

Full Scan Quantitative Analysis of Semivolatile Organic Compounds

Evaluating the performance of an Agilent 7000D GC/TQ in full scan data acquisition mode for SVOCs analysis

Authors

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Abstract

The Agilent 7000D triple quadrupole GC/MS system (GC/TQ) operating in full scan data acquisition mode was used for the quantitative analysis of semivolatile organic compounds (SVOCs) in environmental samples. Under appropriately selected operating conditions, the GC/TQ system was shown to provide excellent spectral library matching scores, high sensitivity, and linearity over a wide dynamic range. The retention time locking (RTL) functionality enabled the same retention times with the GC/TQ and the GC/MSD systems, hence, simplifying the review process. This application note provides the guidelines for data acquisition and processing with GC/TQ operating in full scan data acquisition mode. Following these guidelines, the full scan performance of the GC/TQ was comparable to that of the single quadrupole GC/MSD system when tested for the analysis of SVOCs over a working range of 0.4 to 100 ppm.

Introduction

The analysis of SVOCs by GC/MS is challenging due to the array of target analytes, including bases, neutrals, and acids that span broad molecular weight and boiling point ranges. EPA Method 8270D/E provides guidelines for conditions and quality control checks to facilitate successful analysis of SVOCs using GC/MS.¹ A previous application note² describes the use of the Agilent 5977 GC/MSD operated in full scan data acquisition mode, coupled to the Agilent 7890B GC, to meet the performance requirements and be in compliance with USEPA Method 8270D/E with calibration over a working range of 0.2 to 160 ppm in a single method. EPA 8270E revision 6 was the first version of the method to include use of GC/MS/MS (GC/TQ) for the analysis of SVOCs. GC/TQ operated in multiple reaction monitoring (MRM) mode delivers increased sensitivity, high selectivity afforded by MRM, robust data, and faster batch review due to the elimination of matrix interferences compared to GC/MSD as demonstrated in a previous application note.³ If needed for a standard operating procedure (SOP), method validation, or sample screening, the GC/TQ can also be used in full scan data acquisition mode.

This study demonstrates that the 7000D GC/TQ system operating in full scan mode can be used to identify compounds using spectral library matching, with comparable performance to GC/MSD. This application note outlines the best practices for full scan data acquisition and processing using GC/TQ. The objective was to achieve excellent spectral library matching scores over 90, high sensitivity with limits of detection (LODs) at or below 50 ppb for most compounds, and linearity over a wide dynamic range of 0.4 to 100 ppm.

Experimental

The GC/TQ and GC/MSD systems used in this work were configured to achieve the best performance for the analysis of SVOCs as described in two previous studies.^{2,3} The Agilent 7890B GC was coupled to either a 7000D GC/TQ or a 5977 Series GC/MSD, both equipped with an Inert Plus EI source, as shown in Figure 1A. The GC was equipped with a split/splitless (SSL) inlet, low pressure-drop (LPD) GC inlet liner (part number 5190-2295) shown in Figure 1B, and a 30 m × 0.25 mm,

0.25 μm 5% phenyl (polysiloxane) column for best separation (part number DB-UI 8270D). The instrument operating parameters are listed in Table 1.

The 9 mm diameter extractor lens (part number G3870-20449) was used with both the GC/TQ and GC/MSD systems, as the lens was shown to greatly enhance method performance in SVOCs analysis.³

The injection volume was 1 μL in split mode, with a split ratio of 10:1 for GC/TQ, and pulsed split mode, with a split ratio of 5:1 for GC/MSD. The split ratio was optimized to meet the resolution requirement for benzo[b]fluoranthene and benzo[k]fluoranthene as specified in method 8270. The TQ was tuned with Atunes.eiex.tune.xml and the MSD was tuned with Atune.u. The electron multiplier gain setting was set to 1 for the GC/TQ and 0.3 for the GC/MSD. These settings ensured that the tallest peak in the base peak chromatogram (BPC) for the highest-level calibration standard used was in the range of 3 to 6 × 10⁷ counts for GC/TQ and 3 to 6 × 10⁶ counts for GC/MSD.

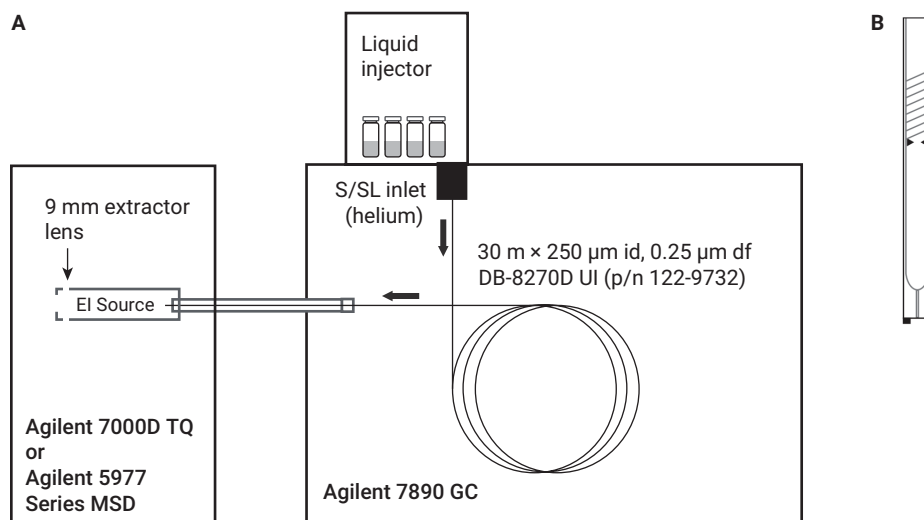


Figure 1. (A) Configuration of the Agilent 7890/7000D GC/TQ or Agilent 7890/5977 Series GC/MSD. (B) Ultra Inert (UI) Universal Low Pressure Drop Liner (part number 5190-2295).

