

Poster Reprint

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Optimized Analysis of Semivolatile Organic Compounds (sVOCs) with EPA 8270E Using GC Triple Quadrupole MS (GC/TQ)

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This work illustrates an optimized sensitive method used to analyze semivolatile organic compounds (SVOCs) on an Agilent 7000E Gas Chromatograph/Triple Quadrupole (GC/TQ) Mass Spectrometer. Two key analytical techniques which facilitated this work were Retention Time Locking (RTL) and dynamic Multiple Reaction Monitoring (dMRM). The utilization of GC/TQ instrumentation for analysis of SVOCs offers significant advantages. High selectivity afforded by Multiple Reaction Monitoring (MRM) mode results in faster batch review and increased confidence due to the elimination of matrix interferences often present when using GC/MS acquisition modes. Increased sensitivity can facilitate smaller extraction volumes which improves sustainability, reduces waste, and decreases costs associated with sample preparation, solvent usage, and waste disposal. A primary objective of this work was to demonstrate the ability of a GC/TQ to detect SVOCs at low levels to meet these laboratory needs while maintaining an excellent dynamic range.



Figure 1 Agilent 8890 GC and 7000E GC/TQ

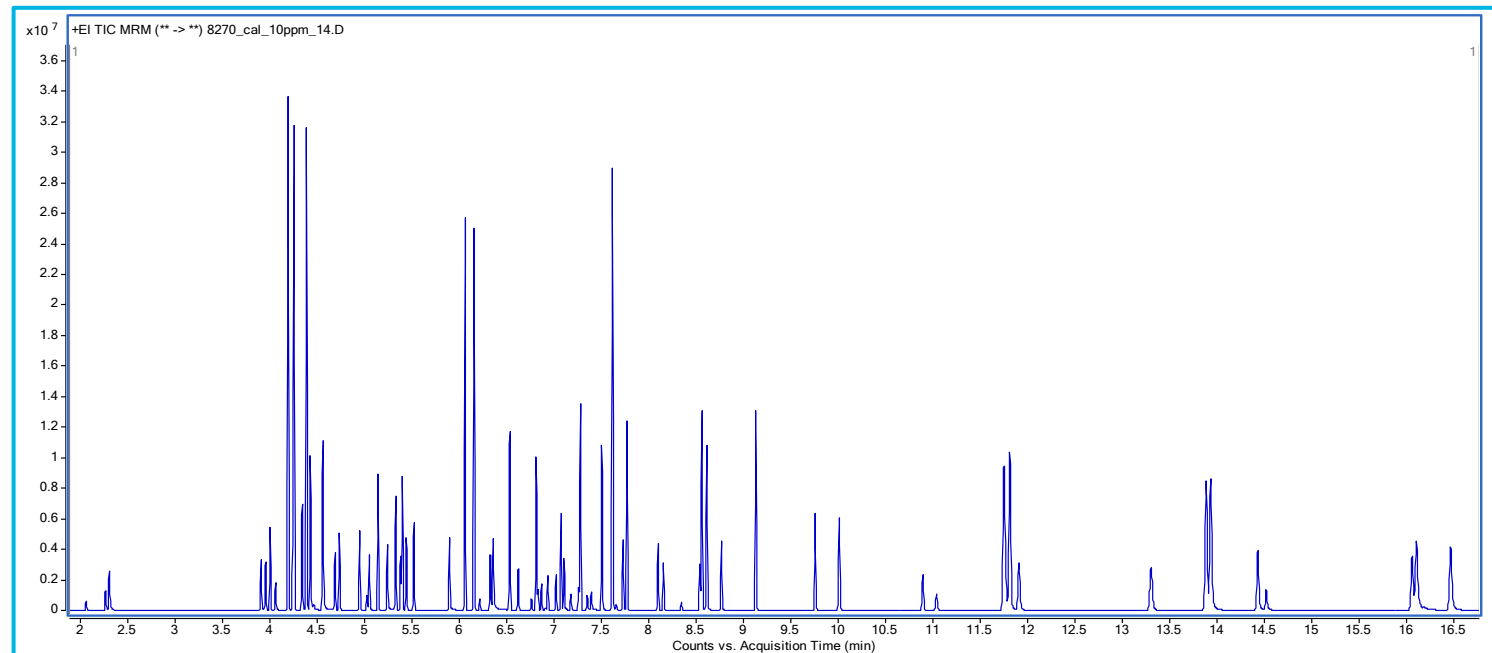


Figure 2 dMRM Total Ion Chromatogram showing separation in 16.9 minutes.

