

Industrial

Analysis of aromatics in gasoline by ASTM D5769 using gas chromatography–single quadrupole mass spectrometry

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Keywords

Benzene, toluene, total aromatics,
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Goal

The goal of this application note is to demonstrate the capability of the Thermo Scientific™ ISQ™ 7610 single quadrupole GC-MS to deliver accurate quantitation of aromatics in gasoline in accordance with ASTM Method D5769.

Introduction

Monocyclic aromatics, unsaturated hydrocarbons containing a benzene ring, are inherent components of gasoline refined from crude oil. Refineries manipulate the content of aromatics in gasoline to increase the octane rating and overall performance. However, there is considerable concern over the current allowable content of aromatics in gasoline, with growing evidence of their detrimental effects on human and environmental health. The content of benzene, a known carcinogen, in gasoline is restricted to 1.0%^{1,2} with total content of aromatics not to exceed 42%². Thus, gasoline producers must be able to accurately assess fuel purity to ensure compliance with regulatory standards.

The ASTM Method D5769 is a standardized method for the determination of aromatics in gasoline by gas chromatography-mass spectrometry (GC-MS).³ A major challenge of performing this analysis is the high content (%vol) of individual aromatics present, which can cause instrument detector saturation. This can result in a non-linear response in the concentration range of gasoline samples, yielding inaccurate quantitation.

In this application note, the performance of the ISQ 7610 single quadrupole GC-MS towards the analysis of aromatics in gasoline is highlighted. Using the new Thermo Scientific™ XLXR™ (extend life, extended range) detector system, saturation was avoided at %vol concentration levels with linear response over the entire calibration range without ion source or hardware modifications. The XLXR detector system consists of a new electron multiplier design and new electronics that enable higher linear dynamic range.⁴ Additional criteria specified by ASTM Method D5769 regarding resolution, sensitivity, spectral and sample accuracy were all achieved, demonstrating the suitability of the ISQ 7610 GC-MS for the analysis of aromatics using ASTM Method D5769.

Experimental

Standard and sample preparation

Reagent quality used in standard and sample preparation adhered to the criteria outlined in ASTM Method D5769. The following standards were purchased through Accustandard, (USA):

- Deuterated internal standard mixtures (P/N D-5769-CAL6-IS-R-SET)
- Resolution criteria standard of 3% wet weight (w/w) of 1-methyl-2-ethylbenzene and 1,3,5-trimethylbenzene (M-GRA-Res)
- Fragmentation pattern criteria standard of 3% w/w 1,2,3-trimethylbenzene (M-GRA-FP)
- Sensitivity criteria solution 0.01% w/w 1,4-diethylbenzene in isooctane (M-GRA-ST)
- Daily quality control standard (M-5769-QC-IS-5 ML)

All solutions were prepared in iso-octane with targeted analytes outlined in Table 1. Analytes were quantified using a 6-point calibration curve with internal standard calibration. The calibration range was analyte-dependent, ranging between 0.17 to 5.56% w/w, with exception to toluene, where calibration standards between 1.4 to 17.7% w/w were assessed. Accuracy and

Table 1. Compound quantification and confirmation ions, percent relative standard deviation (%RSD), and coefficient of determination

