Application Note

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Enhancing Sensitivity in Analysis of Semivolatile Organic Compounds with the Agilent 8890/5977C GC/MSD

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Abstract

This application note evaluates the performance of an Agilent 8890/5977C gas chromatography/mass selective detector (GC/MSD) in the analysis of semivolatile organic compounds (SVOCs) at both traditional and enhanced sensitivity levels. The GC/MSD system was initially calibrated with a range of 0.2 to 150 µg/mL with 97% of the 76 evaluated analytes meeting the requirement for average response factor (RF) curve fits. Method modifications to enhance sensitivity were applied to challenge a lower calibration range of 0.01 to 10 µg/mL. Under these amended conditions, 97% of the tested compounds also met or exceeded the United States Environmental Protection Agency (US EPA) Method 8270E criteria for average RF fits. These results demonstrated a potential for lower detection of analytes.

Introduction

The analysis of semivolatile organic compounds (SVOCs) provides a critical evaluation of our environment for persistent pollutants. The United States Environmental Protection Agency (US EPA) has issued regulations and guidelines in Method 8270E[1] for the analysis of these analytes by gas chromatography/mass spectrometry (GC/MS). The analysis of SVOCs as a class comes with challenges and is a reasonable method of testing the performance of a GC/MS platform. The diverse set of analytes include phthalates, phenols, nitrosamines, aromatic nitro compounds, and polynuclear aromatic hydrocarbons (PAHs), among others. These analytes span a wide range of molecular weights and have a wide range of vapor pressures. Some of the analytes are well disposed to analysis by gas chromatography while others present significant challenges relating to stability, reproducibility, and chromatographic integrity.

Many laboratories had originally established methods with a working concentration range of 20 to 160 µg/mL. There has been a desire to expand the dynamic range and increase sensitivity in the analysis. There are several different motivations for improving sensitivity of analysis for SVOCs. These motivations include increasing environmental protection and improving laboratory sustainability. Cost savings and sustainability objectives can be reached with smaller extraction volumes that reduce waste and reduce costs associated with solvent usage, sample shipping, extract preparation, and waste disposal. In recent years, modern instrumentation and improved techniques have allowed laboratories to improve with many methods, reaching lower limits in the range of 0.2 µg/mL.[2] This application note details the use of the sensitive Agilent 5977C mass selective detector (MSD) combined with an Agilent 8890 gas chromatograph (GC). This system was demonstrated to first meet performance requirements of the US EPA 8270E method over a working range of 0.2 to 150 µg/mL. Then, the system was challenged to meet calibration performance requirements over a wider working range at lower concentrations, from 0.01 to 10 µg/mL. The techniques applied to improve GC/MSD sensitivity are discussed.

Experimental

Instrumental method

The samples were introduced on an Agilent 8890 GC with an Agilent 7693A automatic liquid sampler (ALS). This instrument was equipped with a split/splitless (SSL) inlet and a 30 m DB-UI8270D column with an internal diameter of 0.25 mm and a 0.25 µm film thickness. An Ultra Inert, split, low pressure drop liner with glass wool was used.

An Agilent 5977C GC/MSD was used as the detector. A 9 mm diameter extractor lens (part number G3870-20449) was selected for use in the GC/MSD source. This lens was selected as previous work[2,3] has illustrated that it can produce enhanced method performance over a wide dynamic range for semivolatile analytes.

A split injection technique was selected. Although even greater method sensitivity can be achieved with a splitless injection mode, the advantages of a split injection are compelling. Split injections focus the introduction of the analytes from the inlet to the column in a narrow band, which improves peak shapes and resolution, particularly for early eluting analytes. The higher overall flows of a split injection decrease residence time in the hot inlet, which can be a benefit when analyzing compounds that are thermally labile. Another important benefit of split injections is that they reduce the deposition of nonvolatile contaminants at the head of the GC column, which could reduce the frequency of maintenance performed on the inlet and GC column.

As an enhancement to a standard split injection, a pulsed split injection was found to be advantageous. During a pulsed injection, the GC inlet pressure is increased for a short time during sample introduction. After a short time, the inlet pressure is reduced back to the level needed to obtain the optimal column flow rate. This technique can help contain the solvent vapor in the inlet, further narrows the analyte band introduced to the column, and improves analyte response. The pulsed split also allows low split ratios, which would have too little flow through the liner without the pulse.

Retention time locking (RTL) is another critical tool that is used to ensure retention time fidelity in the method. As a common practice for SVOC analysis during inlet maintenance, the analytical column is often trimmed at the head to remove nonvolatile deposits that degrade instrument performance.

The problem this creates is that the analyst must verify and may need to adjust the retention times of all analytes (numbering 76 in this application), as retention times can shift after trimming. With retention time locking, a single injection of a known analyte is used by the Agilent MassHunter acquisition software for GC/MS systems to calculate a minor adjustment to the GC column flow that will align all the analyte retention times. In this method, the retention time was locked to acenaphthene-d10 at 10.93 minutes. Retention time locking can be used to align the retention times of all analytes across multiple instruments and even across multiple laboratories, which will improve consistency and simplify data review.

Initial instrument parameters were sourced from previous Agilent application notes.[2,4,5] GC and MSD settings are outlined in Table 1.

Table 1. GC and MSD parameters.