Table 1. Gas chromatograph and mass spectrometer conditions for SVOCs analysis using GC/TQ and GC/MSD.

	GC/TQ	GC/MSD
GC		
Model	Agilent 7890 with fast oven, autoinjector, and tray	
Inlet	Split/splitless inlet (SSL)	
Mode	Split	Pulsed Split
Split Ratio	10:1	5:1
Injection Pulse Pressure	–	30 psi until 0.6 min
Septum Purge Flow	3 mL/min	
Injection Volume	1.0 µL	
Injection Type	Standard	
L1 Air Gap	0.2 µL	
Inlet Temperature	280 °C	
Carrier Gas	Helium	
Inlet Liner	Agilent universal low pressure drop liner, with glass wool (p/n 5190-2295)	
Oven		
Gradient	40 °C, hold 0.5 min, 10 °C/min to 100 °C, 25 °C/min to 260 °C, 5 °C/min to 280 °C	
Total Run Time	21.567 min	
Postrun Time	0 min	
Equilibration Time	0.5 min	
Column 1		
Type	Agilent DB-8270D UI, 30 m × 0.25 mm, 0.25 µm (p/n 122-9732)	
Control Mode	Constant flow	
Flow	0.992 mL/min	1.292 mL/min
Inlet Connection	Split/splitless inlet (SSL)	
Outlet Connection	MSD	
MS		
Model	Agilent 7000D TQ	Agilent 5977 Series MSD
Source	Agilent Inert Extractor Source with a 9 mm extractor lens	
Extraction Lens	9 mm (p/n G3870-20449)	
Vacuum Pump	Performance turbo	
Tune File	Atunes.eiex.tune.xml	Atune.u
Mode	MS1 Scan	Scan
Start Mass	35	
End Mass	500	
Scan Speed	220 ms	N = 2
Time Filter	On	–
Solvent Delay	2.5 min	
EM Voltage Gain Mode	1	0.3
Quad Temperature (MS1 and MS2)	150 °C	180 °C
Source Temperature	300 °C	
Transfer line Temperature	320 °C	
He Quench Gas	2.25 mL/min	–
N ₂ Collision Gas	1.5 mL/min	–

For GC/TQ full scan acquisition mode, the following parameters were selected: MS1 Scan, 35 to 500 m/z , 220 ms scan speed, time filter – ON. These parameters were set in the TQ MS method editor of Agilent MassHunter workstation software, as shown in Figure 2. The default parameters were used for collision cell gases, i.e., 2.25 mL/min and 1.5 mL/min for He quench gas and N_2 collision gas, respectively.

For GC/TQ analysis in full scan data acquisition mode, 12 calibration levels were prepared from 0.4 to 100 ppm using a 68-compound mix and six internal standards (ISTDs). ISTD concentration was at the midpoint, at 20 ppm. LODs were calculated using a 0.5 ppm calibration standard injected in a split mode with a split ratio of 10:1, nine consecutive times. MassHunter workstation software was used for data acquisition and processing.

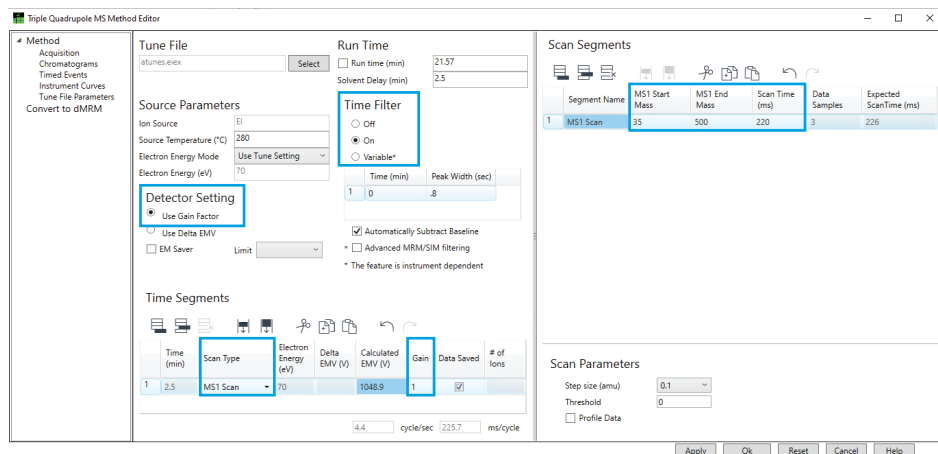


Figure 2. TQ MS Method Editor showing the full scan acquisition parameters used in this work.

Results and discussion

The use of GC/TQ operated in MRM for EPA 8270E SVOCs analysis is described in a previous application note.³ The aim of this study was to show that the Agilent 7000D GC/TQ system operating in full scan mode can be used to identify compounds using spectral library matching and quantitate them, with comparable performance to GC/MSD.