Compound	Quantification ion (m/z)	Confirming ion 1 (m/z)	Confirming ion 2 (m/z)	%RSD	Coefficient of determination (r ²)
1. Benzene-d ₆ (ISTD)	84, 83	82	56	-	-
2. Benzene	78	77	79	2.2	0.99921
3. Toluene-d ₈ (ISTD)	100, 99	98	70	-	-
4. Toluene	92	91	89	2.8	0.99849
5. Ethylbenzene-d ₁₀ (ISTD)	116, 115	98	70	-	-
6. Ethylbenzene	106	91	105	3.1	0.99831
7. <i>m</i> -Xylene + <i>p</i> -Xylene	106	91	105	2.3	0.99902
8. <i>o</i> -Xylene	106	91	105	3.1	0.99829
9. Isopropylbenzene	120	105	77	3.1	0.99829
10. <i>n</i> -Propylbenzene	120	91	92	3.2	0.99808
11. 3-Ethyltoluene	120	105	91	2.5	0.99889
12. 4-Ethyltoluene	120	105	91	4.9	0.99542
13. 1,3,5-Trimethylbenzene	120	105	119	4.8	0.9957
14. 2-Ethyltoluene	120	105	91	4.1	0.99693
15. 1,2,4-Trimethylbenzene	120	105	119	4	0.99705
16. 1,2,3-Trimethylbenzene	120	105	119	3.5	0.99772
17. Indan	117	118	115	5.8	0.99344
18. 1,4-Diethylbenzene + <i>n</i> -Butylbenzene	134	105	91	0.6	0.99993
19. 1,2-Diethylbenzene	134	105	91	1	0.99984
20. 1,2,4,5-Tetramethylbenzene	134	120	91	1	0.99981
21. 1,2,3,5-Tetramethylbenzene	134	120	91	1.7	0.99948
22. Naphthalene-d ₈ (ISTD)	136, 135	137	108	-	-
23. Naphthalene	128	127	102	0.5	0.99996
24. Naphthalene, 2-methyl-	142	141	115	1.3	0.9997
25. Naphthalene, 1-methyl-	142	141	115	2.8	0.99856

ISTD – Internal standard

precision were evaluated through the analysis of a gasoline proficiency sample (RFG-2101) obtained from an interlaboratory study.

Instrument and method setup

Details on the instrumental configuration of the ISQ 7610 GC-MS are provided in Tables 2 and 3. Automated liquid injection was carried out by a Thermo Scientific™ AI/AS 1610 autosampler with a 0.5 µL syringe (P/N 36504045). Chromatographic separation of targeted aromatics was performed on the Thermo Scientific™ TRACE™ 1610 GC equipped with a Thermo Scientific™ TraceGOLD™ TG-1MS 20 m x 0.18 mm i.d. x 0.40 µm film capillary column (P/N 26099-5680). Sample analysis was performed in full scan acquisition.

Table 2. GC injection and column conditions

Trace 1610 GC system parameters	
Injection volume (µL)	0.2
Liner	Thermo Scientific™ Straight liner with quartz wool, 4 mm (P/N 453A2265)
Injection mode	Split
Split ratio	1:500
Injector temperature (°C)	300
Carrier gas, (mL·min ⁻¹)	He, 0.5 (constant flow)
Oven temperature program	
Initial temperature (°C)	35
Hold time (min)	1
Temperature 1 (°C)	210
Rate (°C·min ⁻¹)	25
Hold time (min)	1
Total run time (min)	9

Table 3. Mass spectrometer conditions for using simultaneous full scan and timed acquisition (t-SIM)

ISQ single quadrupole GC-MS parameters	
Transfer line (°C)	280
Thermo Scientific™ ExtractaBrite™ ion source (°C)	300
Ionization mode	EI
Electron energy (eV)	70
Full scan range (<i>m/z</i>)	45–300
Full scan time (s)	0.1
Emission current (µA)	10
Detector gain (V)	1.0e ⁵

Results and discussion

Chromatography and resolution

Chromatographic separation of the targeted analytes was achieved in under 8 min (Figure 1). Although chromatographic separation between the deuterated internal standards of benzene and naphthalene could not be completely achieved, the analytes can be easily identified based on mass selective separation. A resolution of 3.23 was achieved between 3% w/w solution of 1,3,5-trimethylbenzene and 2-ethyltoluene, surpassing the resolution criteria of 2 described in ASTM Method D5769 (Figure 2).

Linearity and sensitivity

Despite the high concentration levels (%vol) applied for the investigated analyte calibration ranges, coefficients of determination of 0.99 or greater were achieved without the need for detector modifications (Table 1). An example of this can be observed with toluene, whose calibration range extends from 1.4 to 17.7% vol due to its high content present in gasoline (Figure 3). High linearity is observed over the entire calibration range for toluene ($r^2 = 0.9985$) with no evidence of detector saturation at the highest calibration point and demonstrates the high dynamic linear response of the XLXR detector.