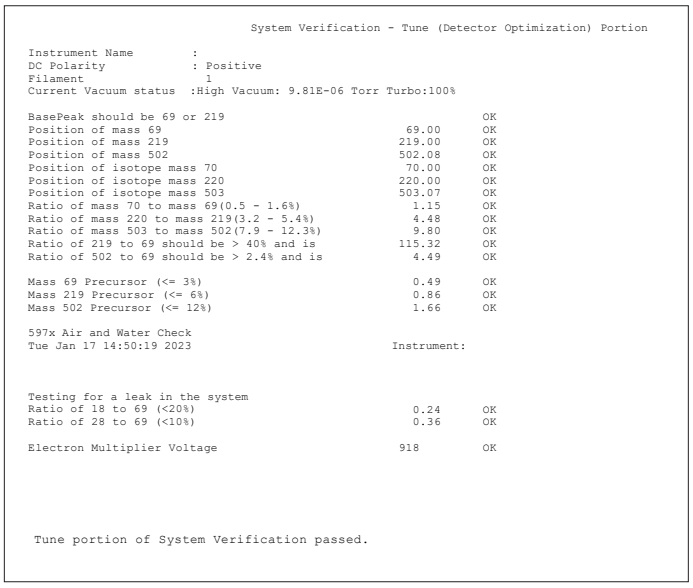
Parameter	Value
GC Settings	
Analytical Column	Agilent J&W DB-8270D UI, 30 m × 0.25 mm, 0.25 µm (part number 122-9732)
Injection Volume	1 µL
Inlet Temperature	Isothermal 280 °C
Injection Mode	Pulsed split
Split Ratio	10:1 / 25:1
Injection Pulse Pressure	30 psi until 0.6 min
Liner	Ultra Inert split, low pressure drop glass wool (part number 5190-2295)
Oven Temperature Program	40 °C, hold for 0.5 min Ramp at 10 °C/min to 100 °C, hold 0 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 15 °C/min to 320 °C, hold 2 min
Run Time	21.6 min
Equilibration Time	1 min
Carrier Gas	Helium, constant flow at 1.25 mL/min (adjusted by RT locking)
Transfer Line Temperature	320 °C
MSD Settings	
Ion Source	Extractor with 9 mm lens
Ion Source Temperature	300 °C
Quadrupole Temperature	150 °C
Ionization Mode	EI
Solvent Delay	2.1 min
EMV Mode	Gain factor
Gain Factor	0.4 / 0.8
Scan Type	Scan

System optimization

Mass spectrometer tuning and verification

The 5977C GC/MSD was tuned with PFTBA (perfluorotributylamine) using the Etune autotune algorithm. This is an automatic tune, which is implemented with a selection in the tune menu in the tune and vacuum control screen of the MassHunter acquisition software for GC/MS systems. The Etune is a modification of the traditional Atune algorithm, which takes advantage of applying voltage to the MS source extractor lens and ion body to improve sensitivity.

Method 8270E requires the MS tune to be verified. First, the MassHunter tune evaluation program was used. This tune system verification function introduces PFTBA into the source and verifies that the manufacturer's recommended performance criteria are met for mass accuracy, mass resolution, and isotopic ratios. An example tune evaluation report is shown in Figure 1.



System Verification - Tune (Detector Optimization) Portion

Instrument Name :
DC Polarity : Positive
Filament 1
Current Vacuum status :High Vacuum: 9.81E-06 Torr Turbo:100%

BasePeak should be 69 or 219		OK
Position of mass 69	69.00	OK
Position of mass 219	219.00	OK
Position of mass 502	502.08	OK
Position of isotope mass 70	70.00	OK
Position of isotope mass 220	220.00	OK
Position of isotope mass 503	503.07	OK
Ratio of mass 70 to mass 69(0.5 - 1.6%)	1.15	OK
Ratio of mass 220 to mass 219(3.2 - 5.4%)	4.48	OK
Ratio of mass 503 to mass 502(7.9 - 12.3%)	9.80	OK
Ratio of 219 to 69 should be > 40% and is	115.32	OK
Ratio of 502 to 69 should be > 2.4% and is	4.49	OK
Mass 69 Precursor (<= 3%)	0.49	OK
Mass 219 Precursor (<= 6%)	0.86	OK
Mass 502 Precursor (<= 12%)	1.66	OK

597x Air and Water Check
Tue Jan 17 14:50:19 2023 Instrument:

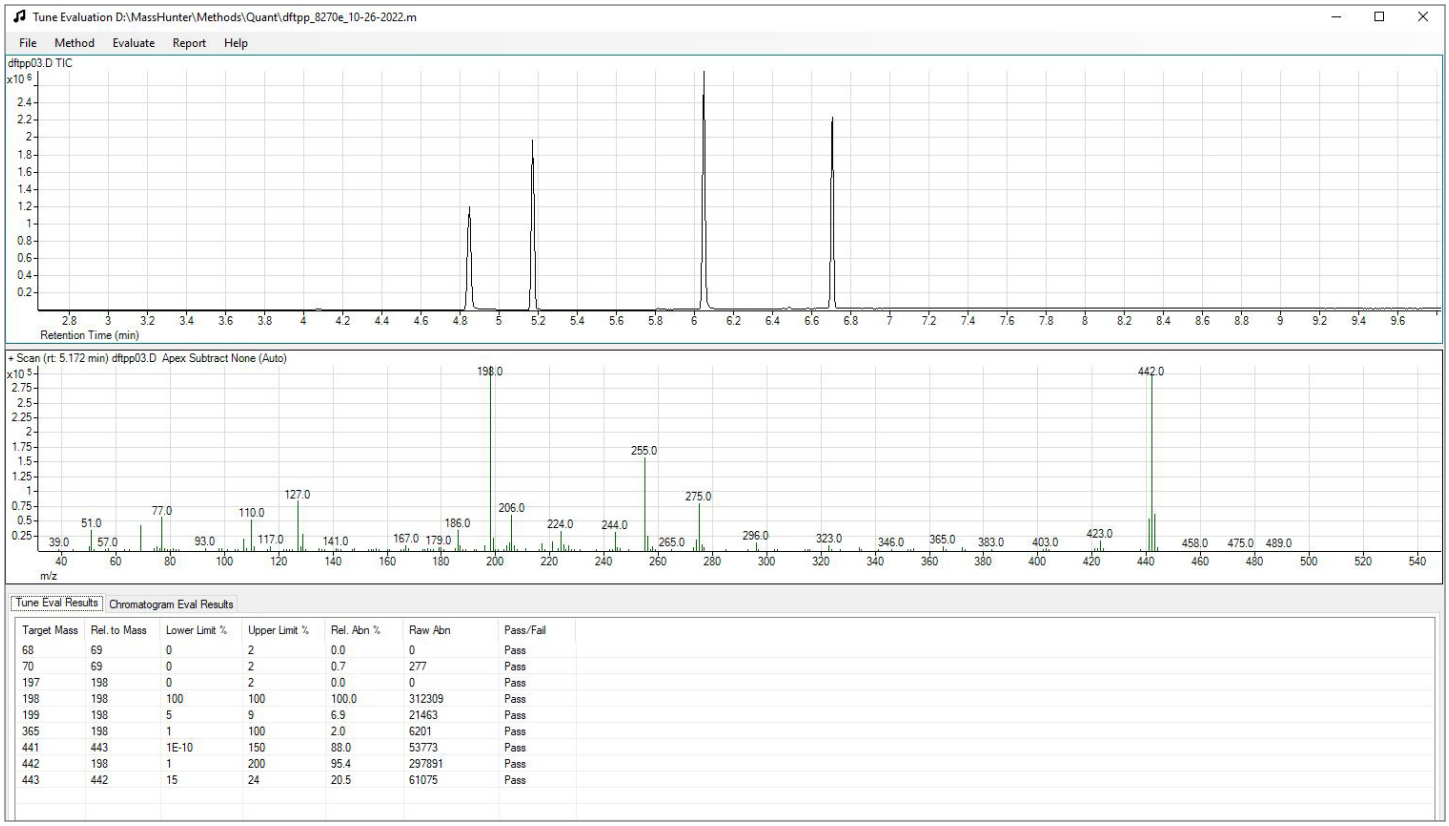
Testing for a leak in the system

Ratio of 18 to 69 (<20%)	0.24	OK
Ratio of 28 to 69 (<10%)	0.36	OK
Electron Multiplier Voltage	918	OK

Tune portion of System Verification passed.

Figure 1. System verification tune report.

Then, an 8270 decafluorotriphenylphosphine (DFTPP) evaluation check was performed. This was done by injecting 1 µL of a 25 ng/mL solution of DFTPP tuning solution and evaluating the performance criteria as outlined in section 11.3 of the 8270E method. The tune evaluation program contained within Agilent MassHunter Environmental Quantitative Analysis software was used to evaluate system performance against these criteria, as shown in Figure 2. All DFTPP tuning mass ratios were found to be within criteria. The tailing factors for pentachlorophenol and benzidine were less than 2. Degradation of 4,4'-DDT was also shown to be minimal.



Target Mass	Rel. to Mass	Lower Limit %	Upper Limit %	Rel. Abn %	Raw Abn	Pass/Fail
68	69	0	2	0.0	0	Pass
70	69	0	2	0.7	277	Pass
197	198	0	2	0.0	0	Pass
198	198	100	100	100.0	312309	Pass
199	198	5	9	6.9	21463	Pass
365	198	1	100	2.0	6201	Pass
441	443	1E-10	150	88.0	53773	Pass
442	198	1	200	95.4	297891	Pass
443	442	15	24	20.5	61075	Pass

Figure 2. DFTPP tune evaluation report.

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. The 14 calibration levels were prepared at the following concentrations: 0.01, 0.025, 0.05, 0.1, 0.25, 0.5, 1, 2.5, 5, 10, 20, 50, 100, and 150 µg/mL. The standard calibration curve covered a range from 0.2 to 150 µg/mL, while the enhanced sensitivity curve covered a range from 0.01 to 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, peneanthrene-d10, and perylene-d12. This ISTD solution was diluted and added to the calibration vials at a concentration of 4 µg/mL.

Workflow for setting the split ratio and detector gain

One of the first parameters that must be optimized is the determination of the split ratio. Setting the split ratio too low can result in poor peak shapes, particularly for early eluting analytes. A low split ratio can also result in poor resolution of critical pairs of analytes. The benzo[b] and benzo[k] fluoranthene peak resolution is checked to help determine an appropriate split ratio. Setting the split ratio too high results in reduced sensitivity and can waste carrier gas. It is also a good recommendation to keep the total inlet flow above 20 mL/min and keep the column pressure above 10 psi. There is some flexibility in these guidelines but, if the column pressure is set too low, it can increase analyte discrimination and result in poor precision of repeat injections. For the initial data set, an initial split ratio of 25:1 was selected.

Once the split ratio is determined, the highest level standard (150 µg/mL) is analyzed to verify sufficient resolution between all peaks and to verify that the MS detector is not saturated. The acquired data file from this test is loaded into MassHunter Qualitative Analysis software. The base peak chromatogram (BPC) is then extracted from the data file. Analysis of the BPC is used to determine the initial gain setting for the MS detector. For best linearity, maximum peak height should be no more than 5 million counts, and

ideally less than 2 million. In this work, the gain setting was adjusted to 0.4, which resulted in the height of the tallest peak (di-*n*-butylphthalate) at approximately 1.7 million counts. This adjustment is easy to determine as the detector response scales linearly with the gain setting. The purpose of this exercise is to ensure that the highest responding peak in the most concentrated standard is near to the top but not above the end of the linear region of the detector response. If the gain is set too high, there is a risk of saturating the MS detector, which will result in a loss of linearity at the top end of the calibration curve. This procedure helps to achieve the widest dynamic range without overloading the detector.

Once the standard calibration was established and verified, the next step was to increase the sensitivity of the analysis and create an enhanced calibration capable of detection of the analyte list at much lower concentrations. As mentioned earlier, the first two parameters to optimize when setting the dynamic range are the split ratio and the detector gain setting. Again, first the split ratio is adjusted. As the goal was to increase sensitivity, the split ratio was reduced. Although successful experiments were made with a split ratio as low as 5:1, a split ratio of 10:1 was selected as it was the lowest split ratio that followed the general guideline of keeping a minimum of 20 mL/min total flow through the inlet. Once the split ratio was determined, a test injection was again made with the highest level standard of the enhanced sensitivity calibration (10 µg/mL). The BPC was extracted from this data file and used to set a new gain parameter for the new method at 0.8. With a new split ratio and detector gain setting, a new enhanced sensitivity method was created and a calibration was run, the results of which can be seen in the data section of this note.