This application note outlines the best practices for full scan data acquisition and processing using GC/TQ.

The performance of GC/TQ operated in full scan acquisition mode for SVOCs analysis was compared to that of GC/MSD operating in scan mode. Figure 3 shows a total ion chromatogram (TIC) for full scan data acquired with GC/TQ for a 1 ppm standard with a 10:1

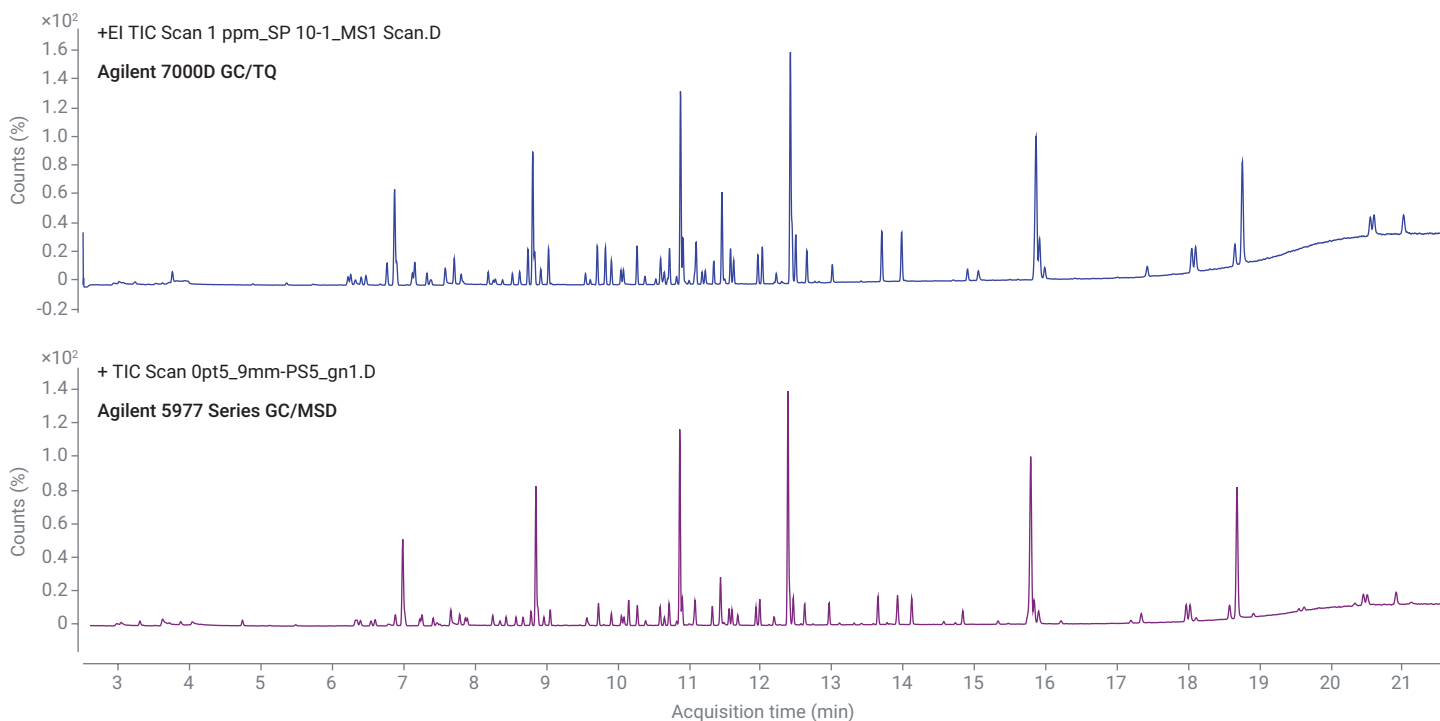


Figure 3. Scan TIC for a 1 ppm standard with a 10:1 split (0.1 ng on-column) analyzed with Agilent 7890/7000D GC/TQ (top). Scan TIC for a 0.5 ppm standard with a 5:1 pulsed split (0.1 ng on-column) analyzed with Agilent 7890/5977 Series GC/MSD (bottom).

split (0.1 ng on-column). A TIC acquired in scan with GC/MSD for a 0.5 ppm standard with a 5:1 pulsed split (0.1 ng on-column) is also shown in Figure 3.

Agilent RTL technology enables the same retention times for all target analytes between different Agilent GC/MS systems.⁴ RTL is achieved by making an adjustment to column flow, so that the retention times on one system can be maintained after maintenance. RTL also allows close matching between instruments using the same nominal column, as shown in Figure 3.

Spectral fidelity with GC/TQ in full scan mode

Excellent spectral library match scores (LMS) for all SVOCs were observed with GC/TQ in full scan data acquisition mode against the NIST spectral library, as shown in Figure 4. To obtain the LMS values, a 10 ppm standard analyzed with a 10:1 GC inlet split was processed with MassHunter Unknowns Analysis

software against the NIST spectral library. The observed LMS values are comparable to those obtained with GC/MS, with an average LMS of 95 for all 74 compounds. The results demonstrate that GC/TQ system can be used for sample screening to identify compounds using spectral library matching.