In addition to providing high selectivity at the %vol concentration ranges, high sensitivity is also achieved using the XLXR detector. The ASTM Method D5769 sensitivity criteria require a signal to noise (S/N) ratio of 5 or greater for a 0.01% w/w solution of 1-4-diethylbenzene. Using the ISQ 7610 GC-MS system, a S/N ratio of 48 is achieved (Figure 4), well surpassing sensitivity requirements.

Spectral accuracy

Mass spectrometer calibration and spectral accuracy are important for confirmation and identification of aromatics present in gasoline samples. Criteria listed under ASTM Method D5769 are provided in Figure 5 together with results obtained from the analysis of 1,2,3-trimethylbenzene (3% w/w) using the ISQ 7610 GC-MS system. Fragmentation results and compliance with method criteria are automatically generated in Chromeleon CDS, simplifying the analyst's assessment of analysis accuracy.

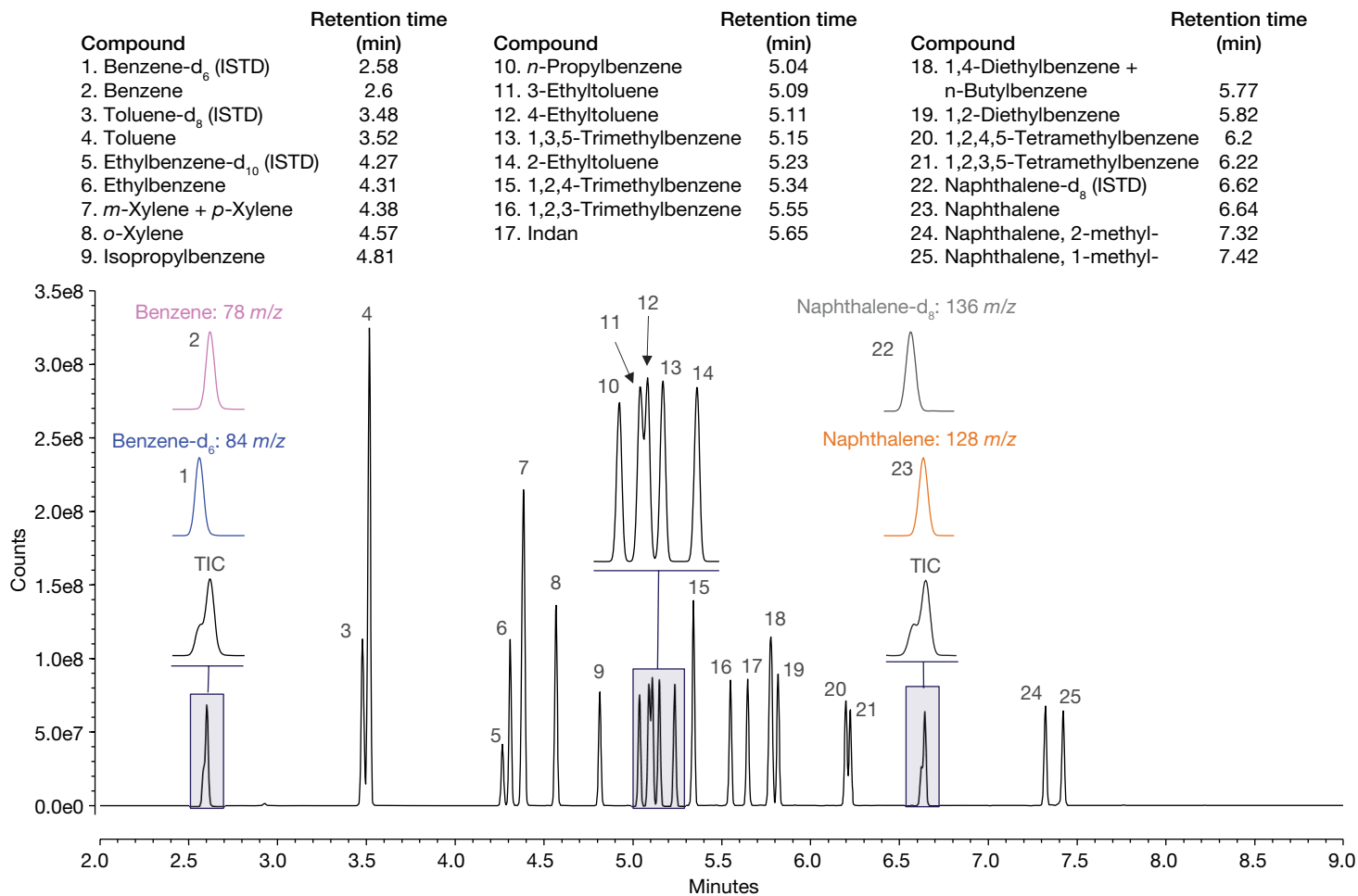


Figure 1. Full scan acquisition of the highest calibration standard for targeted aromatics

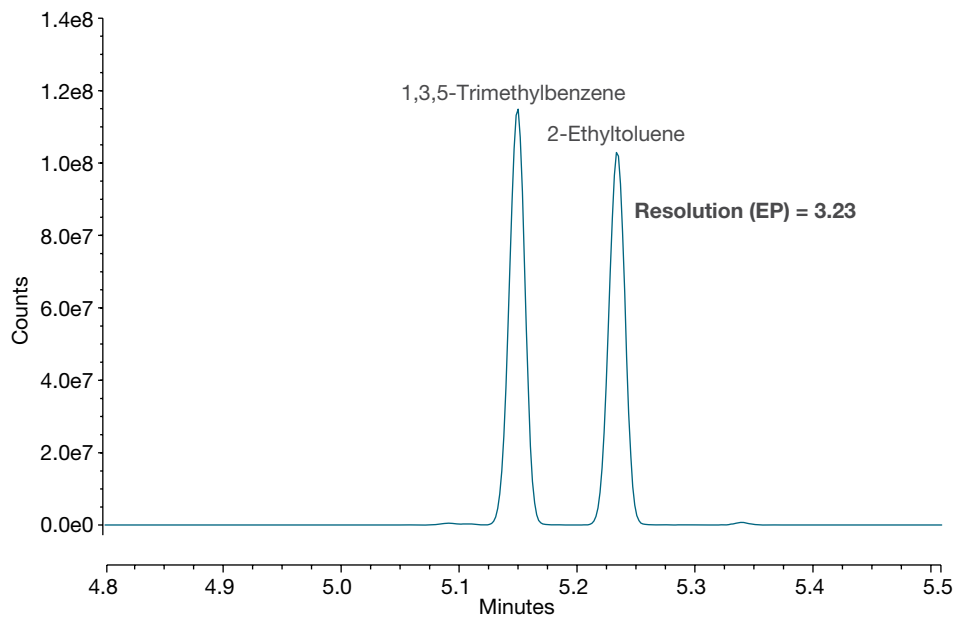


Figure 2. Chromatographic resolution between 3% w/w solution of 1, 2, 5- trimethylbenzene and 2-ethyltoluene

