 mm, 0.4 µm (p/n G3903-63014)
Column Oven	50 °C (hold 0.5 minutes), ramp 20 °C/min to 100 °C (hold 0.0 minutes), ramp 5 °C/min to 120 °C (hold 0.0 minutes), ramp 30 °C/min to 250 °C (hold 0.0 minutes)

Table 2. Mass spectrometer conditions.

Parameter	Value
Acquisition Mode	Scan
Scanning Mode	Normal
Ionization Voltage	(eV) 70, fixed operating condition
Mass Scan Range	*m/z* 28.5 to 300
A/D Samples	4
MS Source	230 °C
MS Quadrupole	150 °C

Results and discussion

The performance was evaluated by 21 injections of an aromatic performance standard containing a mixture of aromatic compounds, as shown in Table 3. The repeatability of the system is excellent, with 1% or less RSD. The chromatogram of the aromatics performance standard is shown in Figure 1.

Table 3. Aromatic performance standard.

Compound Name	Mass %	% RSD
Benzene	2.49	0.73
Toluene	16.34	0.9
Ethylbenzene	4.86	0.85
p-Xylene	4.87	0.85
o-Xylene	5.04	0.85
Isopropylbenzene	2.45	0.93
1,3,5-Trimethylbenzene	2.42	0.85
2-Ethyltoluene	2.58	0.85
1,2,3-Trimethylbenzene	2.31	0.85
Indan	2.67	1.01
1,4-Diethylbenzene	2.96	0.85
1,2,4,5-Tetramethylbenzene	4.07	1.06
Total Aromatics	53.07	0.85

The HP-RFG phase column used in this study provided excellent resolution. Column resolution was tested by injecting a solution containing 3% each of 1,3,5-trimethylbenzene and 1-methyl-2-ethylbenzene. The system provided a resolution factor of 5.3, exceeding the required 2.0 resolution defined by D5769.

Standard D5769 allows for the use of a fourth internal standard, toluene-d_8, which is sometimes required when the GC/MS system cannot provide acceptable linearity. The use of toluene-d_8 poses a potential coelution issue with toluene. The GC/MS system was tested by injecting a standard prepared using toluene-d_8 and the chromatogram shown in Figure 2. The GC/MS system and HP-RFG column used provided near baseline resolution between toluene and toluene-d_8.

1. Benzene-d_6
2. Benzene
3. Ethylbenzene-d_{10}
4. Toluene
5. Ethylbenzene
6. 1,3-Dimethylbenzene, 1,4-Dimethylbenzene
7. 1,2-Dimethylbenzene
8. Isopropylbenzene
9. *n*-Propylbenzene
10. 1-Methyl-3-ethylbenzene
11. 1-Methyl-4-ethylbenzene
12. 1,3,5-Trimethylbenzene
13. 1-Methyl-2-ethylbenzene
14. 1,2,4-Trimethylbenzene
15. 1,2,3-Trimethylbenzene
16. Indan
17. Alkyl Indan group (not present)
18. Naphthalene-d_8
19. 1,4-Diethylbenzene, Butylbenzene
20. 1,2-Diethylbenzene
21. 1,2,4,5-Tetramethylbenzene
22. 1,2,3,5-Tetramethylbenzene
23. Naphthalene
24. 2-Methylnaphthalene
25. 1-Methylnaphthalene
26. C10-Benzene group (not present)
27. C11-Benzene group (not present)
28. C12-Benzene group (not present)