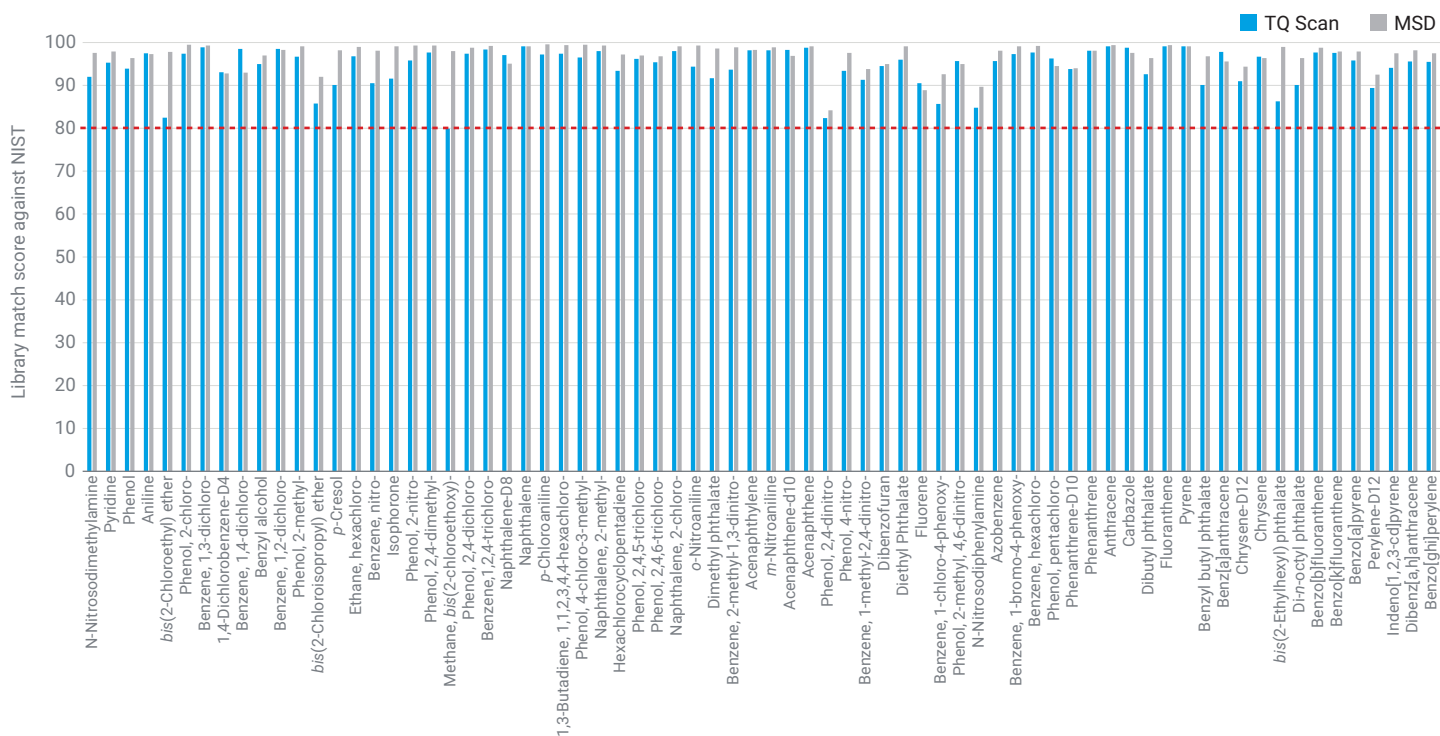


Figure 4. Library match score (LMS) against the NIST spectral library. Blue bars: results for a 10 ppm standard analyzed with Agilent 7890/7000D GC/TQ with a 10:1 split (1 ng of each component on-column). Gray bars: results for a 5 ppm standard analyzed with Agilent 7890/5977 Series GC/MSD with a 5:1 pulsed split (1 ng of each component on-column) in full scan data acquisition mode.

Analyzing GC/TQ full scan data against GC/MSD RTL library

The LMS values shown in Figure 4 were obtained when analyzing the sample against the NIST library. However, the sample can also be analyzed against the custom-built retention time-locked SVOCs library that was created using full scan data for an EPA 8270 SVOCs standard acquired with GC/MSD or GC/TQ. The advantage of analyzing the GC/TQ full scan sample against the custom library is that the compound hits can be filtered based on their retention times.⁵ The RTL functionality provided the same retention times with the 7890/7000D GC/TQ and the 7890/5977 Series GC/MSD (Figure 3). Therefore, when the GC/TQ full scan sample was analyzed against the library built with the GC/MSD data, the compound hits could be filtered based on their retention times, simplifying the review process.

Figure 5 shows the Unknowns Analysis window for a sample analyzed with GC/TQ in full scan mode against a spectral library built in-house using GC/MSD SVOCs analysis results. The average LMS for all 74 compounds was 95, which is the same as the average LMS observed when searching the spectra acquired with GC/TQ against the NIST spectral library.

The components table in Figure 5 shows the identified components arranged in elution order, the match factor against the custom SVOCs library built with GC/MSD data, the component areas, and the delta RT. Delta RT is the difference between the observed retention time and the retention time for the target in the library. Small values of delta RT indicate a good alignment between the retention times observed with GC/TQ and GC/MSD. This workflow is useful when migrating the methods from GC/MSD to GC/TQ.

