

Analysis of Semivolatile Organic Compounds with US EPA 8270E Using the Agilent 7000E Triple Quadrupole GC/MS



Authors

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Abstract

This application note illustrates a sensitive method used to analyze semivolatile organic compounds (SVOCs) on an Agilent 7000E triple quadrupole GC/MS system (GC/TQ). The use 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. These interferences are often present when using selective ion monitoring (SIM) or scan acquisition modes. Increased sensitivity can facilitate smaller extraction volumes that improve sustainability, reduce waste, and decrease 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.

Introduction

The analysis of SVOCs can be challenging as there is a wide variety of target analytes that include bases, neutrals, and acids. These analytes span a wide range of molecular weights and boiling points. The United States Environmental Protection Agency (US EPA) has issued regulations and guidelines in Method 8270E for the analysis of these analytes by GC/TQ. Typical samples that are analyzed for SVOCs include surface or ground water as well as solid samples. These samples are then extracted before analysis. If method sensitivity can be improved, there is an opportunity to reduce sample and extract volumes that can result in decreased costs and increased lab sustainability. A preferable analytical method can also demonstrate a wide dynamic range to reduce the need for sample dilution and reanalysis.

Experimental

Sample preparation

A 2,000 µg/mL stock standard of SVOCs was sourced from Agilent (part number US201-1). Initial calibration curve standards were prepared by dilution of the stock and working standards into dichloromethane. Eleven calibration levels were prepared at the following concentrations: 0.005, 0.01, 0.025, 0.05, 0.1, 0.25, 0.5, 1, 2.5, 5, and 10 µg/mL. A 2,000 µg/mL internal standard (ISTD) solution was also sourced from Agilent (part number ISM-560-1). This solution contained six internal standards: 1,4-dichlorobenzene-d4, acenaphthene-d10, chrysene-d12, naphthalene-d8, phenanthrene-d10, and perylene-d12. This ISTD solution was diluted and added to the calibration vials at a concentration of 4 µg/mL.

Instrumental method

An Agilent 8890 GC system and 7693A automatic liquid sampler (ALS) were used for sample introduction. The 8890 GC was configured with a split/splitless (SSL) inlet. An **Agilent 7000E triple quadrupole mass spectrometer (TQ/MS)** was used as the detector.

Initial method parameters were obtained from two Agilent application notes.^{1,2} GC and MS method settings are shown in in the following tables.

The key techniques below were employed which increased method success:

- Using a GC/TQ provided greater sensitivity for low level analysis and simplified data reduction due to increased selectivity.

- A pulsed split injection with a 5:1 split ratio offered excellent sensitivity while preserving the advantages of a split injection.
- The 9 mm extractor lens enhanced linearity and improved overall performance for challenging analytes.
- Retention time locking protected against losing peaks, which may have otherwise drifted out of an MRM analysis window after column trimming.
- Dynamic MRM (dMRM) analysis mode reduced the number of simultaneous transitions that were monitored and simplified the process of adding and removing analytes.

| GC Settings | |
|---------------------------|--|
| Analytical Column | Agilent J&W DB-8270D UI, 30 m x 0.25 mm, 0.25 µm (p/n 122-9732) |
| Injection Volume | 1 µL |
| Inlet Temperature | Isothermal 280 °C |
| Injection Mode | Pulsed split |
| Split Ratio | 5:1 |
| Injection Pulse Pressure | 30 psi until 0.6 min |
| Liner | Ultra Inert split, low pressure drop glass wool (p/n 5190-2295) |
| Oven Temperature Program | 40 °C, hold for 0.5 min Ramp at 25 °C /min to 260 °C, hold 0 min Ramp at 5 °C /min to 280 °C, hold 0 min Ramp at 25 °C /min to 320 °C, hold 2 min |
| Run Time | 16.9 min |
| Equilibration Time | 1 min |
| Carrier Gas | Helium, constant flow at 1.55 mL/min (adjusted by RT locking) |
| Transfer Line Temperature | 320 °C |

| MS Settings | |
|------------------------|--------------------------|
| Ion Source | Extractor with 9 mm lens |
| Ion Source Temperature | 300 °C |
| Quadrupole Temperature | 150 °C |
| Collision Gas | Nitrogen at 1.5 mL/min |
| Quench Gas | Helium at 2.25 mL/min |
| Ionization Mode | EI |
| Solvent Delay | 1.7 min |
| EMV mode | Gain factor |
| Gain Factor | 3 |
| Scan Type | Dynamic MRM |

Several injection techniques were evaluated including split and splitless modes, with and without pulsed injections. 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. Split injections allow for faster sample transfer from the inlet to the column. This faster transfer can improve performance for thermally sensitive analytes as they spend less time at high temperature in the GC inlet. Split injections also diminish the deposition of nonvolatile matter at the head of the GC column.

This method also used a 9 mm diameter extractor lens (part number G3870-20449) in the MS source. The 9 mm lens has been shown to significantly enhance method performance for polycyclic aromatic hydrocarbons and for many other challenging analytes such as 2,4-dinitrophenol by Anderson *et al.*³

The implementation of retention time locking (RTL) was critical to ensure exact retention time fidelity even after repeated inlet maintenance and column trimming. After trimming the column during maintenance, a single injection was made that allowed the Agilent MassHunter acquisition software for GC/MS systems to make a slight adjustment to the GC flow. This adjustment realigned all the analyte retention times. The method was retention time locked to acenaphthene-d10 at 7.08 minutes. This technique protects against losing peaks that may otherwise drift out of a dMRM analysis window after column maintenance.

The method also used dMRM acquisition mode. This approach addresses the limitations of time segment methods for a large batch of compounds by replacing the group segmentation with individual time windows for every analyte transition. It also dramatically reduces the number of individual MRM transitions that are monitored during each MS scan.⁴ Dynamic MRM mode simplifies the addition and removal of analytes of interest. The dMRM mode overcomes many challenges associated with time segmented methods targeting an abundance of analytes in a short elution window.

Early method experiments used a 25 °C oven ramp from 40 to 320 °C. The oven ramp was modified such that the oven ramp rate from 260 to 280 °C was decreased to 5 °C per minute. By optimizing the oven ramp, improved chromatographic resolution was achieved for benzo[b]fluoranthene and benzo[k]fluoranthene. Isomers are considered resolved if the height of the valley between two isomer peaks is less than 50% of the average of the two peak heights.⁵ As shown in Figure 1, 88.6% resolution was achieved at a concentration of 2.0 µg/mL. Indeno[1,2,3-cd]pyrene and dibenz[a,h]anthracene were also acceptably separated at 62.6% resolution, as shown in Figure 2.

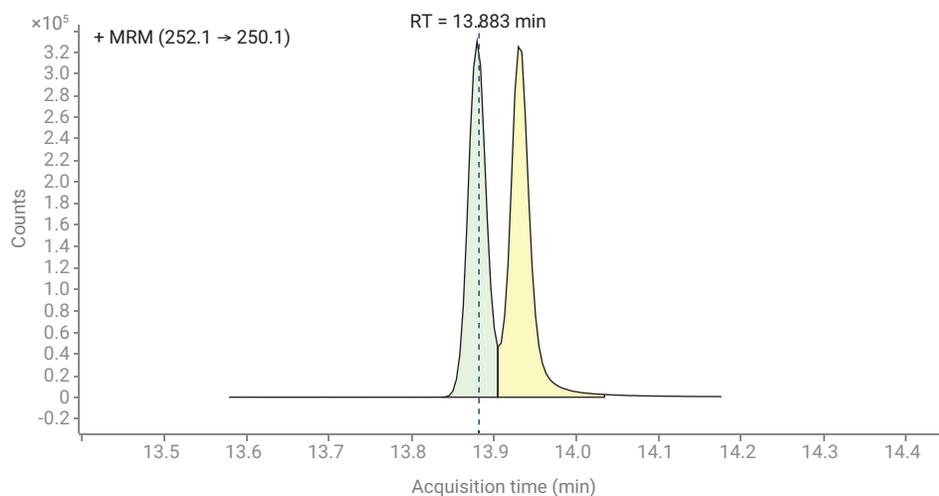


Figure 1. Benzo(b)fluoranthene and benzo(k)fluoranthene at 2.0 µg/mL (88.6% resolution).