Additional considerations for improvement in high sensitivity analysis

This application note takes some initial steps in demonstrating the ability of 5977C MSD to be used as a tool to modify baseline methods for enhanced sensitivity analysis. There exists the capability to push the analysis levels much lower for many analytes, but there are constraints that will be encountered with some analytes that may be active or labile in the GC inlet or encounter other problems at very low concentrations. An analyst will never be able to analyze a compound on the MS detector in a GC/MS system that gets consistently caught in the GC inlet at low concentrations. Section 1.4.7 of the 8270E method[1] lists several such analytes and notes that they may be subject to erratic chromatographic behavior. It can be expected that analytes that are difficult to analyze will be even more difficult at even lower concentrations.

Also, the data presented here were acquired in GC/MS scan mode as has been done historically for SVOC analysis at both low and high levels for comparison purposes. Selected ion monitoring (SIM) mode is a powerful tool which should be considered to detect specific compounds at very high sensitivity. SIM mode is not appropriate for unknowns analysis, but it allows the collection of more points across the chromatographic peak. This mode results in significantly better sensitivity in SIM mode if the analytes are known beforehand.

If even greater sensitivity is needed, another available technology is the use of a triple quadrupole mass spectrometer such as the Agilent 7000E triple quadrupole GC/MS system in multiple reaction monitoring (MRM) mode. The MRM mode greatly increases sensitivity beyond what can be achieved with a standard MSD by reducing noise, and it has shown to be very successful for semivolatiles analysis.[5,7]

When enhancing a method for lower detection limits, there are additional challenges to encounter. Trace contamination and low-level interferents that may have been insignificant previously may present problems for enhanced sensitivity analysis. These are a few key guidelines to consider:

1. Use the Agilent 8890 GC automated maintenance procedures built into the keypad that cool the heated zones to minimize degradation of the flow path during maintenance.
2. Keep the MS system free of leaks. A small leak in a GC/MS fitting may allow a small amount of oxygen into the GC column. Such a leak can increase column bleed that is even more impactful for low-level analysis work.
3. Keep standard, sample preparation, and extraction areas very clean and use new gloves when manipulating any samples or standards.
4. Use only high purity solvents for sample and standard preparation and store these solvents in an isolated area.
5. Use gloves and/or tweezers when manipulating any GC consumables (liners, gold seals, septa, etc.)
6. Use ample blank injections and QC injections at the limit of quantitation (LOQ) to verify instrument cleanliness before sample analysis.
7. Use ample solvent washes and be sure to empty and refill them frequently. This is a frequent place to find low-level contamination in a GC system if not maintained. If sample overlap is enabled on the 7693 autosampler, additional washes may not extend analysis run time as the washes will be done while the previous sample is running.

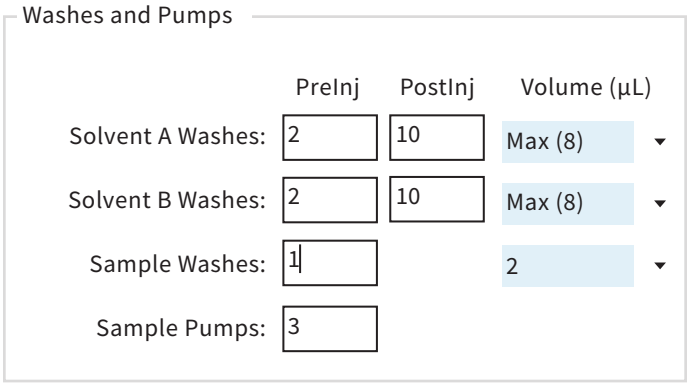


Figure 3. Syringe Wash setting from GC Driver.

Results and discussion

Initial calibration

The initial calibration included 76 analytes. Under the prescribed conditions, 3- and 4-methyl phenol isomers coelute. These two compounds are reported as a combined result. The calibration was achieved by introducing 11 calibration standards spanning a range of 0.2 to 150 µg/mL in sequence on the system. For five of the 76 analytes, one calibration point was trimmed from the bottom of the calibration curve working range to meet method criteria. All calibrated compounds include at least nine calibration levels.

Linearity is tested within MassHunter Quantitative Analysis software by calculating the average response factor (RF) relative standard deviation (RSD) for each analyte across all included calibration points. As per method 8270E Section 11.7.5, the response factor is assumed to be constant if the RSD is 20% or less. Results showed 97% of the analytes (74 of the 76 calibrated compounds) met the criteria average response factor curve fits with an average RF RSD of <20%. The remaining two analytes (2,4-dinitrophenol and 4,6-dinitro-2-methylphenol) were successfully calibrated with quadratic curve fits. As many analytes in the 8270E list can be difficult to calibrate with average response factor criteria due to activity in the GC inlet or other chromatographic challenges, an alternate calibration criterion may be selected, as per 8270E guidelines. When alternate curve fits are used, the coefficient of determination (R^2) should be greater than 0.99. The R^2 values for these two compounds were 0.9997 and 0.9992 respectively. The relative standard error was calculated for each analyte and found to be less than 20% for each calibration curve. The mean relative standard error across all analytes was 9.09%.

Enhanced sensitivity calibration

The enhanced sensitivity calibration included the same 76 analytes. This calibration included up to 10 calibration points and spanned a range of 0.01 to 10 µg/mL. For some analytes, up to three calibration points from the bottom end of the curve and/or one calibration point from the top end of the curve were trimmed to meet method criteria. All calibration curves included at least seven points. Again, 97% of the analytes (74 of the 76 calibrated compounds) met the criteria of an average RF RSD of <20%. The same two analytes (2,4-dinitrophenol and 4,6-dinitro-2-methylphenol) were calibrated with quadratic curve fits. The R^2 values for these compounds were 0.9991 and 0.9992, respectively. The relative standard error was calculated for each analyte and found to be less than 20% for each calibration curve. The mean relative standard error across all analytes was 8.66%.