The GC/TQ chromatogram acquired in full scan data acquisition mode is shown on the top right of Figure 5, as a black trace. The identified components are highlighted using the green trace, and the selected component (benzyl alcohol at 7.121 minutes) is highlighted in red. The mirror plot (middle, right of Figure 5) shows the comparison between the deconvoluted mass spectrum of the highlighted component (benzyl alcohol) and the corresponding library spectrum. The spectrum below the mirror plot is the raw mass spectrum before deconvolution. The overlaid ions are shown under the Ion Peaks window to demonstrate that the ions that belong to the component have the same retention time apexes and chromatographic peak shapes.

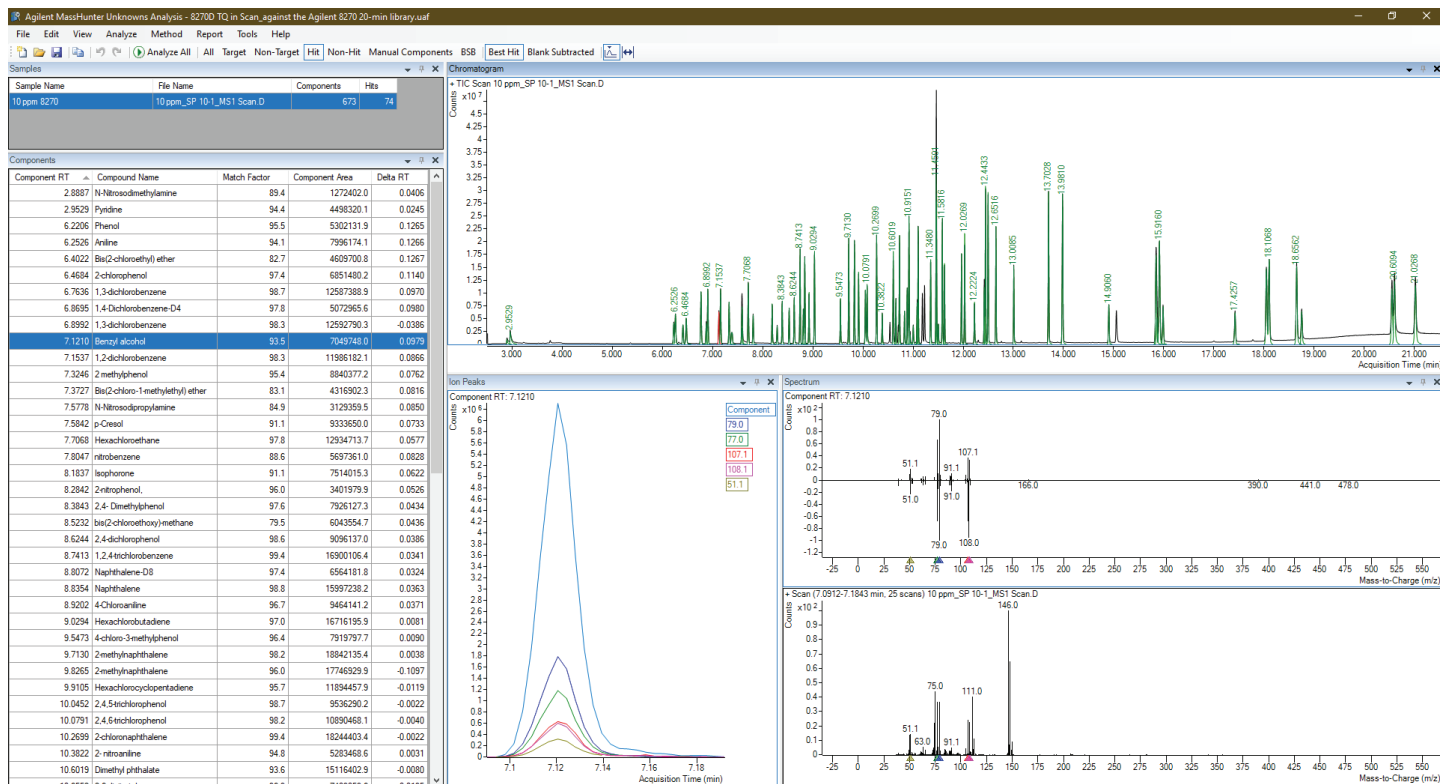


Figure 5. The Unknowns Analysis window featuring a 10 ppm SVOCs standard (10:1 GC inlet split) analyzed with GC/TQ in full scan data acquisition mode against a spectral library built in-house using GC/MSD SVOCs analysis results.

Sensitivity with GC/TQ in full scan mode

Figures 6A and 6B show the comparison of the extracted ion chromatograms (EICs) for hexachlorobenzene and acenaphthene analyzed with GC/TQ in full scan data acquisition mode (top) and GC/MSD (bottom). The loading on-column was 40 pg per analyte as a 0.4 ppm standard was analyzed in 10:1 GC inlet split with GC/TQ, and a 0.2 ppm standard was analyzed in 5:1 GC inlet pulsed split with GC/MSD. The signal-to-noise ratio for EICs achieved with GC/TQ in full scan mode operated under the conditions described in this work was comparable to that observed with GC/MSD in full scan data acquisition mode.

The LODs obtained with the 7890/7000D GC/TQ operated in full scan data acquisition mode are shown in Figure 7. The LODs for most compounds were under 50 ppb (pg/ μ L), comparable to LODs observed with GC/MSD. The compounds with higher observed LODs are known to be challenging for GC/MS analysis at low levels. These compounds include N-nitrosodimethylamine, 2-nitrophenol, 2,4 dinitrophenol, and 2-methyl-4,6-dinitrophenol.

