

Title: GC/MS Analysis for Aromatic Content of gasoline

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Abstracts

The performance of an Agilent Intuvo 9000 GC set under ASTM D5769 conditions is presented in this application note. The GC/MS calibration was carried out in accordance with ASTM D5769 requirements. 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.

2. Experimental

2.1. 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.

2.2. 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-d6, ethylbenzene-d10, and naphthalene-d8, as defined in D5769.

2.3. 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 chromatographic 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, 0.4µm (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
Mass Scan Range	m/z 28.5 to 300
A/D samples	4
MS Source	230 °C
MS Quadrupole	150 °C

3. 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
sopropylbenzene	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-d₈, which is sometimes required when the GC/MS system cannot provide acceptable linearity. The use of toluene-d₈ poses a potential coelution issue with toluene. The GC/MS system was tested by injecting a standard prepared using toluene-d₈ and the chromatogram shown in Figure 2. The GC/MS system and HP-RFG column used provided near baseline resolution between toluene and toluene-d₈.

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

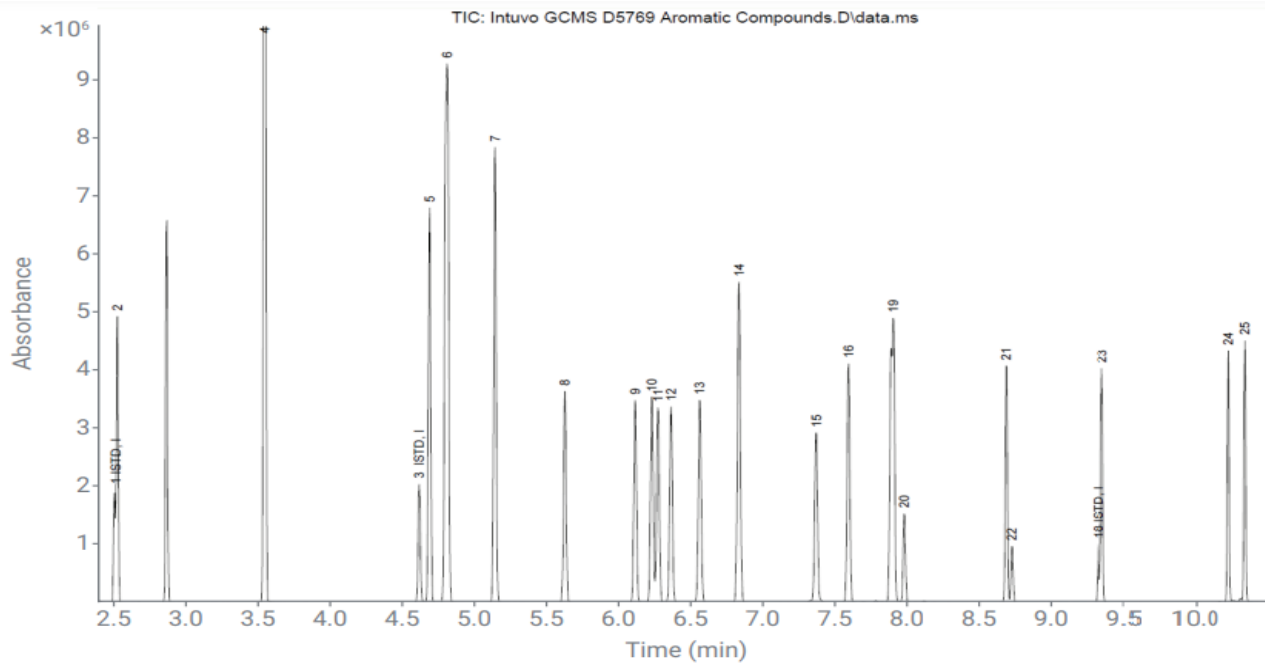


Figure 1 Aromatic performance standard

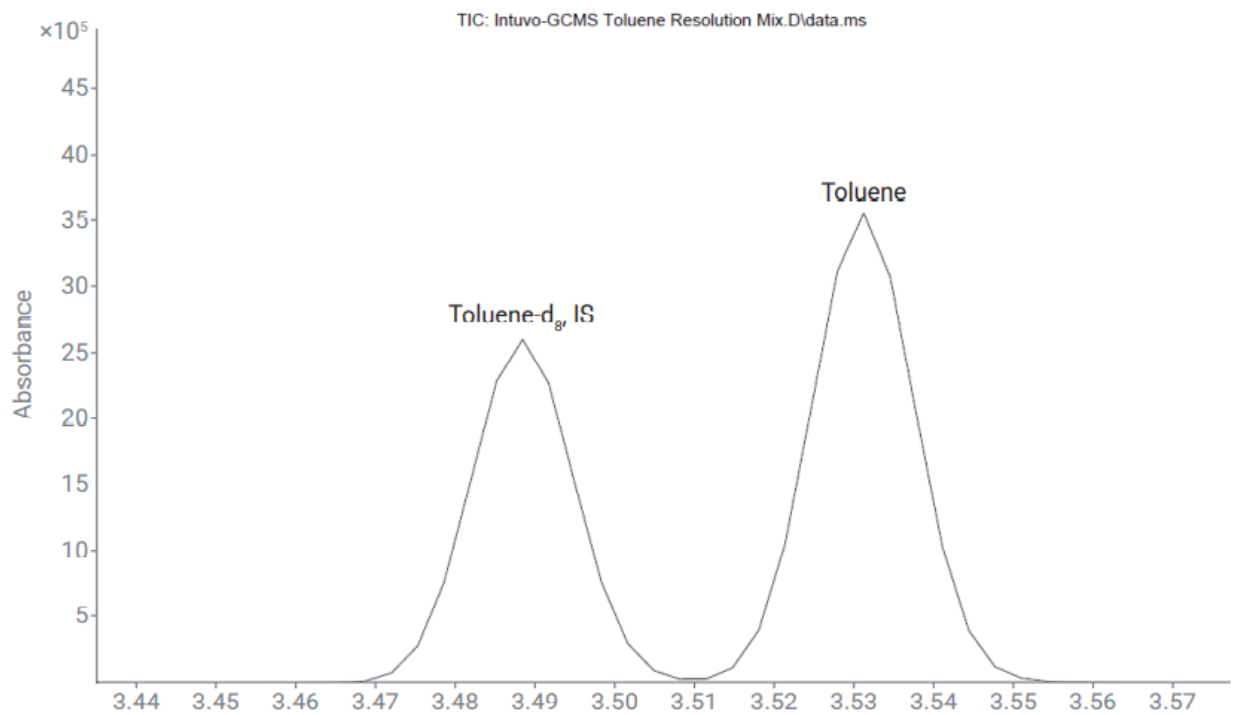


Figure 2 Toluene/Toluene d_8 resolution

3.1. Linearity

The calibration standards used produced R2 values of 0.999 for all compounds, except toluene. Establishing linear response for toluene can be challenging; the GC/MS system provided R2 values of 0.997 for toluene in the 1.55 to 20.01 weight percent, as shown in Figure 3.

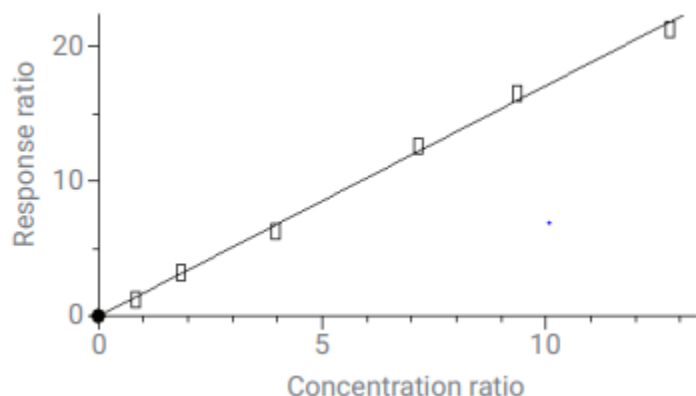


Figure 3 Toluene calibration response $R^2 = 0.997$

3.2. 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

3.3. 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 PTP Data	ASTM RFG Proficiency Samples					
	#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

4. 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.