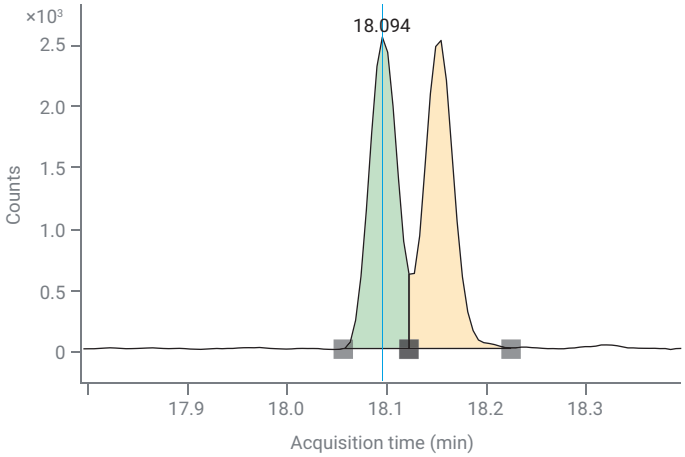


Figure 4. Benzo[b] and benzo[k]fluoranthene at 0.05 µg/mL, showing separation of critical pairs.

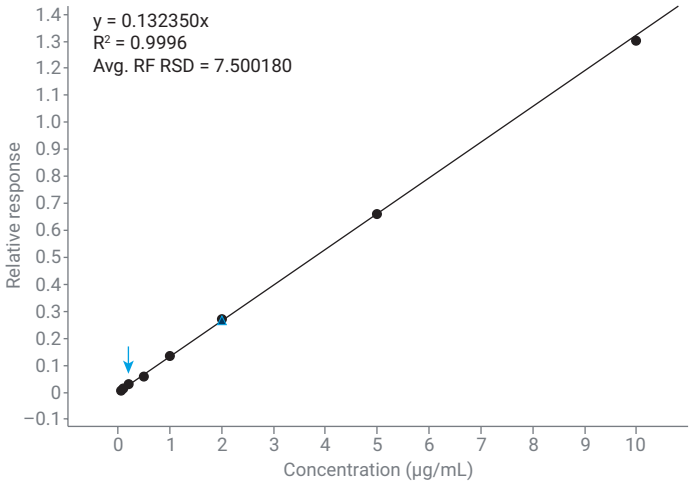


Figure 5. Calibration curve for NDMA 0.05 to 10 µg/mL.

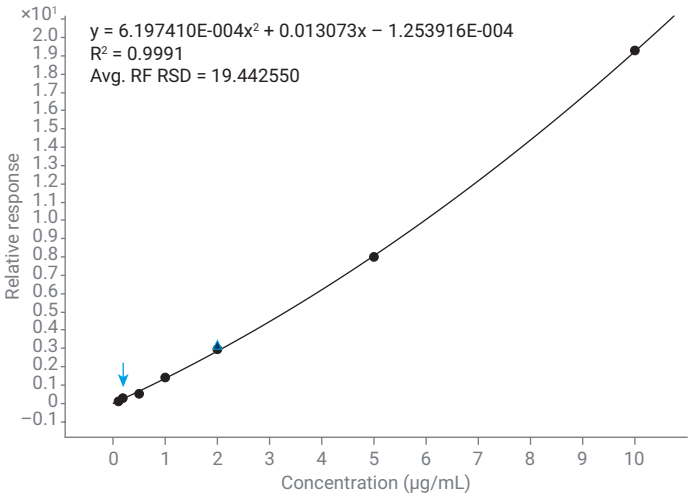


Figure 6. Quadradic calibration curve for 2,4-dinitrophenol 0.1 to 10 µg/mL.

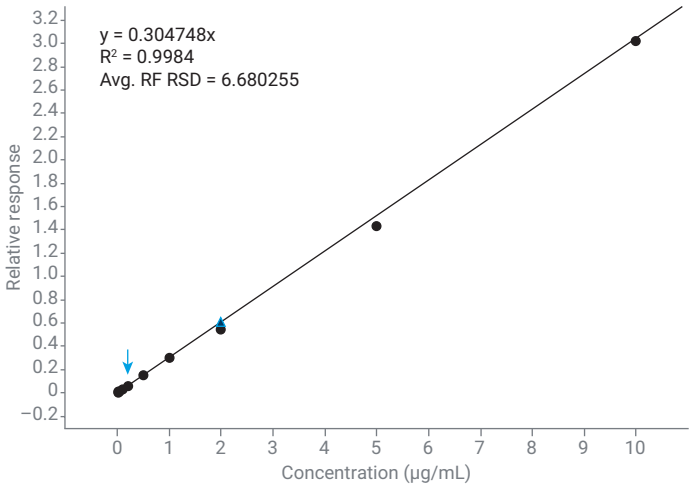


Figure 7. Calibration curve for chrysene 0.01 to 10 µg/mL.

For both the initial and the enhanced sensitivity calibrations, the accuracy for all calibration points was calculated to be within ±35% of the theoretical value for the low point of the calibration curve and ±30% of the theoretical value for all other calibration points.