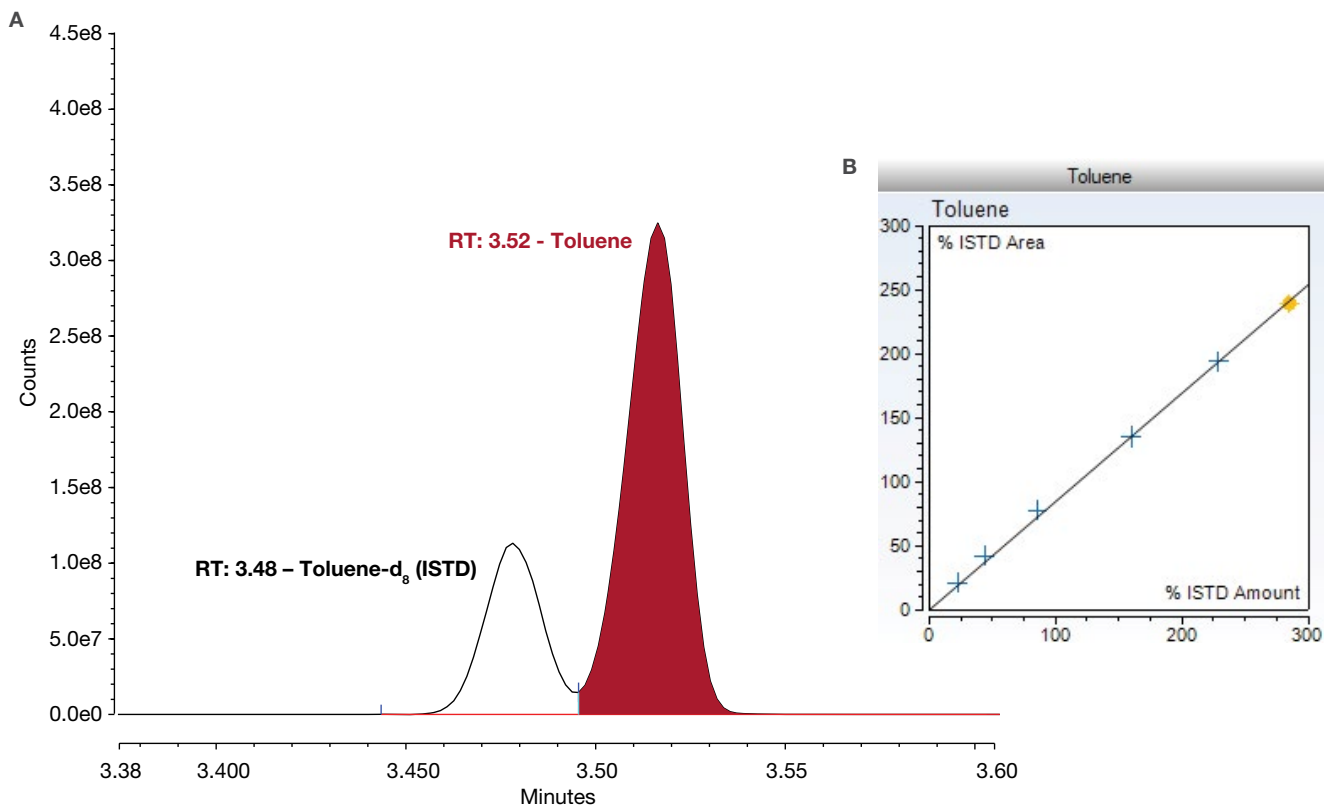


Figure 3. Chromatographic separation of toluene and deuterated toluene internal standard in the highest calibration point (17.7% vol) (A) and its calibration curve (B)