Experimental

Several Key factors and techniques increased method success:

- Eleven calibration levels from 0.005 to 10 ppm were prepared in dichloromethane with internal standards at 4ppm.
- A pulsed split injection with a 5:1 split ratio was selected as it offered excellent sensitivity while preserving the advantages of a split injection. The pulse pressure was set to 30psi for 0.6 minutes.
- The 9mm extractor lens (p/n G3870-20449) has been shown to significantly enhance method performance for polycyclic aromatic hydrocarbons and for many challenging analytes such as 2,4-dinitrophenol.¹
- Retention Time Locking (RTL) was utilized on Acenaphthene-d10 at 7.08 minutes. This technique protected against losing peaks which may otherwise drift out of an MRM analysis window after column trimming.
- Dynamic MRM (dMRM) acquisition mode “addresses the limitations of the time segment methods for a large batch of compounds by replacing the group segmentation with individual time windows for every analyte transition and by dramatically reducing, on average, the number of individual MRM transitions that are monitored during each MS scan.”²

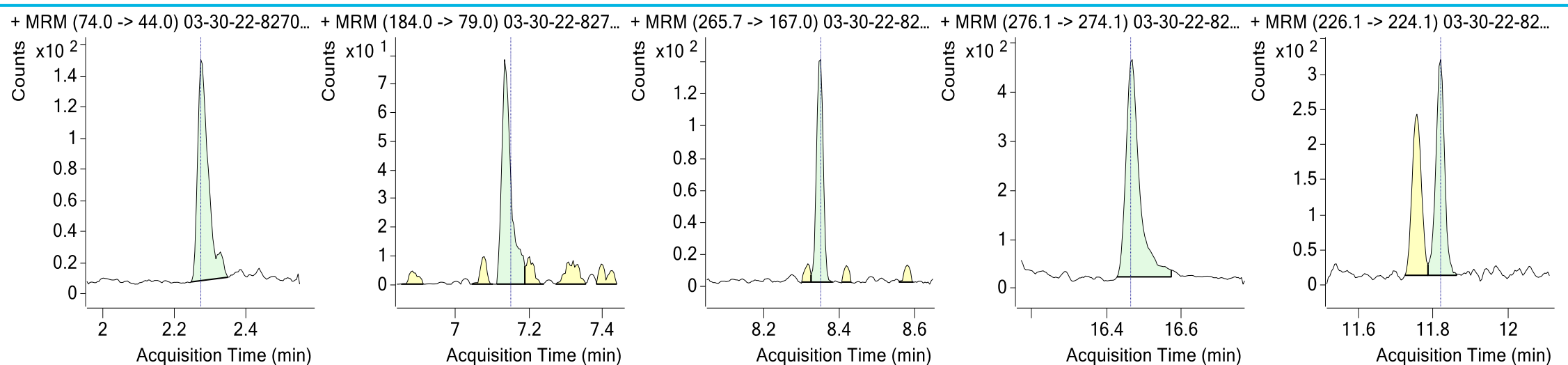


Figure 3 NDMA 0.01ppm, 2,4-Dinitrophenol 0.05ppm, PCP 0.01ppm, Benzo[g,h,i]perylene 0.005ppm, Chrysene 0.005ppm

The GC/TQ showed excellent sensitivity and was calibrated for most analytes from 0.005 to 10ppm.

- 69 of the 74 analytes were calibrated using an average response factor (Avg RF) fit with a relative standard deviation $\leq 20\%$.
- The mean Avg RF %RSD across the entire batch was 6.98%.
- 5 analytes (2,4-Dinitrotoluene, 2,6-Dinitrotoluene, 4-Nitroaniline, Di-n-octyl phthalate, and Pentachlorophenol) were calibrated using weighted least squares regression with quadratic fits having R^2 values above 0.99.
- The accuracy for all calibration points used was within $\pm 30\%$ of the theoretical value for each concentration.
- At least six data points were used for each calibration curve.