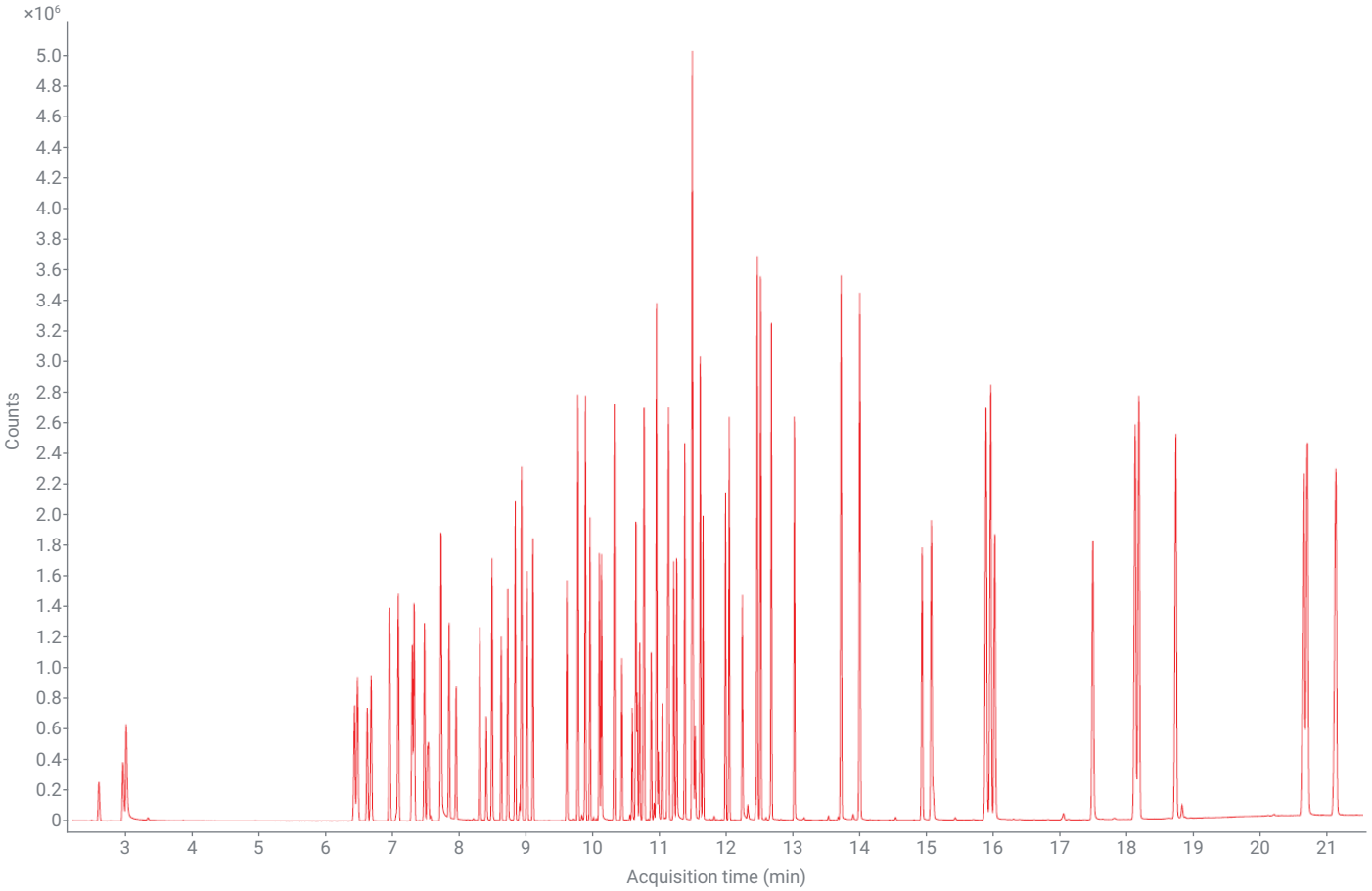


Figure 8. Total ion chromatogram from scan mode showing separation within 22 minutes.

Table 2. Analyte curve fits, % RSE, and calibrated range (continued on next page).