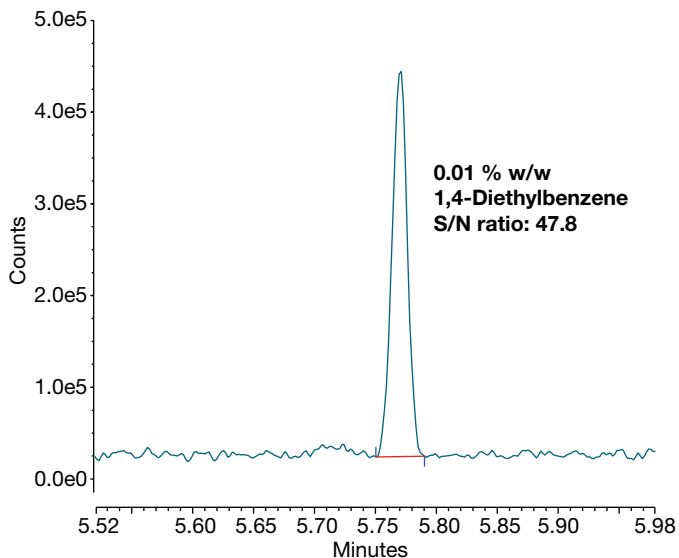


Figure 4. Chromatogram of 0.01% 1, 4-diethylbenzene sensitivity check solution

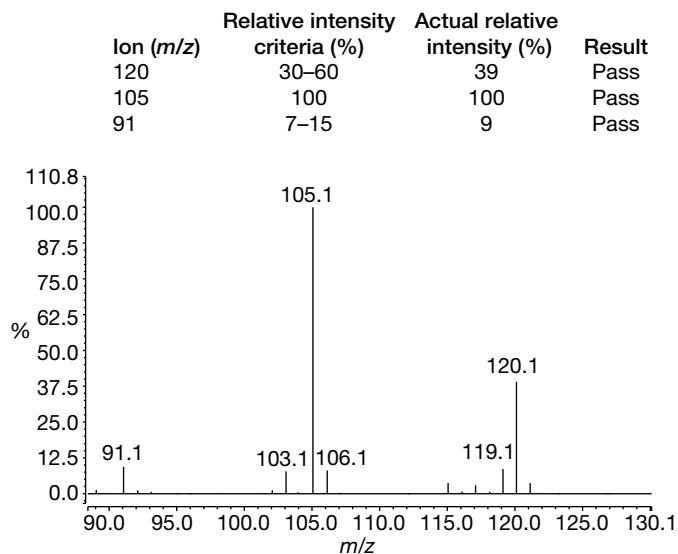


Figure 5. Mass spectrum of 1, 2, 3-trimethylbenzene with measured relative intensity of *m/z* 120, 105, and 91 comparisons to ASTM Method D5769 criteria

Sample accuracy

To ensure accuracy of the results delivered by the ISQ 7610 GC-MS system, a quality reference control standard was analyzed using the method described here. To fulfill the criteria of ASTM Method D5769, quantified results must be within 5% of the certified reference values of the standard with the exception of 1,2,3,4-tetramethylbenzene and naphthalene, which should be within 10%. Results from the quality reference control standard show all aromatics detected were less than 5%, including 1,2,3,4-tetramethylbenzene and naphthalene (Figure 6).

Method accuracy was also evaluated using a gasoline sample (RFG 2101) obtained from an interlaboratory study (Figure 7).

Results obtained for benzene, toluene, and total aromatics were within 1 standard deviation from the true sample mean, demonstrating the accuracy of the applied method.

Advanced GC-MS technology enabling productivity

The TRACE 1600 series GC has a modular detector and injector design. This allows exchange within minutes, providing versatility towards different analysis requirements or maintenance offline without interrupting system operation. The modular design allows for dedicated injectors and detectors for a specific analysis, enabling efficient use of the GC system while significantly minimizing downtime and maximizing productivity.

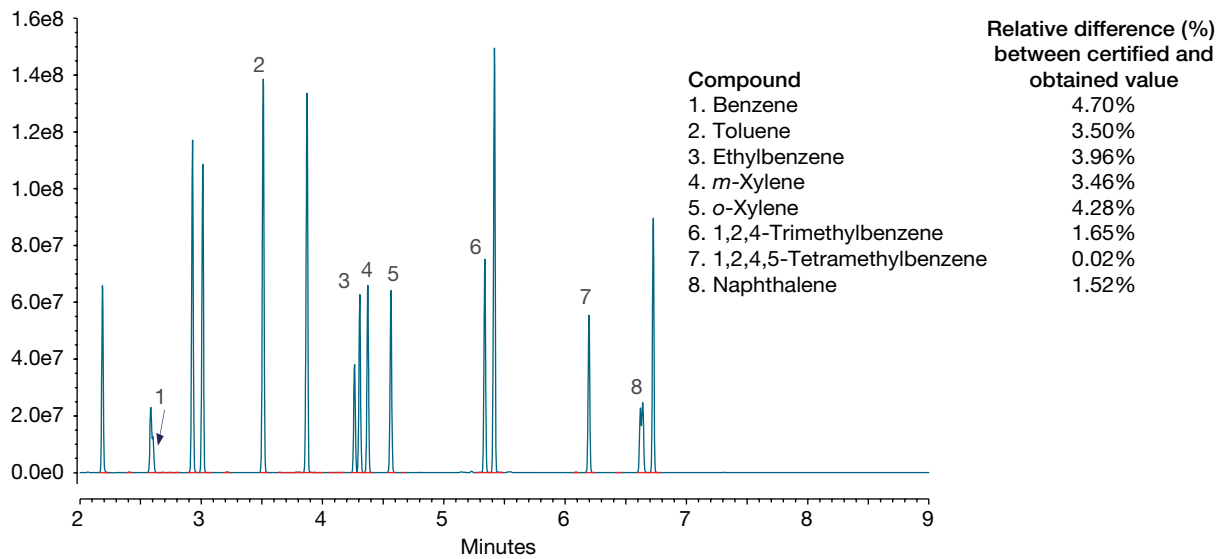


Figure 6. Chromatogram and relative difference (%) obtained from the quality control reference standard