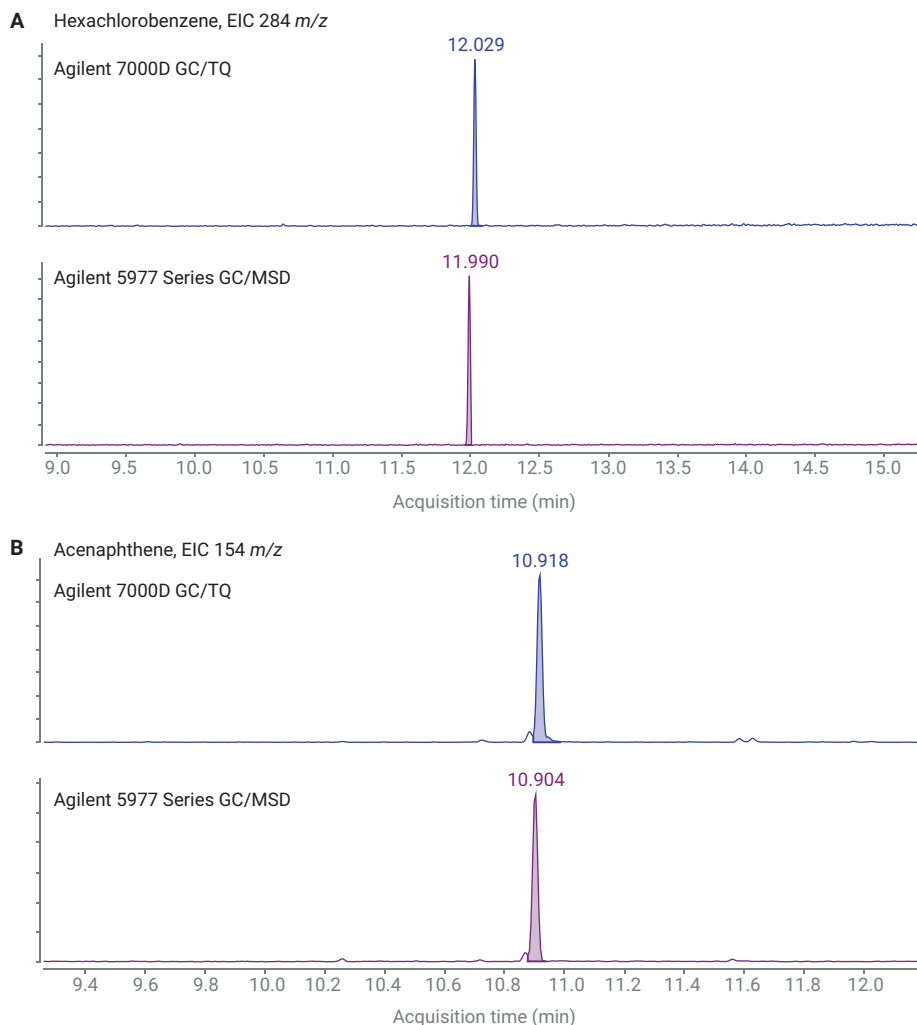


Figure 6. EICs acquired with GC/TQ in full scan data acquisition mode (top chromatograms in blue) and with GC/MSD in full scan mode (bottom chromatograms in purple) for: (A) 40 pg of hexachlorobenzene (m/z 284); (B) 40 pg of acenaphthene (m/z 154).