The Manufacturer's Recommended Tune protocol was utilized to verify mass accuracy and resolution on the GC/TQ

- On a single quadrupole GC/MS, the instrument would be challenged with a Decafluorotriphenylphosphine (DFTPP) solution to verify mass accuracy and resolution.
- As specified in EPA 8270E, DFTPP tune checks are not appropriate for TQ/MS³
- The GC/TQ tune was verified using Agilent's Manufacturer's Recommended Tune protocol.
- This procedure quickly generates tune evaluation tests and reports to evaluate and document the operability of the MS system.

Triple Quadrupole GC/MS Checktune Report

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Instrument Information: EI with Extractor Ion Source - High Sensitivity Tune

MS Model: G7000E | Tune Timestamp: 2022-03-30 11:30:51-04:00
 Instrument Name: Perseverance / US1943U315 | Save Timestamp: 2022-03-30 11:30:56-04:00
 SW/FW Version: 10.2.382 / 7.10.16 | Tune File: first.exe
 Tune Level: Full Autotune

Instrument Actuals

Emission (A)	35.1	Rough Vac (mTorr)	1.04E+2	Column 1 (mL/min)	1.550
Source Temp. (°C)	300	High Vac (Torr)	7.64E-5	Column 2 (mL/min)	0.000
MS1 Quad Temp. (°C)	150	Turbo 1 Speed (%)	100.0	Collision Cell (mL/min)	1.500
MS2 Quad Temp. (°C)	150	Turbo 1 Power (W)	0.0	Quench Flow (mL/min)	2.250
Transfer Line (°C)	320				

MS1/MS2 Quadrupole Checktune Results

Target Mass (m/z)	MS1	MS2	Abundance	Ratio %	Acceptable %	Abundance	Ratio %	Acceptable %
69.0	69.0	69.0	11,924,296	100.00	50.0 - 110.0	39,580,079	100.00	50.0 - 110.0
219.0	219.0	219.0	10,837,233	90.88	70.0 - 110.0	15,324,358	38.72	10.0 - 40.0
264.0	264.0	264.0	3,749,068	31.44	10.0 - 60.0	12,500,412	31.58	10.0 - 60.0
414.0	414.0	414.0	952,894	7.99	0.1 - 40.0	3,333,806	8.42	0.1 - 20.0
502.0	502.0	502.0	560,982	4.70	0.1 - 40.0	964,475	2.44	0.1 - 12.0

Detector Checktune Results

Detector Checktune Results	Value	Recommended Limit
EMV (V)	1159	$\leq 2,900$
Maximum Gain Factor	100	≥ 100

Air and Water Checktune Results

Air / Water	Absolute Abundance	Relative Abundance (%)	Recommended Limit
PFTBA(69)	11,357,567	100	---
Water	21,511	0.19	≤ 20
Oxygen*	22,816	0.20	≤ 2.5
Nitrogen*	85,036	0.75	≤ 10

* Nitrogen values are calculated from oxygen abundance.