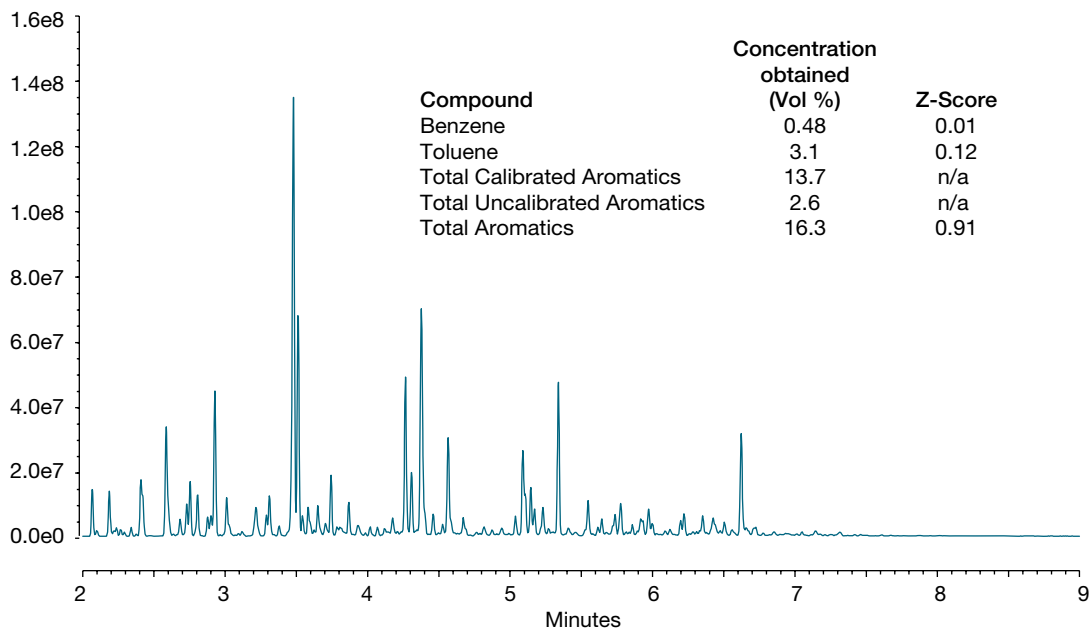


Figure 7. Chromatogram, concentrations, and z-score obtained from the interlaboratory gasoline sample RFG 2101

The ISQ 7610 GC-MS system is available with Thermo Scientific™ NeverVent™ technology, which includes the proprietary vacuum probe interlock (VPI) and the V-lock. This allows ion source cleaning or column replacement to be performed quickly without breaking the MS vacuum. Figure 8 shows the VPI being removed from the ISQ 7610 GC-MS system. NeverVent technology was specifically designed to simplify maintenance and maximize instrument uptime. After ionization source cleaning or column exchange with NeverVent technology, the system is ready to run samples within hours and not days.



Figure 8. VPI being removed from the ISQ 7610 GC-MS system

Conclusion

This application note demonstrates the suitability of the ISQ 7610 single quadrupole GC-MS system for accurate quantification of individual and total aromatics at high concentrations within gasoline.

- Separation of targeted aromatics achieved in under 8 minutes while meeting resolution (R_s) requirements between 1,3,5-trimethylbenzene and 2-ethyltoluene ($R_s > 2$).
- Linear response observed at %vol concentrations without of detector saturation.
- Sensitivity obtained by the ISQ 7610 GC-MS system was a factor of 9 times greater than criteria outlined by ASTM Method D5769.
- Ion ratios for 1,2,3-trimethylbenzene passed the method criteria ranges for relative intensity.
- Accurate quantitation was achieved with both a quality control reference standard and interlaboratory gasoline sample, with deviation from reference values well within accepted criteria.

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