Results and discussion

Manufacturer recommended tune

On a single quadrupole MS, the instrument would be challenged with a DFTPP (decafluorotriphenylphosphine) solution to verify mass accuracy and resolution. DFTPP tune checks are not appropriate for tandem MS analysis using MRM. However, the laboratory must demonstrate, prior to the initial calibration, that the MS system achieves mass accuracy and mass resolution criteria specified by the instrument manufacturer for the perfluorotributylamine (PFTBA) internal calibrant or another appropriate chemical.⁵ The MS tune was verified using the Agilent manufacturer recommended tune protocol for the GC/TQ. Figure 4 shows an example check tune report from the Agilent manufacturer recommended tune. This procedure assists the analyst in using the GC/TQ by generating tune evaluation tests and reports to quickly evaluate and document the operability of the MS system.

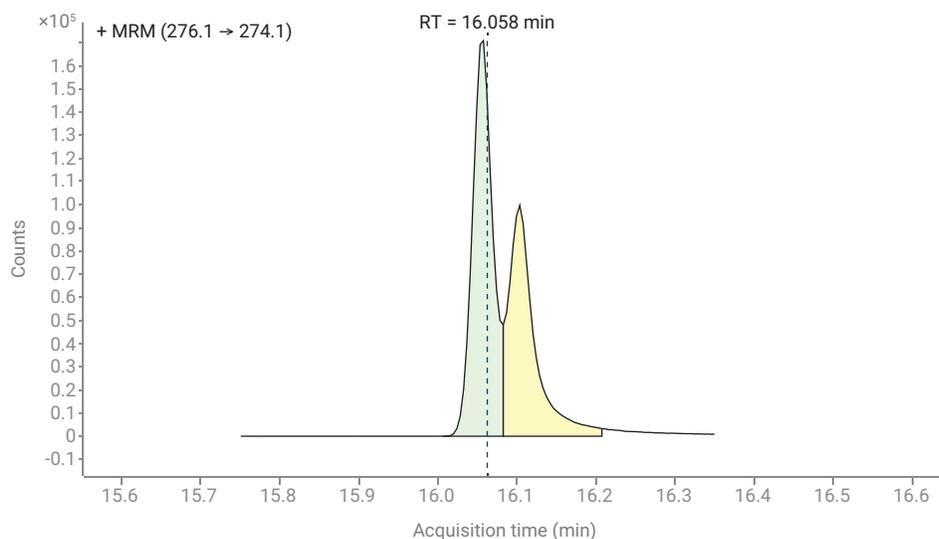


Figure 2. Indeno[1,2,3-cd]pyrene and dibenz[a,h]anthracene at 2.0 $\mu\text{g}/\text{mL}$ (62.6% resolution).

Calibration

The initial calibration included 74 analytes. The 3- and 4-methyl phenol isomers were not separated and were reported as a combined result. The initial calibration was performed by introducing 11 different calibration solutions across more than three orders of magnitude in

the range of 0.005 to 10 $\mu\text{g}/\text{mL}$. Each analyte was monitored using at least two MRM transitions, one of which was selected to quantify the results while the second was used as a qualifier. Some calibration curve ranges were trimmed at the top and/or bottom of the working range to meet method criteria.

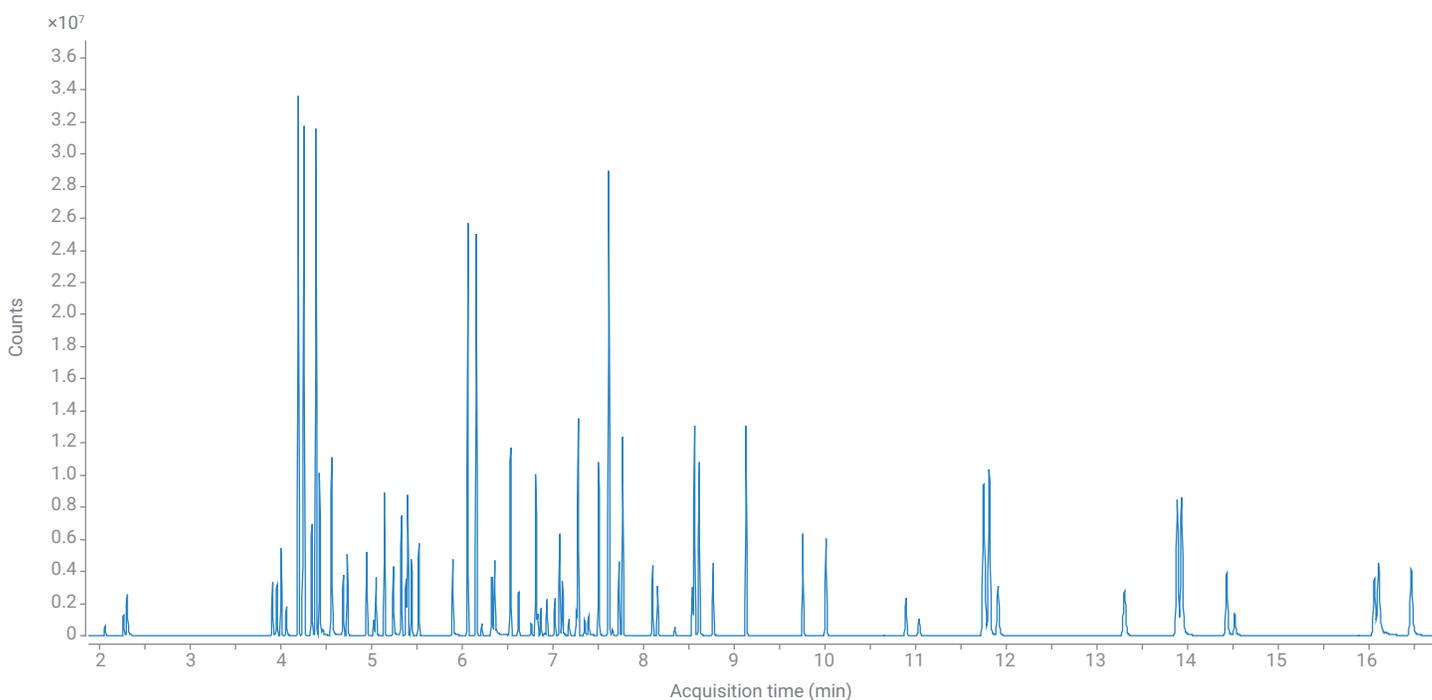


Figure 3. Total ion chromatogram from composite of all DMRM transitions showing separation in 16.9 minutes.