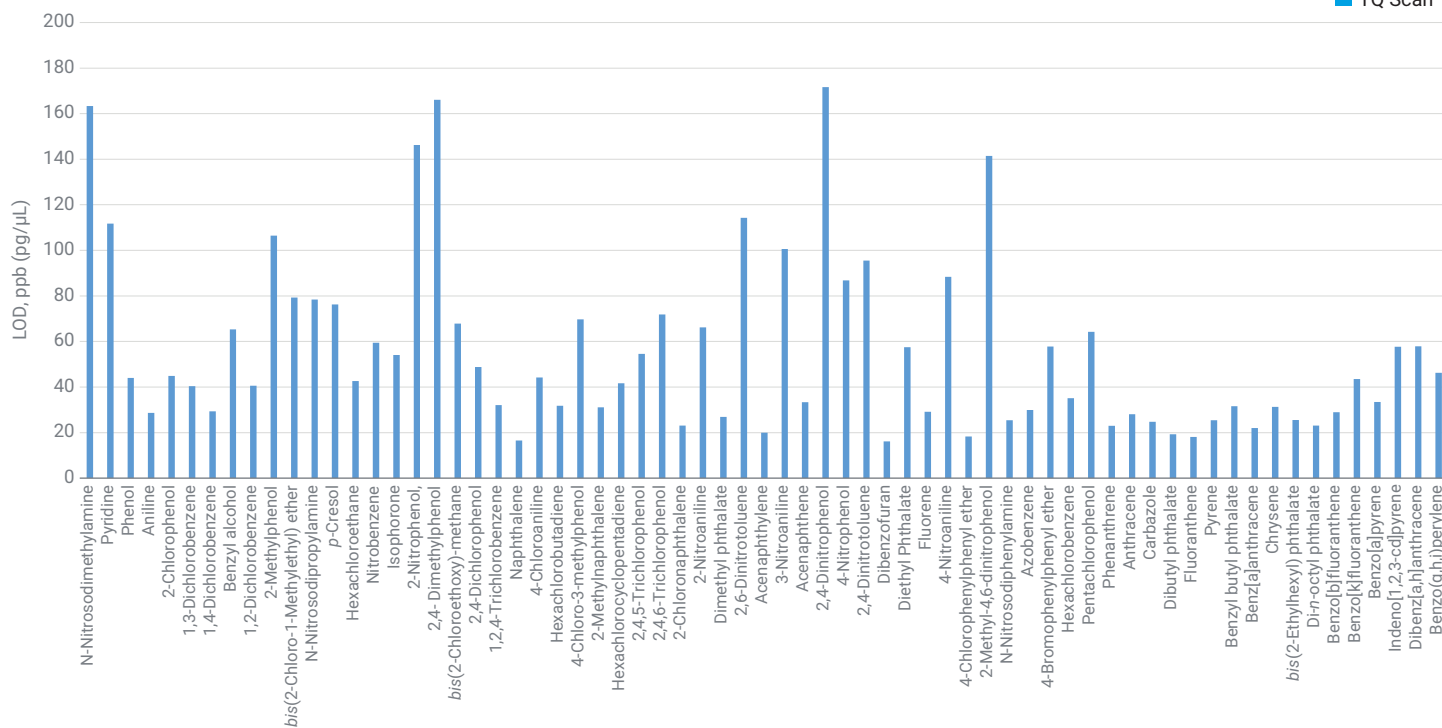


Figure 7. LODs with the 7890/7000D GC/TQ in full scan data acquisition mode obtained when performing nine sequential injections of a 0.5 ppm standard with a GC inlet split ratio of 10:1.

Resolution between benzo[b]- and benzo[k]fluoranthene

Chromatographic resolution between two isomer peaks for benzo[b]fluoranthene and benzo[k]fluoranthene was evaluated as this is commonly used as a marker of chromatographic performance in many standard methods. Figure 8 shows that the chromatographic resolution of the height of the valley between two isomer peaks for benzo[b]fluoranthene and benzo[k]fluoranthene was less than 50% of the average of the two peak heights at the midpoint concentration level with GC/TQ analysis in full scan mode.

Initial calibration performance with GC/TQ in full scan mode

To evaluate the calibration performance with GC/TQ in full scan mode, a 12-point calibration from 0.4 to 100 ppm using a 68-compound mix and six ISTDs was

analyzed. Using MassHunter Quantitative Analysis, the relative response factor was determined for each component at each calibration level. The mean response factor was then calculated across the average relative response factors for the calibration curve of each compound,

along with its relative standard deviation (RSD). Passing criteria state that the average response factor %RSD must be ≤ 20 (this is the preferred passing criteria). If this is not met, $R^2 \geq 0.990$ is required for a linear curve fit. Finally, a quadratic fit with $R^2 \geq 0.990$ that results

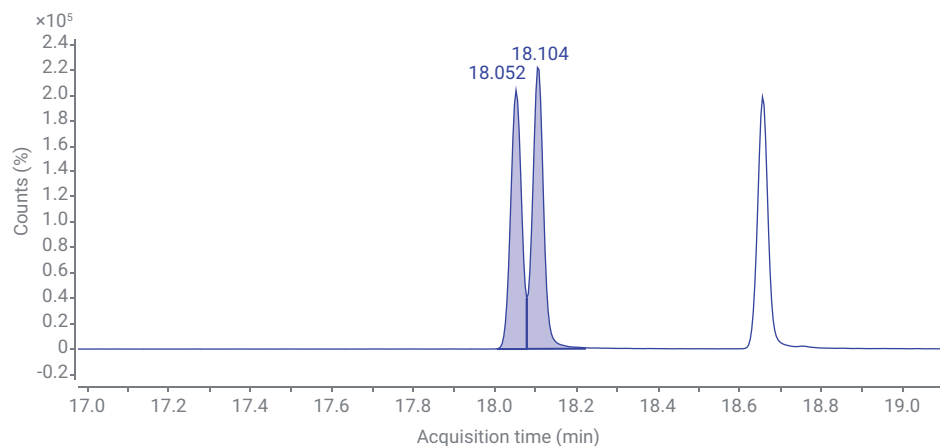


Figure 8. Benzo[b]- and benzo[k]fluoranthene resolution at 10 ppm with GC/TQ in full scan mode, EIC 252 m/z.

in the recalculated concentration of the low calibration point within $\pm 30\%$ of the standard's true concentration may be used. Accuracy for the lowest data point must be $\pm 30\%$, and six points are needed when a curve fit is used. Relative standard error (RSE) was also calculated in MassHunter Quantitative Analysis to provide a measure of curve quality.

Table 2 summarizes the initial calibration performance for the SVOCs analysis achieved with GC/TQ in full scan mode over the evaluated concentration range of 0.4 to 100 ppm. The average response factor %RSD for 68 compounds was 16.1, with 47 out of 68 compounds meeting the average response factor %RSD passing criteria of ≤ 20 . Either linear or quadratic calibration curve fit was used for the remaining 21 compounds.

The initial calibration curves for all 68 compounds had the RSE ≤ 20 , with an average RSE of 11.0 across all the targets.