Compound	Retention Time (min)	Initial Calibration Curve				Enhanced Calibration Curve			
		Curve Fit	% RSE	R^2 (If Quadratic)	Calibration Range	Curve Fit	% RSE	R^2 (If Quadratic)	Calibration Range
N-Nitrosodimethylamine	2.99	Avg RF	9.28		0.5 to 150 µg/mL	Avg RF	7.50		0.05 to 10 µg/mL
Pyridine	3.04	Avg RF	13.24		0.5 to 150 µg/mL	Avg RF	16.43		0.1 to 10 µg/mL
Phenol	6.44	Avg RF	7.38		0.2 to 150 µg/mL	Avg RF	9.97		0.01 to 10 µg/mL
Aniline	6.49	Avg RF	5.64		0.2 to 150 µg/mL	Avg RF	5.45		0.01 to 10 µg/mL
Bis(2-chloroethyl) Ether	6.64	Avg RF	6.05		0.2 to 150 µg/mL	Avg RF	6.89		0.01 to 10 µg/mL
2-Chlorophenol	6.70	Avg RF	5.95		0.2 to 150 µg/mL	Avg RF	6.20		0.01 to 10 µg/mL
1,3-Dichlorobenzene	6.97	Avg RF	7.67		0.2 to 150 µg/mL	Avg RF	7.30		0.01 to 10 µg/mL
1,4-Dichlorobenzene	7.10	Avg RF	7.27		0.2 to 150 µg/mL	Avg RF	6.48		0.01 to 10 µg/mL
Benzyl Alcohol	7.31	Avg RF	8.84		0.2 to 150 µg/mL	Avg RF	9.29		0.02 to 10 µg/mL
1,2-Dichlorobenzene	7.34	Avg RF	7.63		0.2 to 150 µg/mL	Avg RF	8.64		0.01 to 10 µg/mL
2-Methylphenol	7.49	Avg RF	4.73		0.2 to 150 µg/mL	Avg RF	3.20		0.05 to 10 µg/mL
2,2'-Oxybis(1-chloropropane)	7.55	Avg RF	7.23		0.2 to 150 µg/mL	Avg RF	10.44		0.01 to 10 µg/mL
N-Nitrosodi-*n*-propylamine	7.74	Avg RF	8.85		0.2 to 150 µg/mL	Avg RF	3.15		0.05 to 10 µg/mL
3/4-Methylphenol	7.74	Avg RF	6.00		0.2 to 150 µg/mL	Avg RF	6.47		0.01 to 10 µg/mL
Hexachloroethane	7.86	Avg RF	5.59		0.2 to 150 µg/mL	Avg RF	11.60		0.01 to 10 µg/mL
Nitrobenzene	7.96	Avg RF	4.73		0.2 to 150 µg/mL	Avg RF	2.12		0.05 to 10 µg/mL
Isophorone	8.32	Avg RF	6.42		0.2 to 150 µg/mL	Avg RF	7.64		0.02 to 10 µg/mL
2-Nitrophenol	8.42	Avg RF	12.45		0.2 to 150 µg/mL	Avg RF	8.77		0.05 to 10 µg/mL
2,4-Dimethylphenol	8.50	Avg RF	5.69		0.2 to 150 µg/mL	Avg RF	4.92		0.01 to 10 µg/mL
Bis(2-chloroethoxy) Methane	8.64	Avg RF	6.11		0.2 to 150 µg/mL	Avg RF	5.39		0.01 to 10 µg/mL
2,4-Dichlorophenol	8.74	Avg RF	8.66		0.2 to 150 µg/mL	Avg RF	7.22		0.01 to 10 µg/mL
1,2,4-Trichlorobenzene	8.85	Avg RF	7.20		0.2 to 150 µg/mL	Avg RF	7.02		0.01 to 10 µg/mL
Naphthalene	8.94	Avg RF	9.87		0.2 to 150 µg/mL	Avg RF	6.77		0.01 to 10 µg/mL
4-Chloroaniline	9.03	Avg RF	6.66		0.2 to 150 µg/mL	Avg RF	3.42		0.02 to 10 µg/mL
Hexachlorobutadiene	9.11	Avg RF	6.39		0.2 to 150 µg/mL	Avg RF	11.18		0.01 to 10 µg/mL
4-Chloro-3-methylphenol	9.62	Avg RF	6.00		0.2 to 150 µg/mL	Avg RF	7.26		0.01 to 10 µg/mL
2-Methylnaphthalene	9.79	Avg RF	9.12		0.2 to 150 µg/mL	Avg RF	5.05		0.01 to 10 µg/mL
1-Methylnaphthalene	9.90	Avg RF	9.30		0.2 to 150 µg/mL	Avg RF	5.36		0.01 to 10 µg/mL
Hexachlorocyclopentadiene	9.97	Avg RF	5.67		0.2 to 150 µg/mL	Avg RF	5.46		0.01 to 10 µg/mL
2,4,6-Trichlorophenol	10.11	Avg RF	8.07		0.2 to 150 µg/mL	Avg RF	11.61		0.01 to 10 µg/mL
2,4,5-Trichlorophenol	10.14	Avg RF	7.28		0.2 to 150 µg/mL	Avg RF	12.51		0.02 to 10 µg/mL
2-Chloronaphthalene	10.33	Avg RF	8.81		0.2 to 150 µg/mL	Avg RF	5.19		0.02 to 10 µg/mL
2-Nitroaniline	10.45	Avg RF	6.20		0.2 to 150 µg/mL	Avg RF	14.39		0.05 to 10 µg/mL
1,4-Dinitrobenzene	10.60	Avg RF	13.96		0.5 to 150 µg/mL	Avg RF	12.08		0.02 to 10 µg/mL
Dimethyl Phthalate	10.65	Avg RF	7.08		0.2 to 150 µg/mL	Avg RF	5.61		0.01 to 10 µg/mL
1,3-Dinitrobenzene	10.68	Avg RF	12.08		0.2 to 150 µg/mL	Avg RF	11.64		0.1 to 10 µg/mL
2,6-Dinitrotoluene	10.71	Avg RF	17.16		0.2 to 150 µg/mL	Avg RF	9.50		0.05 to 5 µg/mL
1,2-Dinitrobenzene	10.76	Avg RF	13.09		0.2 to 150 µg/mL	Avg RF	17.02		0.02 to 10 µg/mL

Table 2. Analyte curve fits, % RSE, and calibrated range (continued).