Triple Quadrupole GC/MS Checktune Report



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 | | Save Timestamp | 2022-03-30 11:30:56-04:00 |
| SW/FW Version | | Tune File | first.eiex |
| | | Tune Level | Full Autotune |

Instrument Actuals

| | | | | | |
|---------------------|------|-------------------|---------|-------------------------|-------|
| Emission (µA) | 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) | Actual Mass (m/z) | | MS1 Abundance | | | MS2 Abundance | | |
|-------------------|-------------------|-------|---------------|---------|--------------|---------------|---------|--------------|
| | 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 - 80.0 | 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 |

| Isotope M+1 (m/z) | MS1 Abundance | | | MS2 Abundance | | |
|-------------------|---------------|-----------------|--------------|---------------|-----------------|--------------|
| | Iso M+1 Abund | Iso M+1 Ratio % | Acceptable % | Iso M+1 Abund | Iso M+1 Ratio % | Acceptable % |
| 70.0 | 137,009 | 1.15 | 0.63 - 1.72 | 545,237 | 1.38 | 0.63 - 1.72 |
| 220.0 | 471,869 | 4.35 | 2.94 - 6.42 | 687,613 | 4.49 | 2.94 - 6.42 |
| 265.0 | 213,584 | 5.70 | 4.09 - 8.37 | 731,141 | 5.85 | 4.09 - 8.37 |
| 415.0 | 84,401 | 8.86 | 7.29 - 12.08 | 294,690 | 8.84 | 7.29 - 12.08 |
| 503.0 | 55,587 | 9.91 | 8.75 - 12.88 | 94,539 | 9.80 | 8.75 - 12.88 |

Detector Checktune Results

| Detector Checktune Results | Value | Recommended Limit |
|----------------------------|-------|-------------------|
| EMV (V) | 1158 | ≤ 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. Example check tune report for manufacturer recommended tune.

Some analytes in the 8270 list are prone to difficulty in calibration. These analytes may be labile or active in the GC inlet, particularly at lower concentrations. This may manifest as variation in response factor relative to analyte concentration. Section 1.4.7 of the 8270 method⁵ lists several such analytes and notes that they may be subject to erratic chromatographic behavior. 2,4-Dinitrophenol is one of the most difficult from this list and the calibration is shown in Figure 5. The response factor moderately increases with concentration, but method requirements were met as the average response factor (avg RF) relative standard deviation was 18.07%, which is less than the requirement of 20%. Method 8270 allows curve fitting for some analytes to alleviate this difficulty, provided that the coefficient of determination (R^2) is greater than 0.99. An alternate quadratic curve fit for 2-4-dinitrophenol is shown in Figure 6 with a R^2 of 0.9979. Pentachlorophenol is another of these listed potentially difficult analytes and the calibration curve is shown in Figure 8. In this case, a quadratic curve fit was selected with a R^2 value of 0.9966. These calibration curves demonstrate that calibration criteria may be met even with difficult analytes at low concentrations. An example of a more ideal calibration curve is shown for NDMA in Figure 9. NDMA itself can be a difficult analyte if chromatographic conditions are not optimized due to early elution and potential difficulty in complete resolution from the solvent. In this example, NDMA has an avg RF relative standard deviation of 5.71% and demonstrates exemplary linearity across the calibrated range.

Table 1. Calibration results.

| Compound | Curve Fit | % RSE | R ² | Low Std (ppm) | High Std (ppm) |
|------------------------------|-----------|-------|----------------|------------------------------|----------------|
| | | | | (default is 0.005 to 10 ppm) | |
| 1,2,4-Trichlorobenzene | Avg RF | 5.7 | | | |
| 1,2-Dichlorobenzene | Avg RF | 5.3 | | | |
| 1,3-Dichlorobenzene | Avg RF | 4.5 | | | |
| 1,3-Dinitrobenzene | Avg RF | 16.4 | | 0.025 | 5 |
| 1,4-Dichlorobenzene | Avg RF | 7.8 | | | |
| 1,4-Dinitrobenzene | Avg RF | 11.8 | | 0.025 | |
| 1-Methylnaphthalene | Avg RF | 6.8 | | | |
| 2,2'-oxybis[1-chloropropane] | Avg RF | 4.3 | | 0.050 | |
| 2,3,4,6-Tetrachlorophenol | Avg RF | 14.1 | | | |
| 2,3,5,6-Tetrachlorophenol | Avg RF | 9.6 | | 0.025 | |
| 2,4,5-Trichlorophenol | Avg RF | 8.2 | | | |
| 2,4,6-Trichlorophenol | Avg RF | 5.2 | | | |
| 2,4-Dichlorophenol | Avg RF | 4.2 | | | |
| 2,4-Dimethylphenol | Avg RF | 3.4 | | 0.010 | |
| 2,4-Dinitrophenol | Avg RF | 18.1 | | 0.050 | 5 |
| 2,4-Dinitrotoluene | Quadratic | 5.4 | 0.9967 | 0.025 | |
| 2,6-Dinitrotoluene | Quadratic | 8.3 | 0.9937 | 0.010 | |
| 2-Chloronaphthalene | Avg RF | 3.5 | | | |
| 2-Chlorophenol | Avg RF | 6.5 | | | |
| 2-methyl-4,6-dinitrophenol | Avg RF | 13.0 | | 0.025 | 5 |
| 2-Methylnaphthalene | Avg RF | 4.1 | | | |
| 2-Methylphenol | Avg RF | 6.7 | | 0.010 | |
| 2-Nitroaniline | Avg RF | 10.4 | | | |
| 2-Nitrophenol | Avg RF | 7.8 | | | |
| 3+4-Methylphenol | Avg RF | 3.5 | | | |
| 3-Nitroaniline | Avg RF | 14.7 | | | 5 |
| 4-bromophenyl phenyl ether | Avg RF | 3.9 | | | |
| 4-chloro-3-methylphenol | Avg RF | 4.9 | | | |
| 4-Chloroaniline | Avg RF | 3.0 | | | |
| 4-Chlorophenyl phenyl ether | Avg RF | 2.1 | | | |
| 4-Nitroaniline | Quadratic | 7.0 | 0.9954 | | |
| 4-Nitrophenol | Avg RF | 11.9 | | | 5 |
| Acenaphthene | Avg RF | 9.8 | | 0.010 | |
| Acenaphthylene | Avg RF | 4.3 | | 0.010 | |
| Aniline | Avg RF | 7.6 | | 0.010 | |
| Anthracene | Avg RF | 5.2 | | | |
| Azobenzene | Avg RF | 3.9 | | | |
| Benz[a]anthracene | Avg RF | 6.7 | | | |
| Benzo[a]pyrene | Avg RF | 7.9 | | | |
| Benzo[b]fluoranthene | Avg RF | 7.2 | | | |
| Benzo[g,h,i]perylene | Avg RF | 8.0 | | | |
| Benzo[k]fluoranthene | Avg RF | 8.7 | | | |
| Benzyl alcohol | Avg RF | 2.7 | | 0.010 | |
| bis(2-Chloroethoxy)methane | Avg RF | 3.2 | | | |
| bis(2-Chloroethyl)ether | Avg RF | 7.1 | | | |