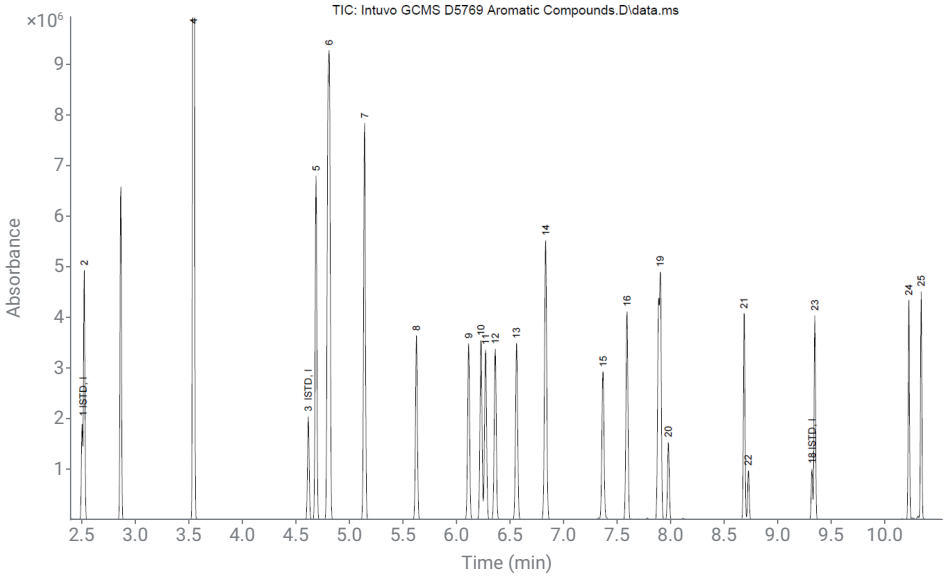

Figure 1. Aromatics performance standard.

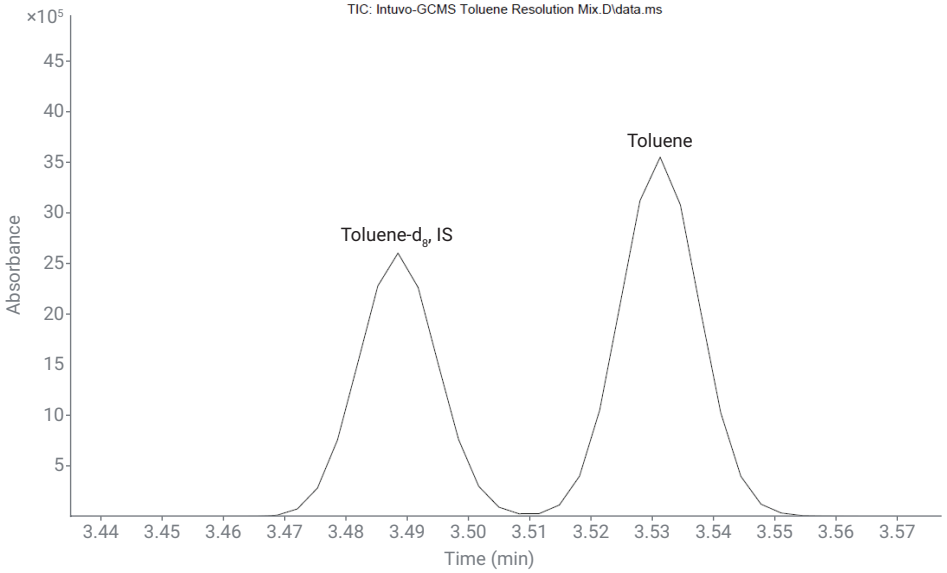

Figure 2. Toluene/toluene-d_8 resolution.

Linearity

The calibration standards used produced R^2 values of 0.999 for all compounds, except toluene. Establishing linear response for toluene can be challenging; the GC/MS system provided R^2 values of 0.997 for toluene in the 1.55 to 20.01 weight percent, as shown in Figure 3.

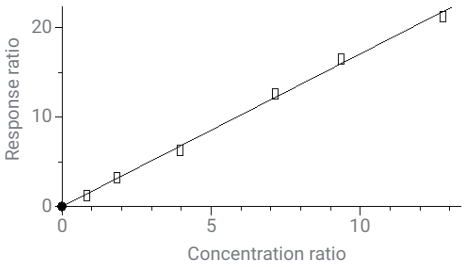

Figure 3. Toluene calibration response R^2 = 0.997.

Precision

Precision was investigated by analyzing 21 consecutive replicates of an aromatics performance standard to determine the relative standard deviation (RSD). RSD performance obtained for benzene, toluene, and total aromatics was 1.06% or less for all compounds, is shown in Table 3.

Verification

The GC/MS system configuration complied with ASTM D5769 specifications. The system validation consisted of testing several ASTM reformulated gasoline (RFG) performance test proficiency (PTP) samples. Mass spectral response performance testing using 1,2,3-trimethylbenzene produced excellent results and complied with ASTM D5769, as shown in Table 4. The calibration was verified using a calibration check standard as defined in ASTM D5769. The results of testing the quality control check standard demonstrated excellent agreement with the gravimetric concentrations, as shown in Table 5. The results of ASTM RFG PTP samples are shown in Table 6. The benzene and total aromatic test results obtained by testing the ASTM RFG PTP samples showed excellent agreement and were all within Z-score values, as shown in Table 6. The example chromatogram obtained by testing a sample of ASTM RFG #1810 motor gasoline is shown in Figure 4.