The calibration curves for N-nitrosodimethylamine and bis(2-chloro-1-methylethyl)ether are shown in Figure 9. The initial calibrations show excellent linearity, with the average response factor %RSD of 8.2 and 1.4, respectively, while maintaining accuracy at low calibration levels.

Table 2. The initial calibration performance for SVOCs analysis achieved with GC/TQ in full scan data acquisition over the evaluated concentration range of 0.4 to 100 ppm.

Number of Compounds with Average Response Factor %RSD ≤ 20	Average Response Factor %RSD for 68 Compounds	Number of Compounds with Relative Standard Error (RSE) ≤ 20	Average Relative Standard Error (RSE) for 68 Compounds	Number of Compounds with Linear Fit Passing $R^2 > 0.99$ and Accuracy 30%	Number of Compounds with Quadratic Fit Passing $R^2 > 0.99$ and Accuracy 30%
47	16.1	68	11.0	10	11

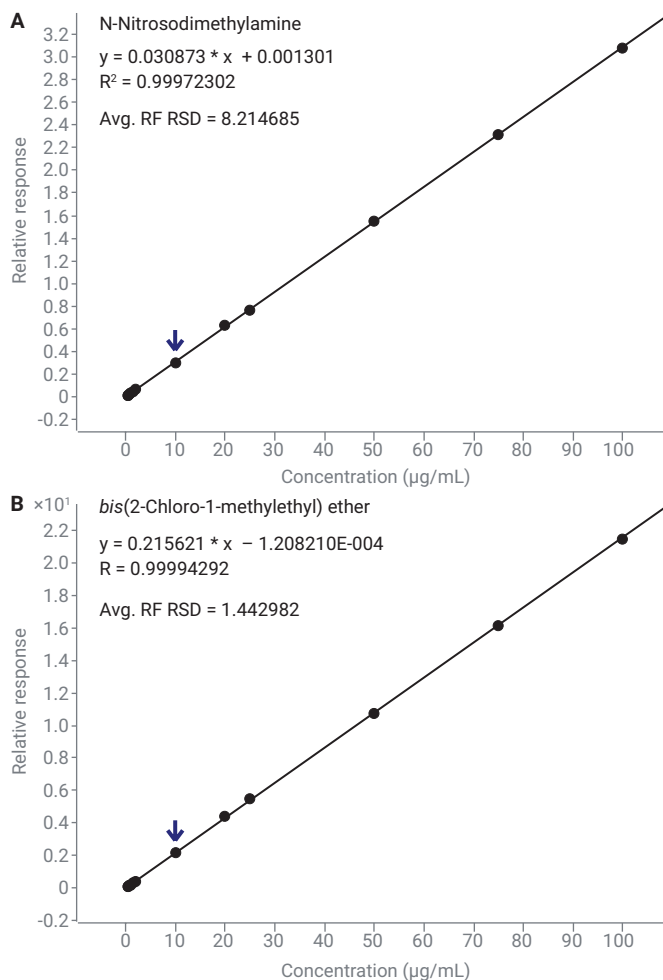


Figure 9. Example calibration curves for N-nitrosodimethylamine and bis(2-chloro-1-methylethyl)ether over the calibration range of 0.4 to 100 ppm acquired with GC/TQ in full scan mode using the GC inlet split ratio of 10:1.

Conclusion

The Agilent 7000D triple quadrupole GC/MS system was used for the analysis of semivolatile organic compounds (SVOCs) in full scan data acquisition mode. Using the operating conditions outlined in this application note, the 7000D GC/TQ system in full scan data acquisition mode enables excellent spectral library matching, high sensitivity, and linearity over a wide dynamic range of 0.4 to 100 ppm.

All the target compounds were identified against both the NIST library and the custom-built SVOCs spectral library, with high library match scores (average of 95) in both cases. The average response factor %RSD for 68 compounds was 10.96, with 47 out of 68 compounds meeting the average response factor %RSD passing criteria of ≤ 20 . The LODs obtained with the GC/TQ for most of the compounds were under 50 ppb (pg/ μ L).

Following the best practices for data acquisition and processing, the full scan data acquisition performance of the GC/TQ was found to be comparable to that of the single quadrupole GC/MS system for SVOCs analysis. This performance enables laboratories to perform single quadrupole GC/MS workflows with GC/TQ when needed, extending the flexibility of GC/TQ for routine workflows, such as sample screening and compound identification in full scan mode.

References

1. Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS); Method 8270E. *United States Environmental Protection Agency* June **2018**, Revision 6. https://www.epa.gov/sites/production/files/2019-01/documents/8270e_revised_6_june_2018.pdf
2. Churley, M.; Szelewski, M.; Quimby, B. EPA 8270 Re-optimized for Widest Calibration Range on the 5977 Inert Plus GC/MSD, *Agilent Technologies application brief*, publication number 5994-0350EN, **2018**.
3. Churley, M.; Quimby, B.; Andrianova, A. A Fast Method for EPA 8270 in MRM Mode Using the 7000 Series Triple Quadrupole GC/MS, *Agilent Technologies application note*, publication number 5994-0691EN, **2019**.
4. Agilent Retention Time Locking <https://www.agilent.com/en/retention-time-locking>.
5. Andrianova, A.; Quimby, B.; Westland, J. GC/MSD Pesticide Screening in Strawberries at Tolerance Levels Using Library Searching of Deconvoluted Spectra. *Agilent Technologies application note*, publication number 5994-0915EN, **2019**.

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