| Compound | Curve Fit | % RSE | R ² | Low Std (ppm) | High Std (ppm) |
|------------------------------------|-----------|-------|----------------|------------------------------|----------------|
| | | | | (default is 0.005 to 10 ppm) | |
| Bis(2-ethylhexyl) phthalate | Avg RF | 14.3 | | 0.025 | |
| Butyl benzyl phthalate | Avg RF | 10.3 | | | |
| Carbazole | Avg RF | 5.0 | | | |
| Chrysene | Avg RF | 5.7 | | | |
| Dibenz[a,h]anthracene | Avg RF | 14.4 | | | 5 |
| Dibenzofuran | Avg RF | 5.0 | | | |
| Diethyl phthalate | Avg RF | 7.6 | | 0.100 | |
| Dimethyl phthalate | Avg RF | 4.1 | | | |
| Di- <i>n</i> -butyl phthalate | Avg RF | 3.2 | | 0.025 | |
| Di- <i>n</i> -octyl phthalate | Quadratic | 6.2 | 0.9960 | | |
| Diphenylamine | Avg RF | 4.9 | | 0.025 | |
| Fluoranthene | Avg RF | 3.9 | | | |
| Fluorene | Avg RF | 3.0 | | | |
| Hexachlorobenzene | Avg RF | 7.1 | | | |
| Hexachlorobutadiene | Avg RF | 3.7 | | | |
| Hexachlorocyclopentadiene | Avg RF | 14.4 | | 0.010 | |
| Hexachloroethane | Avg RF | 2.6 | | 0.010 | |
| Indeno[1,2,3- <i>cd</i>]pyrene | Avg RF | 7.9 | | | 5 |
| Isophorone | Avg RF | 5.6 | | | |
| Naphthalene | Avg RF | 6.8 | | | |
| NDMA | Avg RF | 5.7 | | 0.010 | |
| Nitrobenzene | Avg RF | 10.9 | | 0.010 | |
| N-Nitrosodi- <i>n</i> -propylamine | Avg RF | 3.4 | | 0.050 | |
| Pentachlorophenol | Quadratic | 6.7 | 0.9966 | 0.010 | |
| Phenanthrene | Avg RF | 5.7 | | | |
| Phenol | Avg RF | 5.7 | | | |
| Pyrene | Avg RF | 3.6 | | | |
| Pyridine | Avg RF | 5.2 | | 0.025 | |
| Average = 7.0 | | | | | |

In this data set, 69 of the 74 analytes were calibrated using an avg RF fit with a relative standard deviation of less than or equal to 20%. The remaining five 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 R² values above 0.99. The relative standard error

was calculated for each analyte and found to be less than or equal to 20% for each calibration curve. The mean relative standard error across all analytes was 6.96%. Also, the accuracy for all calibration points used was within ±30% of the theoretical value for each concentration. At least six data points were used for each calibration curve.

If a calibration working range is desired which covers higher concentrations, it is recommended to either dilute the samples or increase the ratio of the pulsed split injection. This modification would have the additional benefit of reducing matrix that reaches the column and detector and would likely reduce maintenance frequency.

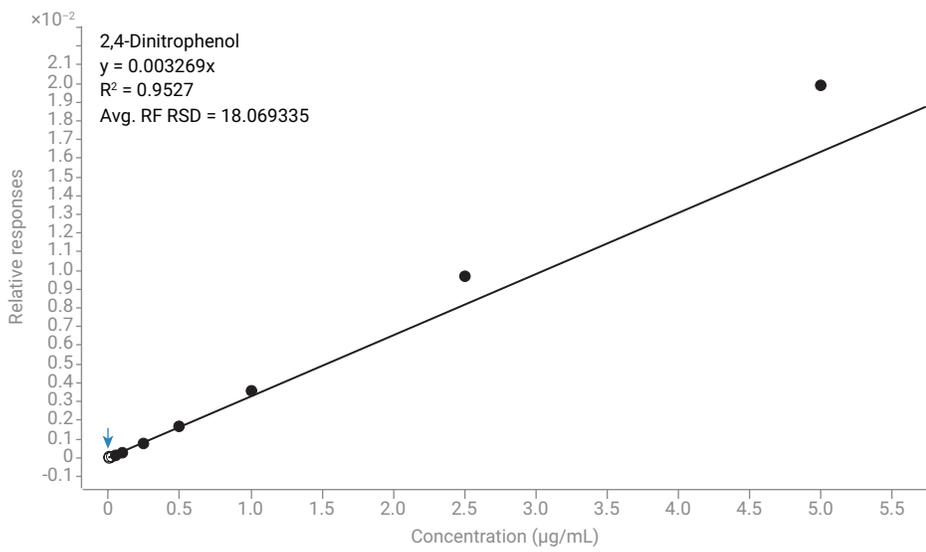


Figure 5. Avg RF calibration curve for challenging analyte 2,4-dinitrophenol 0.05 to 5 µg/mL. Avg. RF RSD = 18.07. Calibration points 1, 2, 3, and 11 are excluded.

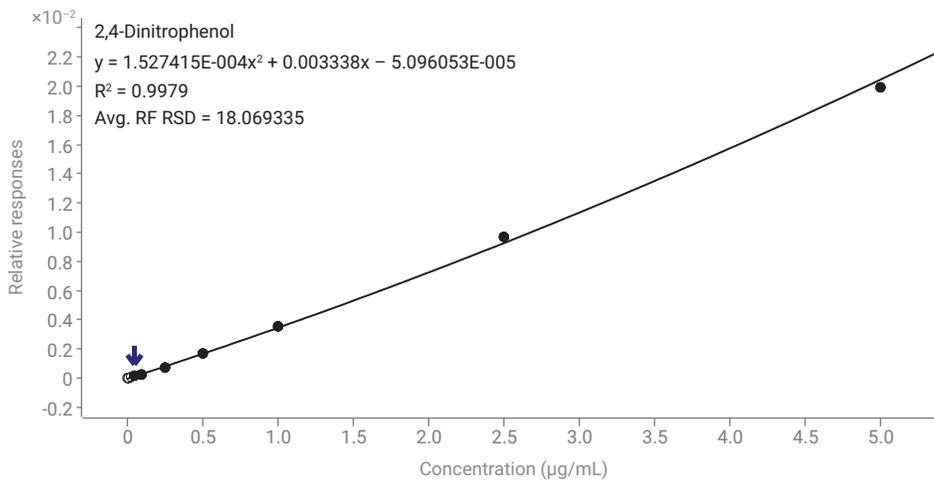


Figure 6. Alternate calibration curve for 2,4-dinitrophenol with a quadratic curve fit 0.05 to 5 µg/mL. $R^2 = 0.9979$. Calibration points 1, 2, 3, and 11 are excluded.

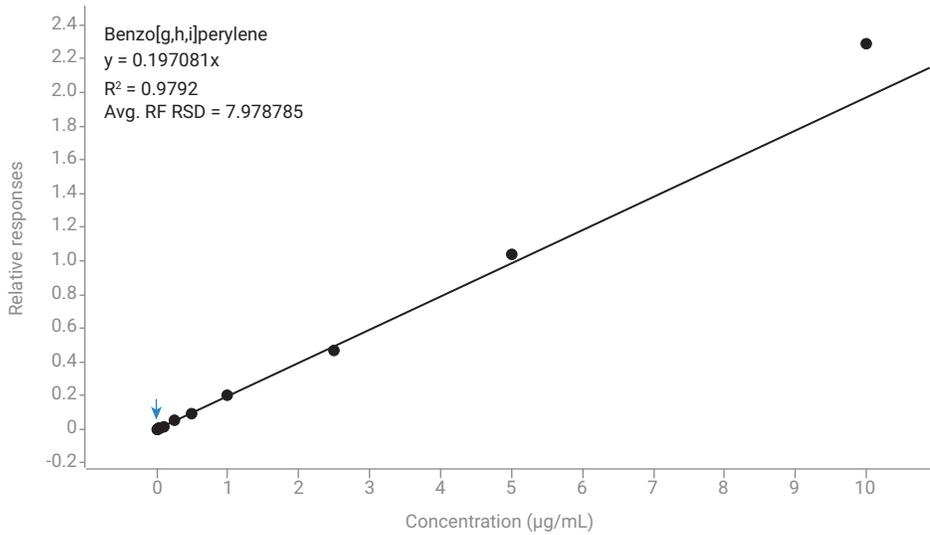


Figure 7. Avg RF calibration curve for benzo[g,h,i]perylene 0.005 to 10 µg/mL. Avg RF RSD = 7.98.