Figure 4 Manufacturer's Checktune Report

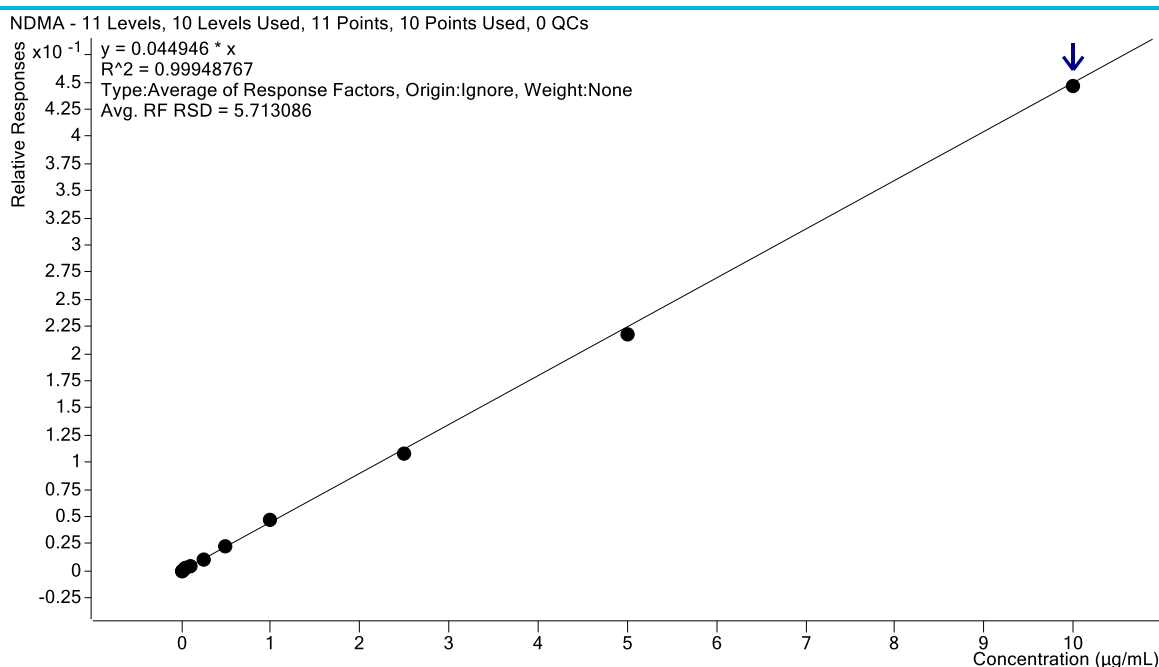


Figure 5 Calibration NDMA 0.01 to 10 ppm

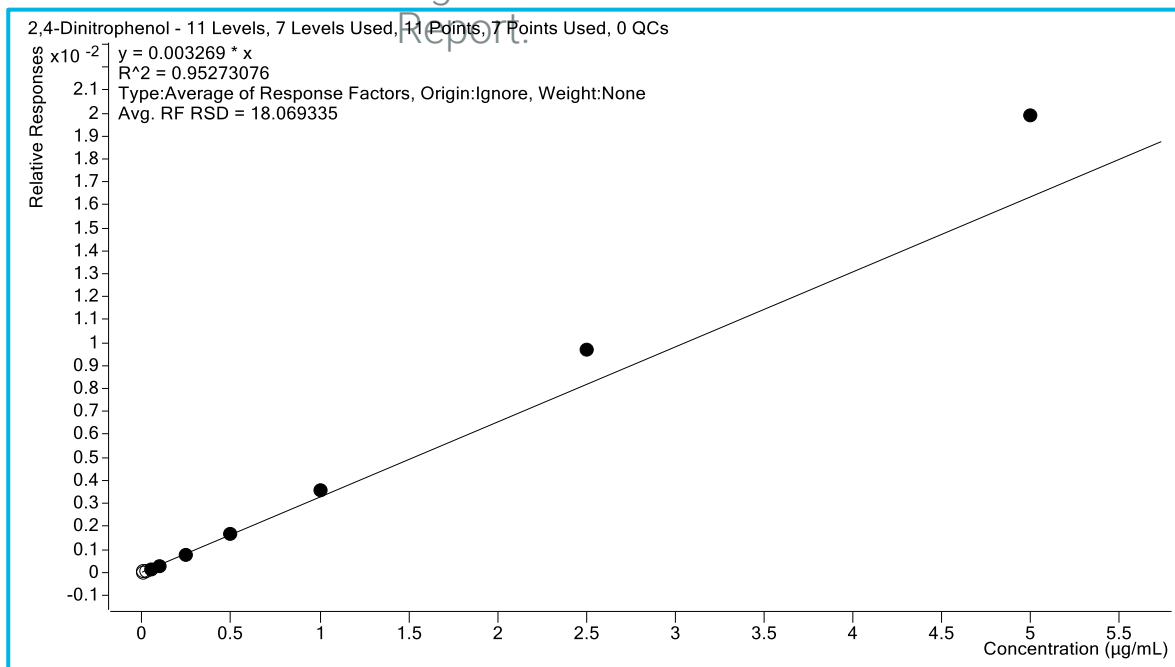


Figure 6 Calibration 2,4-Dinitrophenol 0.05 to 5 ppm

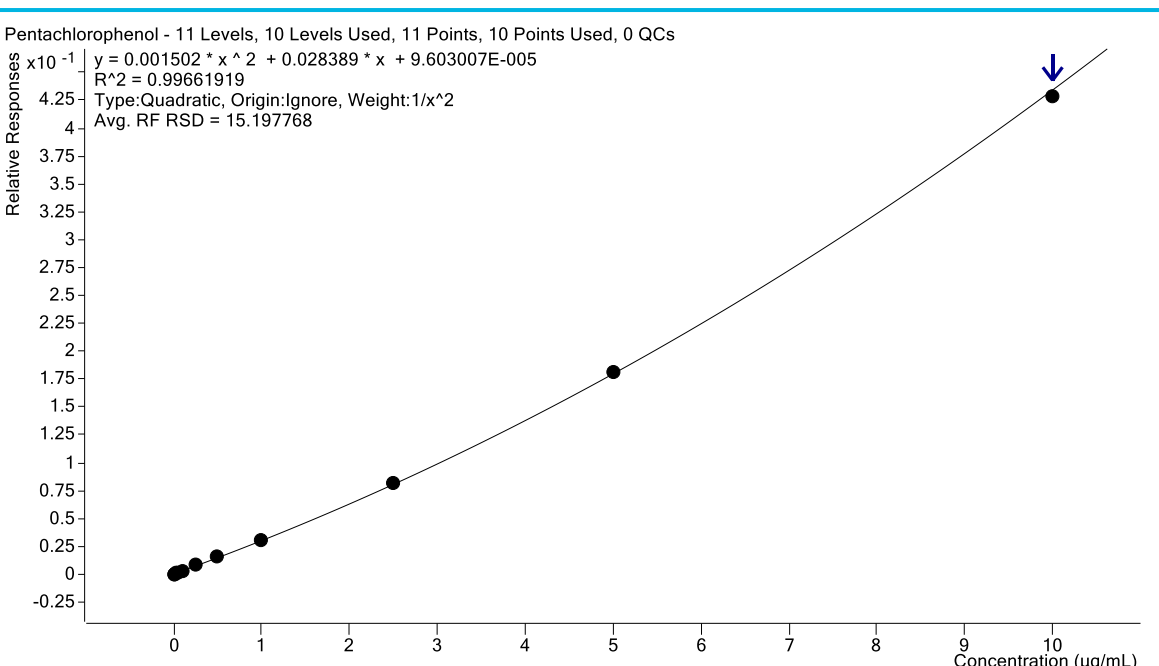


Figure 7 Calibration Pentachlorophenol (PCP) 0.01 to 10 ppm

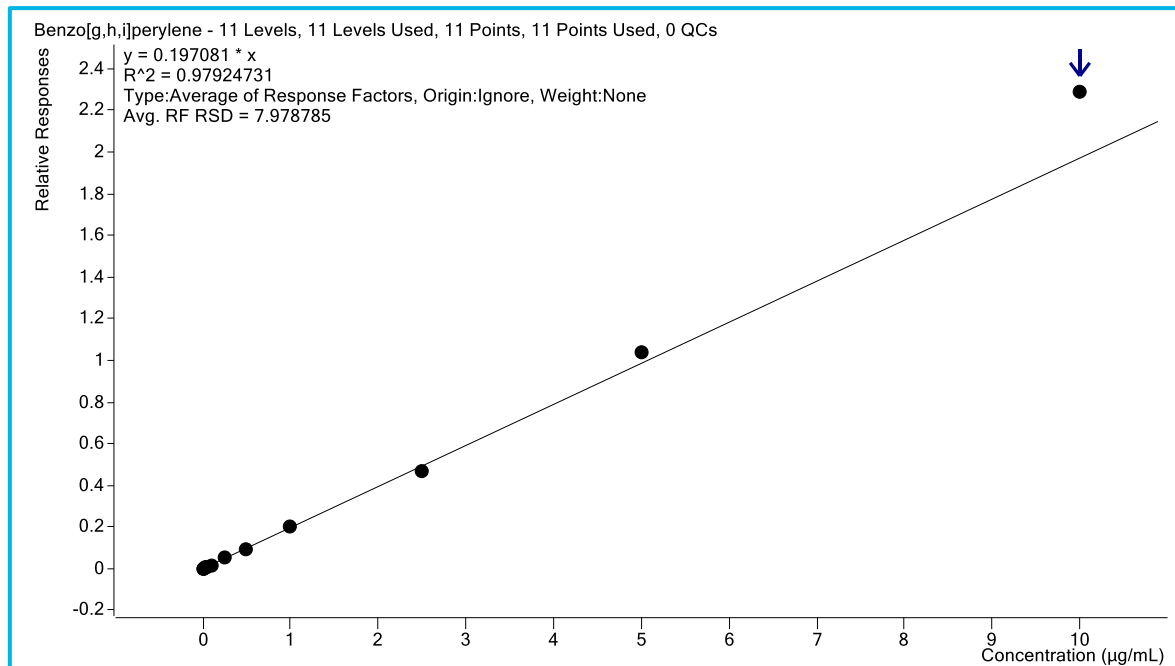


Figure 8 Calibration Benzo[g,h,i]perylene 0.005 to 10 ppm

GC/TQ offers significant advantages over GC/SQ in the analysis of sVOCs

- High selectivity results in faster batch review due to simpler data reduction and increased confidence in results due to elimination of matrix interferences.
- Increased sensitivity facilitates reduced sample sizes and smaller extraction volumes which
 - Reduce waste while improving sustainability.
 - Decrease costs associated with sample transport, solvent usage and waste disposal.
- Dynamic MRM mode generally reduces the number of individual MRM transitions during each MS scan which improves instrument performance and makes adding and removing analytes from your analyte list easy.

The Manufacturer's Recommended Tune procedure simplifies tuning verification for the GC/TQ

Some Key Techniques for sVOC analysis by GC/MS which improve results are:

- Retention time locking ensures exact retention time fidelity even after column trimming which
 - Eliminates the need to manually adjust retention times after maintenance.
 - Makes data interchangeable across multiple instruments and multiple laboratories.
- A Pulsed split injection can enhance sensitivity over a standard split injection while maintaining a wide dynamic range.
- A 9mm extractor lens gives outstanding linearity for all compounds while affording excellent sensitivity for many difficult analytes such as 2,4-Dinitrophenol.