Table 4. Mass spectral response for three ions derived from % 1,2,3-trimethylbenzene.

Ion (*m/z*)	Expected Relative Intensity	Relative Intensity Obtained
120	30 to 60	43
105	100	100
91	7 to 15	12

Table 5. Quality control standard.

Compound Name	Expected Mass %	Results Mass %
Benzene	1	0.99
Toluene	9	9.12
1,3-Diethylbenzene	3	2.98
1,2-Diethylbenzene	3	3.01
Ethylbenzene	3	3.08
1,2,4-Trimethylbenzene	3	2.95
1,2,4,5-Trimethylbenzene	2	2.18
Naphthalene	1	0.97
Total Aromatics	25	25.28

Table 6. ASTM RFG proficiency testing.

	ASTM RFG Proficiency Samples					
ASTM RFG PTP Data	**#1706**	**#1707**	**#1709**	**#1711**	**#1808**	**#1810**
Benzene (vol.%)	0.531	0.466	0.525	0.496	0.379	0.845
Toluene (vol.%)	3.38	2.12	4.55	3.11	1.84	4.74
Total aromatics (vol.%)	18.58	15.31	22.3	15.13	15.7	18.65
Intuvo GC/MS Results	**#1706**	**#1707**	**#1709**	**#1711**	**#1808**	**#1810**
Benzene (vol.%)	0.50	0.46	0.51	0.49	0.35	0.86
Toluene (vol.%)	3.39	2.22	4.68	3.30	1.77	4.94
Total aromatics (vol.%)	19.27	17.46	23.64	16.5	15.94	19.95

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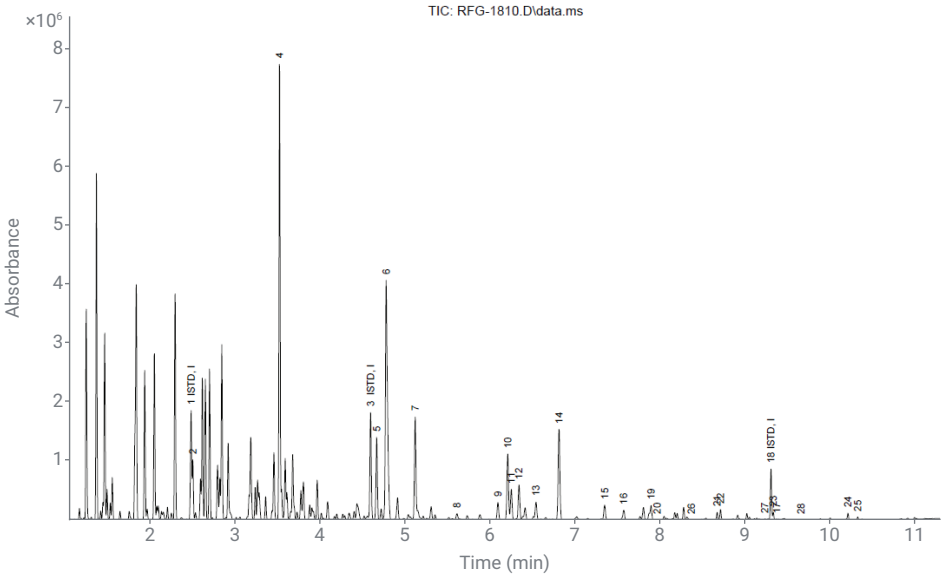

Figure 4. ASTM RFG #1810.

Conclusion

The Intuvo 9000 GC configured with the 5977B GC/MSD has proven to be an effective system for meeting the specifications defined within ASTM D5769. The exceptional performance demonstrated provides a very high level of precision and dynamic range for benzene, toluene, and total aromatics. The conditions used for this method enable a fast 11.3-minute run time. The ASTM RFG PTP sample testing results were in excellent agreement with industry results.

Reference

1. ASTM D5769-15, Standard Test Method for Determination of Benzene, Toluene, and Total Aromatics in Finished Gasolines by Gas Chromatography/Mass Spectrometry, ASTM International, West Conshohocken, PA, **2015**, www.astm.org

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