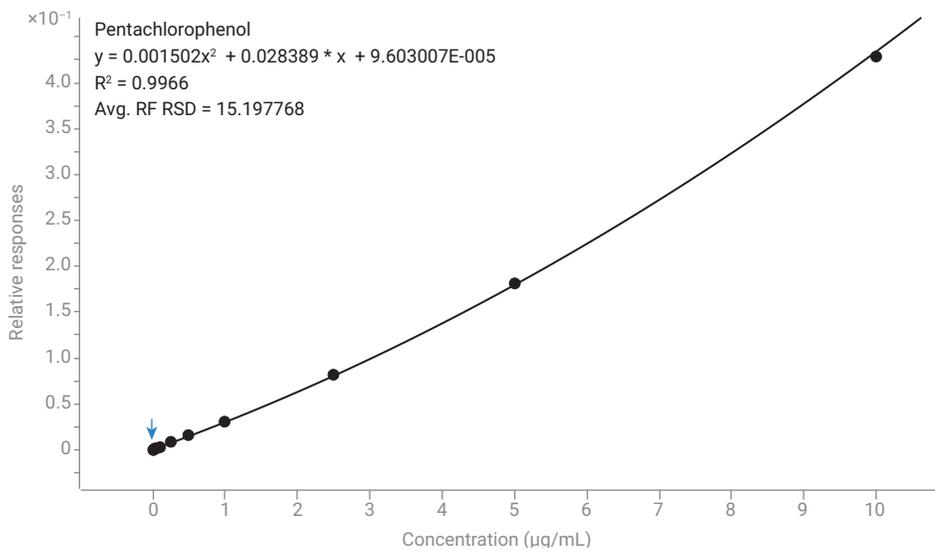


Figure 8. Calibration curve for pentachlorophenol 0.01 to 10 µg/mL. $R^2 = 0.9966$. Calibration point 1 excluded.

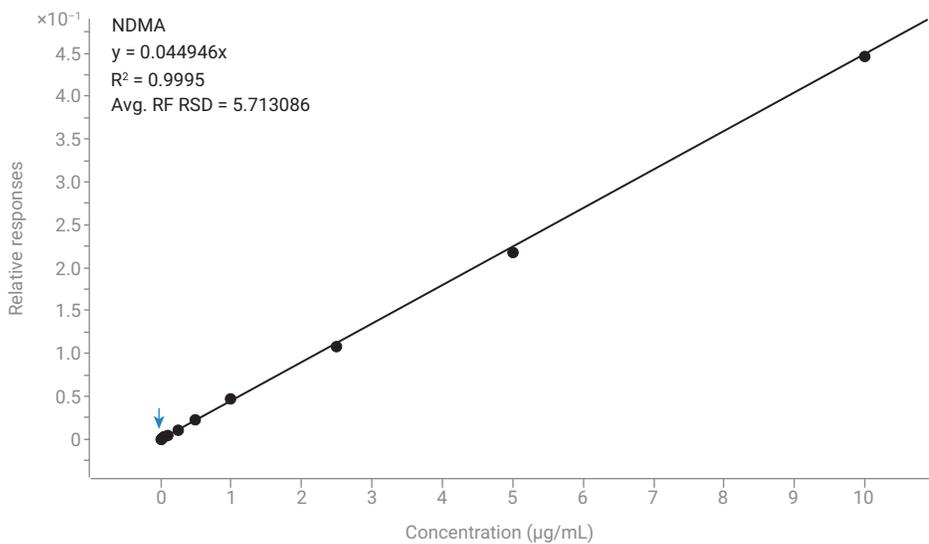


Figure 9. Calibration curve for NDMA. 0.01 to 10 µg/mL. Avg. RF RSD = 5.71. Calibration point 1 excluded.

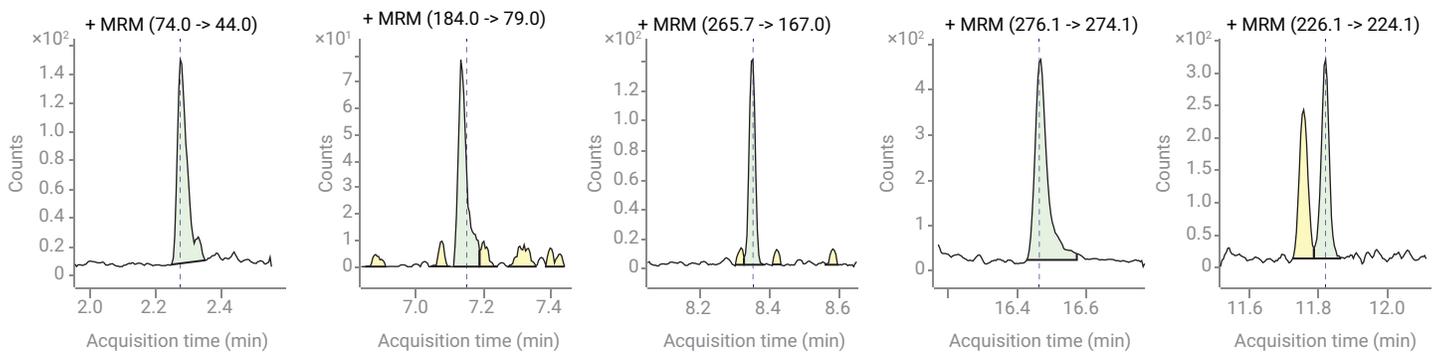


Figure 10. NDMA 0.01 µg/mL, 2,4-dinitrophenol 0.05 µg/mL, PCP 0.01 µg/mL, benzo[g,h,i]perylene 0.005 µg/mL, and chrysene 0.005 µg/mL.

Conclusion

A sensitive method for analysis of SVOCs has been developed that also demonstrates an extended dynamic range. Many analytes were shown to have a wide working calibration range over more than three orders of magnitude from 0.005 to 10 µg/mL. The collected data were evaluated with the quality criteria outlined in EPA 8270E.

GC/TQ offers significant advantages over the single quadrupole GC/MSD system in the analysis of SVOCs:

- High selectivity results in faster batch review by reducing the complexity of the data due to elimination of matrix interferences.
- Increased sensitivity opens the door for reduced sample sizes and smaller extraction volumes, which may:
 - 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. This improves instrument performance and makes adding and removing analytes from the method easy.
- The manufacturer recommended tune protocol simplifies tuning verification on the GC/TQ.

Key techniques for SVOC analysis by GC/MS which can 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 9 mm extractor lens gives outstanding linearity for all compounds while affording excellent sensitivity for many difficult analytes.

References

1. Churley, M. *et al.* A Fast Method for EPA 8270 in MRM Mode Using the 7000 Series Triple Quadrupole GC/MS. *Agilent Technologies application note*, publication number 5991-0694EN, **2019**.
2. M. Churley, *et al.* EPA 8270 Re-Optimized for Widest Calibration Range on the 5977 Inert Plus GC/MSD. *Agilent Technologies application note*, publication number 5994-0349EN, **2018**.

3. Anderson, Kim A. *et al.* Modified ion source triple quadrupole mass spectrometer gas chromatograph for polycyclic aromatic hydrocarbon analyses. *J. Chromatog. A* **2015**, 1419, 89–98. doi:10.1016/j.chroma.2015.09.054
4. Stone, P. *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**.
5. Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS); Method 8270E Sections 1.4.7, 11.3.1.2, and 11.6.1.4; United States Environmental Protection Agency, Revision 4, June **2018**.

Disclaimer

Although reference is made to EPA documents for review of the data, the contents of this publication have not been subjected to EPA review and the opinions of the authors do not reflect EPA policy.