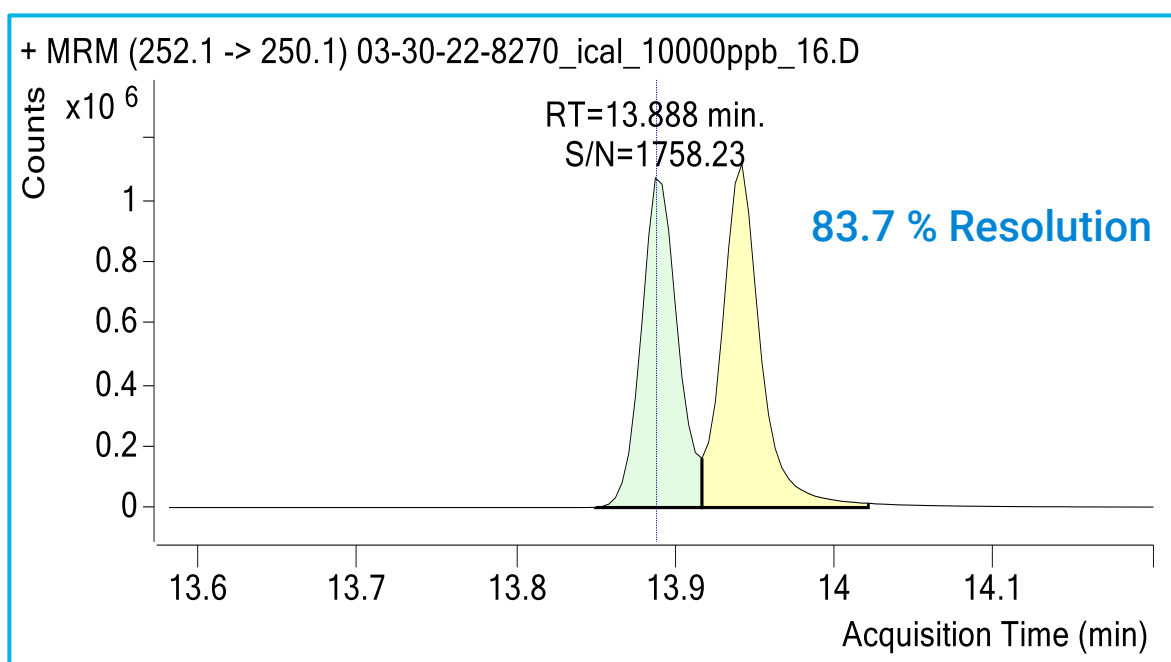


Figure 9 Benzo(b) and Benzo(k)fluoranthene 10ppm

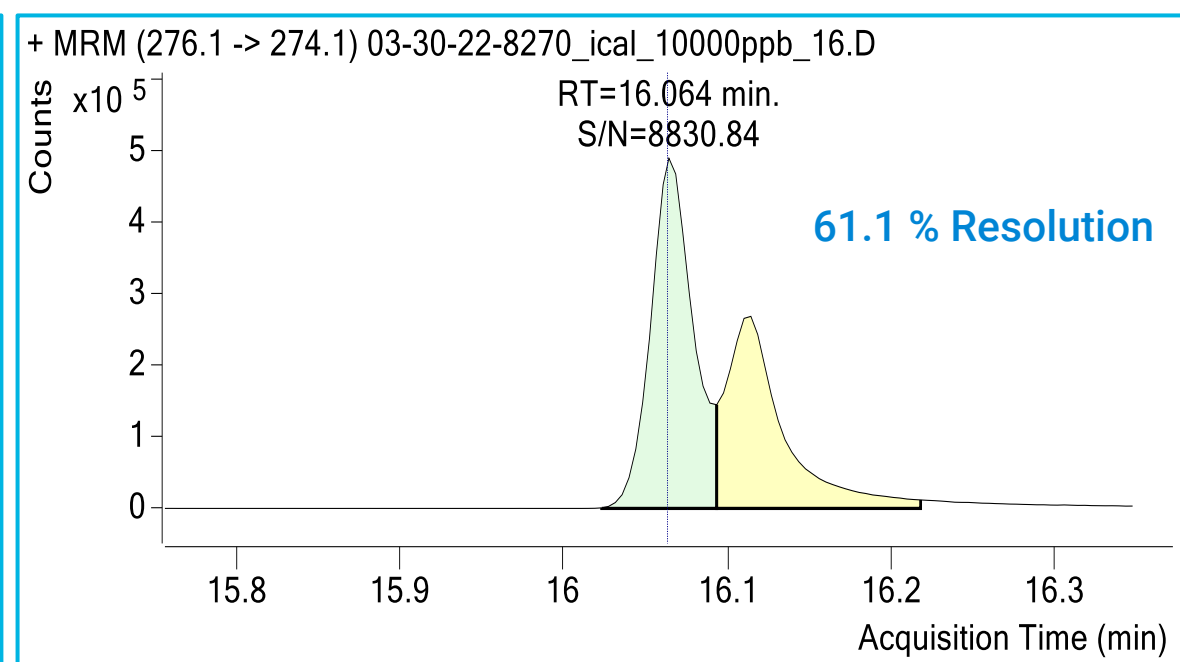


Figure 10 Indeno[1,2,3-cd]pyrene & Dibenz[a,h]anthracene 10ppm

References

1-Anderson, Kim A et al. "Modified ion source triple quadrupole mass spectrometer gas chromatograph for polycyclic aromatic hydrocarbon analyses." Journal of chromatography. A vol. 1419 (2015): 89-98. doi:10.1016/j.chroma.2015.09.054

2- P. Stone, et al. New Dynamic MRM Mode Improves Data Quality and Triple Quad Quantification in Complex Analyses. Agilent Technologies Technical Overview, publication number 5990-3595 (2009).

3-Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS); Method 8270E Section 11.3.1.2 Note; United States Environmental Protection Agency, Revision 4, June 2018.

The author would like to recognize the significant contributions of Dale Walker and Rachael Ciotti in developing and testing this methodology.

<https://explore.agilent.com/asms>

This information is subject to change without notice.

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