Appendix

A List of calibrated compounds and transitions is shown in the following table.

| Compound Name | CAS No. | Retention Time (min) | Precursor Ion | Product Ion | Left RT Delta | Right RT Delta | CE |
|------------------------------------|-----------|----------------------|---------------|-------------|---------------|----------------|----|
| NDMA | 62-75-9 | 2.25 | 74 | 44 | 0.3 | 0.3 | 6 |
| NDMA | 62-75-9 | 2.25 | 74 | 42 | 0.3 | 0.3 | 14 |
| Pyridine | 110-86-1 | 2.4 | 79 | 52 | 0.3 | 0.5 | 25 |
| Pyridine | 110-86-1 | 2.4 | 79 | 51 | 0.3 | 0.5 | 25 |
| Phenol | 108-95-2 | 3.92 | 94 | 66.1 | 0.3 | 0.3 | 15 |
| Phenol | 108-95-2 | 3.92 | 94 | 65.1 | 0.3 | 0.3 | 20 |
| Aniline | 62-53-3 | 3.96 | 93 | 66 | 0.3 | 0.3 | 10 |
| Aniline | 62-53-3 | 3.96 | 92 | 65 | 0.3 | 0.3 | 10 |
| bis(2-Chloroethyl)ether | 111-44-4 | 4.01 | 95.1 | 65 | 0.3 | 0.3 | 5 |
| bis(2-Chloroethyl)ether | 111-44-4 | 4.01 | 93.1 | 63 | 0.3 | 0.3 | 0 |
| 2-Chlorophenol | 95-57-8 | 4.06 | 128 | 64 | 0.3 | 0.3 | 30 |
| 2-Chlorophenol | 95-57-8 | 4.06 | 128 | 63 | 0.3 | 0.3 | 15 |
| 1,3-Dichlorobenzene | 541-73-1 | 4.2 | 146 | 111 | 0.3 | 0.3 | 15 |
| 1,3-Dichlorobenzene | 541-73-1 | 4.2 | 146 | 75 | 0.3 | 0.3 | 30 |
| 1,4-Dichlorobenzene-d4 | 3855-82-1 | 4.25 | 150 | 115 | 0.2 | 0.2 | 15 |
| 1,4-Dichlorobenzene-d4 | 3855-82-1 | 4.25 | 150 | 78 | 0.2 | 0.2 | 30 |
| 1,4-Dichlorobenzene | 106-46-7 | 4.27 | 146 | 111 | 0.3 | 0.3 | 15 |
| 1,4-Dichlorobenzene | 106-46-7 | 4.27 | 146 | 75 | 0.3 | 0.3 | 30 |
| Benzyl alcohol | 100-51-6 | 4.35 | 108 | 79 | 0.3 | 0.3 | 15 |
| Benzyl alcohol | 100-51-6 | 4.35 | 107 | 79 | 0.3 | 0.3 | 5 |
| 1,2-Dichlorobenzene | 95-50-1 | 4.39 | 146 | 111 | 0.3 | 0.3 | 15 |
| 1,2-Dichlorobenzene | 95-50-1 | 4.39 | 146 | 75 | 0.3 | 0.3 | 30 |
| 2-Methylphenol | 95-48-7 | 4.44 | 108 | 107 | 0.3 | 0.3 | 15 |
| 2-Methylphenol | 95-48-7 | 4.44 | 107 | 77 | 0.3 | 0.3 | 15 |
| 2,2'-oxybis[1-chloropropane] | 108-60-1 | 4.47 | 121 | 77 | 0.3 | 0.3 | 5 |
| 2,2'-oxybis[1-chloropropane] | 108-60-1 | 4.47 | 121 | 49 | 0.3 | 0.3 | 30 |
| 3+4-Methylphenol | 108-39-4 | 4.57 | 108 | 107.1 | 0.3 | 0.3 | 15 |
| 3+4-Methylphenol | 108-39-4 | 4.57 | 108 | 80 | 0.3 | 0.3 | 0 |
| N-Nitrosodi- <i>n</i> -propylamine | 621-64-7 | 4.58 | 113.1 | 71 | 0.3 | 0.3 | 10 |
| N-Nitrosodi- <i>n</i> -propylamine | 621-64-7 | 4.58 | 101 | 70 | 0.3 | 0.3 | 0 |
| Hexachloroethane | 67-72-1 | 4.69 | 200.9 | 165.9 | 0.3 | 0.3 | 15 |
| Hexachloroethane | 67-72-1 | 4.69 | 118.9 | 83.9 | 0.3 | 0.3 | 35 |
| Nitrobenzene | 98-95-3 | 4.74 | 123 | 77 | 0.3 | 0.3 | 10 |
| Nitrobenzene | 98-95-3 | 4.74 | 77 | 51 | 0.3 | 0.3 | 15 |
| Isophorone | 78-59-1 | 4.96 | 138 | 82 | 0.3 | 0.3 | 5 |
| Isophorone | 78-59-1 | 4.96 | 82 | 54 | 0.3 | 0.3 | 5 |
| 2-Nitrophenol | 88-75-5 | 5.03 | 138.9 | 81 | 0.3 | 0.3 | 15 |
| 2-Nitrophenol | 88-75-5 | 5.03 | 109 | 81 | 0.3 | 0.3 | 10 |
| 2,4-Dimethylphenol | 105-67-9 | 5.06 | 121 | 107 | 0.3 | 0.3 | 10 |
| 2,4-Dimethylphenol | 105-67-9 | 5.06 | 107.1 | 77.1 | 0.3 | 0.3 | 15 |
| bis(2-Chloroethoxy)methane | 111-91-1 | 5.15 | 95 | 65 | 0.3 | 0.3 | 5 |

| Compound Name | CAS No. | Retention Time (min) | Precursor Ion | Product Ion | Left RT Delta | Right RT Delta | CE |
|----------------------------|------------|----------------------|---------------|-------------|---------------|----------------|----|
| bis(2-Chloroethoxy)methane | 111-91-1 | 5.15 | 93 | 63 | 0.3 | 0.3 | 5 |
| 2,4-Dichlorophenol | 120-83-2 | 5.25 | 163.9 | 63 | 0.3 | 0.3 | 30 |
| 2,4-Dichlorophenol | 120-83-2 | 5.25 | 162 | 63 | 0.3 | 0.3 | 30 |
| 1,2,4-Trichlorobenzene | 120-82-1 | 5.34 | 179.9 | 145 | 0.3 | 0.3 | 15 |
| 1,2,4-Trichlorobenzene | 120-82-1 | 5.34 | 179.9 | 109 | 0.3 | 0.3 | 30 |
| Naphthalene-d8 | 1146-65-2 | 5.39 | 136.1 | 108.1 | 0.2 | 0.2 | 20 |
| Naphthalene-d8 | 1146-65-2 | 5.39 | 136.1 | 84.1 | 0.2 | 0.2 | 25 |
| Naphthalene | 91-20-3 | 5.41 | 128.1 | 102.1 | 0.3 | 0.3 | 20 |
| Naphthalene | 91-20-3 | 5.41 | 128.1 | 78.1 | 0.3 | 0.3 | 20 |
| 4-Chloroaniline | 106-47-8 | 5.46 | 127 | 92 | 0.3 | 0.3 | 15 |
| 4-Chloroaniline | 106-47-8 | 5.46 | 127 | 65 | 0.3 | 0.3 | 20 |
| Hexachloro-1,3-butadiene | 87-68-3 | 5.53 | 226.8 | 191.9 | 0.3 | 0.3 | 15 |
| Hexachloro-1,3-butadiene | 87-68-3 | 5.53 | 224.7 | 189.9 | 0.3 | 0.3 | 15 |
| 4-chloro-3-methylphenol | 59-50-7 | 5.91 | 142 | 107 | 0.3 | 0.3 | 15 |
| 4-chloro-3-methylphenol | 59-50-7 | 5.91 | 107 | 77 | 0.3 | 0.3 | 15 |
| 2-Methylnaphthalene | 91-57-6 | 6.07 | 142 | 141 | 0.3 | 0.3 | 15 |
| 2-Methylnaphthalene | 91-57-6 | 6.07 | 141 | 114.9 | 0.3 | 0.3 | 15 |
| 1-Methylnaphthalene | 90-12-0 | 6.16 | 142 | 114.9 | 0.3 | 0.3 | 30 |
| 1-Methylnaphthalene | 90-12-0 | 6.16 | 114.9 | 89 | 0.3 | 0.3 | 20 |
| Hexachlorocyclopentadiene | 77-47-4 | 6.22 | 236.7 | 143 | 0.3 | 0.3 | 20 |
| Hexachlorocyclopentadiene | 77-47-4 | 6.22 | 236.7 | 119 | 0.3 | 0.3 | 20 |
| 2,4,6-Trichlorophenol | 88-06-2 | 6.34 | 197.8 | 97 | 0.3 | 0.3 | 25 |
| 2,4,6-Trichlorophenol | 88-06-2 | 6.34 | 195.8 | 97 | 0.3 | 0.3 | 25 |
| 2,4,5-Trichlorophenol | 95-95-4 | 6.37 | 197.8 | 97 | 0.3 | 0.3 | 30 |
| 2,4,5-Trichlorophenol | 95-95-4 | 6.37 | 195.8 | 97 | 0.3 | 0.3 | 25 |
| 2-Chloronaphthalene | 91-58-7 | 6.54 | 162 | 126.9 | 0.3 | 0.3 | 20 |
| 2-Chloronaphthalene | 91-58-7 | 6.54 | 162 | 77 | 0.3 | 0.3 | 35 |
| 2-Nitroaniline | 88-74-4 | 6.63 | 138 | 92 | 0.3 | 0.3 | 15 |
| 2-Nitroaniline | 88-74-4 | 6.63 | 138 | 65 | 0.3 | 0.3 | 25 |
| 1,4-Dinitrobenzene | 100-25-4 | 6.77 | 168 | 75 | 0.2 | 0.2 | 20 |
| 1,4-Dinitrobenzene | 100-25-4 | 6.77 | 122 | 92 | 0.2 | 0.2 | 5 |
| Dimethyl phthalate | 131-11-3 | 6.82 | 163 | 92 | 0.3 | 0.3 | 30 |
| Dimethyl phthalate | 131-11-3 | 6.82 | 163 | 77 | 0.3 | 0.3 | 20 |
| 1,3-Dinitrobenzene | 99-65-0 | 6.84 | 168 | 75 | 0.3 | 0.3 | 20 |
| 1,3-Dinitrobenzene | 99-65-0 | 6.84 | 122 | 92 | 0.3 | 0.3 | 5 |
| 2,6-Dinitrotoluene | 606-20-2 | 6.87 | 165 | 90.1 | 0.3 | 0.3 | 15 |
| 2,6-Dinitrotoluene | 606-20-2 | 6.87 | 165 | 63 | 0.3 | 0.3 | 25 |
| Acenaphthylene | 208-96-8 | 6.94 | 151.9 | 102 | 0.3 | 0.3 | 30 |
| Acenaphthylene | 208-96-8 | 6.94 | 150.9 | 77 | 0.3 | 0.3 | 25 |
| 1,2-Dinitrobenzene | 528-29-0 | 6.95 | 168 | 78 | 0.3 | 0.3 | 5 |
| 1,2-Dinitrobenzene | 528-29-0 | 6.95 | 168 | 63 | 0.3 | 0.3 | 35 |
| 3-Nitroaniline | 99-09-2 | 7.03 | 138 | 92 | 0.3 | 0.3 | 15 |
| 3-Nitroaniline | 99-09-2 | 7.03 | 138 | 80 | 0.3 | 0.3 | 5 |
| Acenaphthene-d10 | 15067-26-2 | 7.08 | 164.1 | 162.1 | 0.5 | 0.5 | 15 |
| Acenaphthene-d10 | 15067-26-2 | 7.08 | 162.1 | 160.1 | 0.5 | 0.5 | 20 |
| Acenaphthene | 83-32-9 | 7.11 | 153.9 | 127 | 0.3 | 0.3 | 40 |
| Acenaphthene | 83-32-9 | 7.11 | 152.9 | 77 | 0.3 | 0.3 | 45 |

| Compound Name | CAS No. | Retention Time (min) | Precursor Ion | Product Ion | Left RT Delta | Right RT Delta | CE |
|----------------------------|-----------|----------------------|---------------|-------------|---------------|----------------|----|
| 2,4-Dinitrophenol | 51-28-5 | 7.14 | 184 | 107 | 0.3 | 0.3 | 25 |
| 2,4-Dinitrophenol | 51-28-5 | 7.14 | 184 | 79 | 0.3 | 0.3 | 25 |
| 4-Nitrophenol | 100-02-7 | 7.19 | 138.9 | 109 | 0.3 | 0.3 | 5 |
| 4-Nitrophenol | 100-02-7 | 7.19 | 109 | 81 | 0.3 | 0.3 | 10 |
| 2,4-Dinitrotoluene | 121-14-2 | 7.27 | 165 | 119 | 0.3 | 0.3 | 5 |
| 2,4-Dinitrotoluene | 121-14-2 | 7.27 | 165 | 63 | 0.3 | 0.3 | 45 |
| Dibenzofuran | 132-64-9 | 7.29 | 167.9 | 139.1 | 0.3 | 0.3 | 25 |
| Dibenzofuran | 132-64-9 | 7.29 | 138.9 | 63 | 0.3 | 0.3 | 35 |
| 2,3,5,6-Tetrachlorophenol | 935-95-5 | 7.36 | 232 | 167.9 | 0.2 | 0.2 | 15 |
| 2,3,5,6-Tetrachlorophenol | 935-95-5 | 7.36 | 230 | 165.9 | 0.2 | 0.2 | 15 |
| 2,3,4,6-Tetrachlorophenol | 58-90-2 | 7.4 | 231.9 | 167.9 | 0.3 | 0.3 | 15 |
| 2,3,4,6-Tetrachlorophenol | 58-90-2 | 7.4 | 230 | 165.9 | 0.3 | 0.3 | 15 |
| Diethyl phthalate | 84-66-2 | 7.51 | 149 | 93 | 0.3 | 0.3 | 15 |
| Diethyl phthalate | 84-66-2 | 7.51 | 149 | 65 | 0.3 | 0.3 | 20 |
| 4-Chlorodiphenyl ether | 7005-72-3 | 7.62 | 204 | 77 | 0.3 | 0.3 | 30 |
| 4-Chlorodiphenyl ether | 7005-72-3 | 7.62 | 141.1 | 115.1 | 0.3 | 0.3 | 20 |
| Fluorene | 86-73-7 | 7.62 | 166 | 165.1 | 0.3 | 0.3 | 15 |
| Fluorene | 86-73-7 | 7.62 | 164.9 | 163.1 | 0.3 | 0.3 | 35 |
| 4-Nitroaniline | 100-01-6 | 7.64 | 138 | 108.1 | 0.3 | 0.3 | 5 |
| 4-Nitroaniline | 100-01-6 | 7.64 | 108 | 80 | 0.3 | 0.3 | 15 |
| 4,6-dinitro-o-cresol | 534-52-1 | 7.66 | 198 | 167.9 | 0.3 | 0.3 | 5 |
| 4,6-dinitro-o-cresol | 534-52-1 | 7.66 | 198 | 121 | 0.3 | 0.3 | 10 |
| Diphenylamine | 122-39-4 | 7.75 | 170 | 169.2 | 0.3 | 0.3 | 15 |
| Diphenylamine | 122-39-4 | 7.75 | 167 | 166.2 | 0.3 | 0.3 | 20 |
| Azobenzene | 103-33-3 | 7.79 | 105 | 77.1 | 0.3 | 0.3 | 5 |
| Azobenzene | 103-33-3 | 7.79 | 77 | 51 | 0.3 | 0.3 | 15 |
| 4-bromophenyl phenyl ether | 101-55-3 | 8.1 | 250 | 141 | 0.3 | 0.3 | 20 |
| 4-bromophenyl phenyl ether | 101-55-3 | 8.1 | 248 | 141 | 0.3 | 0.3 | 20 |
| Hexachlorobenzene | 118-74-1 | 8.16 | 283.7 | 213.8 | 0.3 | 0.3 | 30 |
| Hexachlorobenzene | 118-74-1 | 8.16 | 248.7 | 214 | 0.3 | 0.3 | 15 |
| Pentachlorophenol | 87-86-5 | 8.35 | 265.7 | 167 | 0.3 | 0.3 | 25 |
| Pentachlorophenol | 87-86-5 | 8.35 | 165 | 130 | 0.3 | 0.3 | 25 |
| Phenanthrene-d10 | 1517-22-2 | 8.54 | 188.3 | 160.2 | 0.2 | 0.2 | 20 |
| Phenanthrene-d10 | 1517-22-2 | 8.54 | 188.3 | 158.2 | 0.2 | 0.2 | 35 |
| Phenanthrene | 85-01-8 | 8.57 | 177.9 | 152 | 0.3 | 0.3 | 25 |
| Phenanthrene | 85-01-8 | 8.57 | 175.9 | 149.9 | 0.3 | 0.3 | 25 |
| Anthracene | 120-12-7 | 8.62 | 178.1 | 151 | 0.3 | 0.3 | 30 |
| Anthracene | 120-12-7 | 8.62 | 177.9 | 152 | 0.3 | 0.3 | 25 |
| Carbazole | 86-74-8 | 8.77 | 167 | 139 | 0.3 | 0.3 | 45 |
| Carbazole | 86-74-8 | 8.77 | 167 | 89 | 0.3 | 0.3 | 60 |
| Di-n-butyl phthalate | 84-74-2 | 9.13 | 149 | 121 | 0.3 | 0.3 | 15 |
| Di-n-butyl phthalate | 84-74-2 | 9.13 | 149 | 65 | 0.3 | 0.3 | 25 |
| Fluoranthene | 206-44-0 | 9.76 | 201.9 | 151.9 | 0.3 | 0.3 | 30 |
| Fluoranthene | 206-44-0 | 9.76 | 200.9 | 199.9 | 0.3 | 0.3 | 15 |
| Pyrene | 129-00-0 | 10.02 | 202.1 | 151 | 0.3 | 0.3 | 45 |
| Pyrene | 129-00-0 | 10.02 | 201.1 | 200 | 0.3 | 0.3 | 15 |

| Compound Name | CAS No. | Retention Time (min) | Precursor Ion | Product Ion | Left RT Delta | Right RT Delta | CE |
|-----------------------------|-----------|----------------------|---------------|-------------|---------------|----------------|----|
| Butyl benzyl phthalate | 85-68-7 | 10.9 | 149 | 65 | 0.3 | 0.3 | 25 |
| Butyl benzyl phthalate | 85-68-7 | 10.9 | 91 | 65 | 0.3 | 0.3 | 15 |
| Benz[a]anthracene | 56-55-3 | 11.75 | 228.1 | 226.1 | 0.3 | 0.3 | 30 |
| Benz[a]anthracene | 56-55-3 | 11.75 | 226.1 | 224.1 | 0.3 | 0.3 | 35 |
| Chrysene-d12 | 1719-03-5 | 11.77 | 240.2 | 236.2 | 0.3 | 0.3 | 35 |
| Chrysene-d12 | 1719-03-5 | 11.77 | 236.1 | 232.1 | 0.3 | 0.3 | 40 |
| Chrysene | 218-01-9 | 11.81 | 226.1 | 224.1 | 0.3 | 0.3 | 40 |
| Chrysene | 218-01-9 | 11.81 | 113.1 | 112.1 | 0.3 | 0.3 | 10 |
| Bis(2-ethylhexyl) phthalate | 117-81-7 | 11.9 | 167 | 149 | 0.3 | 0.3 | 5 |
| Bis(2-ethylhexyl) phthalate | 117-81-7 | 11.9 | 149 | 65 | 0.3 | 0.3 | 25 |
| Di-n-octyl phthalate | 117-84-0 | 13.29 | 149 | 93 | 0.3 | 0.3 | 20 |
| Di-n-octyl phthalate | 117-84-0 | 13.29 | 149 | 65 | 0.3 | 0.3 | 25 |
| Benzo[b]fluoranthene | 205-99-2 | 13.88 | 252.1 | 250.1 | 0.3 | 0.3 | 35 |
| Benzo[b]fluoranthene | 205-99-2 | 13.88 | 126 | 113.1 | 0.3 | 0.3 | 10 |
| Benzo[k]fluoranthene | 207-08-9 | 13.93 | 252.1 | 250.1 | 0.3 | 0.3 | 30 |
| Benzo[k]fluoranthene | 207-08-9 | 13.93 | 126.1 | 113.1 | 0.3 | 0.3 | 10 |
| Benzo[a]pyrene | 50-32-8 | 14.42 | 252.1 | 250.1 | 0.3 | 0.3 | 35 |
| Benzo[a]pyrene | 50-32-8 | 14.42 | 125 | 124.1 | 0.3 | 0.3 | 10 |
| Perylene-d12 | 1520-96-3 | 14.5 | 264.2 | 260.1 | 0.3 | 0.3 | 35 |
| Perylene-d12 | 1520-96-3 | 14.5 | 260.1 | 256.1 | 0.3 | 0.3 | 40 |
| Indeno[1,2,3-cd]pyrene | 193-39-5 | 16.05 | 276.1 | 274.1 | 0.3 | 0.3 | 40 |
| Indeno[1,2,3-cd]pyrene | 193-39-5 | 16.05 | 137 | 136 | 0.3 | 0.3 | 15 |
| Dibenz[a,h]anthracene | 53-70-3 | 16.1 | 278.1 | 276.1 | 0.3 | 0.3 | 35 |
| Dibenz[a,h]anthracene | 53-70-3 | 16.1 | 125 | 124 | 0.3 | 0.3 | 10 |
| Benzo[g,h,i]perylene | 191-24-2 | 16.47 | 276.1 | 274.1 | 0.3 | 0.3 | 45 |
| Benzo[g,h,i]perylene | 191-24-2 | 16.47 | 138 | 137 | 0.3 | 0.3 | 15 |

| Consumables | Part Number |
|--|-------------|
| Sample Containment | |
| Vials, screw top, amber, deactivated, 2 mL, 100/pk | 5183-2072 |
| Cap, screw, PTFE/silicone septa, 100/pk | 5040-4681 |
| Vial inserts, 250 µL, deactivated, 100/pk | 5181-8872 |
| Instrument Supplies | |
| Syringe, Blue Line, 10 µL, fixed needle, 23-26s/42/cone, 6/pk | G4513-80200 |
| Inlet septa, Advanced Green, nonstick, 11 mm, 50/pk | 5183-4759 |
| Inlet liner, Ultra Inert, split, low pressure drop, glass wool | 5190-2295 |
| GC inlet seal, gold plated, with washer, Ultra Inert, 10/pk | 5190-6145 |
| Lens, extraction, 9 mm | G3870-20449 |
| Separation | |
| J&W DB-8270D Ultra Inert GC column, 30 m × 0.25 mm, 0.25 µm | 122-9732 |

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