Compound	Retention Time (min)	Initial Calibration Curve				Enhanced Calibration Curve			
		Curve Fit	% RSE	R^2 (If Quadratic)	Calibration Range	Curve Fit	% RSE	R^2 (If Quadratic)	Calibration Range
Acenaphthylene	10.78	Avg RF	9.82		0.2 to 150 µg/mL	Avg RF	2.98		0.01 to 10 µg/mL
3-Nitroaniline	10.88	Avg RF	14.47		0.2 to 150 µg/mL	Avg RF	12.14		0.02 to 10 µg/mL
Acenaphthene	10.96	Avg RF	10.03		0.2 to 150 µg/mL	Avg RF	5.99		0.01 to 10 µg/mL
2,4-Dinitrophenol	10.99	Quadratic	7.81	0.9997	0.5 to 150 µg/mL	Quadradic	11.21	0.9991	0.1 to 10 µg/mL
4-Nitrophenol	11.04	Avg RF	16.02		0.2 to 150 µg/mL	Avg RF	12.91		0.05 to 10 µg/mL
2,4-Dinitrotoluene	11.13	Avg RF	18.18		0.2 to 150 µg/mL	Avg RF	10.95		0.02 to 5 µg/mL
Dibenzofuran	11.14	Avg RF	9.48		0.2 to 150 µg/mL	Avg RF	4.65		0.01 to 10 µg/mL
2,3,5,6-Tetrachlorophenol	11.22	Avg RF	11.01		0.2 to 150 µg/mL	Avg RF	13.63		0.02 to 10 µg/mL
2,3,4,6-Tetrachlorophenol	11.26	Avg RF	10.14		0.2 to 150 µg/mL	Avg RF	11.53		0.02 to 10 µg/mL
Diethyl Phthalate	11.38	Avg RF	11.34		0.2 to 150 µg/mL	Avg RF	11.82		0.05 to 10 µg/mL
Fluorene	11.49	Avg RF	11.34		0.2 to 150 µg/mL	Avg RF	7.43		0.01 to 10 µg/mL
4-Chlorophenyl-phenyl Ether	11.50	Avg RF	7.78		0.2 to 150 µg/mL	Avg RF	12.46		0.01 to 10 µg/mL
4-Nitroaniline	11.51	Avg RF	9.78		0.2 to 150 µg/mL	Avg RF	14.04		0.02 to 10 µg/mL
4,6-Dinitro-2-methylphenol	11.54	Quadratic	16.47	0.9992	0.5 to 150 µg/mL	Quadradic	13.36	0.9992	0.05 to 10 µg/mL
Diphenylamine	11.62	Avg RF	10.64		0.2 to 150 µg/mL	Avg RF	9.69		0.05 to 10 µg/mL
Azobenzene	11.66	Avg RF	8.58		0.2 to 150 µg/mL	Avg RF	13.95		0.01 to 10 µg/mL
4-Bromophenyl Phenyl Ether	12.00	Avg RF	5.56		0.2 to 150 µg/mL	Avg RF	7.92		0.01 to 10 µg/mL
Hexachlorobenzene	12.05	Avg RF	7.91		0.2 to 150 µg/mL	Avg RF	5.14		0.02 to 10 µg/mL
Pentachlorophenol	12.25	Avg RF	15.66		0.2 to 150 µg/mL	Avg RF	11.20		0.02 to 10 µg/mL
Phenanthrene	12.47	Avg RF	7.95		0.2 to 150 µg/mL	Avg RF	4.22		0.02 to 10 µg/mL
Anthracene	12.52	Avg RF	7.15		0.2 to 150 µg/mL	Avg RF	4.19		0.01 to 10 µg/mL
Carbazole	12.68	Avg RF	8.57		0.2 to 150 µg/mL	Avg RF	5.21		0.01 to 10 µg/mL
Di-*n*-butylphthalate	13.02	Avg RF	7.61		0.2 to 150 µg/mL	Avg RF	9.13		0.02 to 10 µg/mL
Fluoranthene	13.72	Avg RF	6.29		0.2 to 150 µg/mL	Avg RF	5.70		0.01 to 10 µg/mL
Pyrene	14.00	Avg RF	7.80		0.2 to 150 µg/mL	Avg RF	7.30		0.01 to 10 µg/mL
Butylbenzylphthalate	14.93	Avg RF	15.86		0.2 to 150 µg/mL	Avg RF	13.38		0.01 to 10 µg/mL
Bis(2-ethylhexyl) Adipate	15.07	Avg RF	18.31		0.2 to 150 µg/mL	Avg RF	10.74		0.02 to 5 µg/mL
Benzo[a]anthracene	15.89	Avg RF	7.39		0.2 to 150 µg/mL	Avg RF	6.09		0.05 to 10 µg/mL
Chrysene	15.96	Avg RF	6.76		0.2 to 150 µg/mL	Avg RF	6.68		0.01 to 10 µg/mL
Bis(2-ethylhexyl) Phthalate	16.02	Avg RF	14.87		0.2 to 150 µg/mL	Avg RF	14.18		0.02 to 10 µg/mL
Di-*n*-octyl Phthalate	17.48	Avg RF	18.98		0.2 to 150 µg/mL	Avg RF	8.27		0.01 to 5 µg/mL
Benzo[b]fluoranthene	18.12	Avg RF	5.28		0.2 to 150 µg/mL	Avg RF	6.86		0.01 to 10 µg/mL
Benzo[k]fluoranthene	18.17	Avg RF	5.77		0.2 to 150 µg/mL	Avg RF	8.92		0.01 to 10 µg/mL
Benzo[a]pyrene	18.73	Avg RF	5.11		0.2 to 150 µg/mL	Avg RF	11.56		0.01 to 10 µg/mL
Indeno[1,2,3-cd]pyrene	20.64	Avg RF	4.52		0.2 to 150 µg/mL	Avg RF	8.24		0.01 to 10 µg/mL
Dibenzo[a,h]anthracene	20.69	Avg RF	6.63		0.2 to 150 µg/mL	Avg RF	8.77		0.01 to 10 µg/mL
Benzo[ghi]perylene	21.12	Avg RF	5.87		0.2 to 150 µg/mL	Avg RF	11.16		0.01 to 10 µg/mL

Conclusion

The Agilent 8890/5977C GC/MSD system was configured and calibrated for the analysis of SVOCs with a calibration curve from 0.2 to 150 µg/mL. The 5977C MSD has the capability to reach beyond these historic levels and be configured for enhanced sensitivity analysis. This was demonstrated by presenting a workflow and guidelines for converting a GC/MS method for enhanced sensitivity. These implementations resulted in an enhanced sensitivity calibration curve from 0.01 to 10 µg/mL. Both methods were tested and proven to exceed method calibration criteria as outlined in US EPA Method 8270E.

There are several key techniques that were discussed, which can enable success when converting methods to enhanced sensitivity analysis:

1. Retention time locking results in exact retention time reproducibility, which saves time by avoiding the need to adjust retention times manually after maintenance and enhances data comparability across multiple instruments and laboratories.
2. A pulsed split injection enhances sensitivity over results obtained with a standard split injection and can be used to analyze a wide dynamic range.
3. Set the split flow as outlined previously, considering the total inlet flow and minimum pressure setting for the inlet.
4. Do not exceed 2 to 5 million counts in height in the base peak chromatogram (BPC) chromatogram for the highest responding analyte.
5. Adjust the split flow in the inlet and then the gain setting of the MS detector to modify the dynamic range.
6. Follow the guidelines listed in the workflow section above for improved performance in enhanced sensitivity analysis.

References

1. Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS); Method 8270E United Stated Environmental Protection Agency, Revision 4, June **2018**.
2. Ciotti, R. EPA 8270E with Pulsed Split Injection and Retention Time Locking on an 8890 GC with a 5977 Series MSD, *Agilent Technologies application note*, publication number 5994-1500EN, **2020**.
3. Anderson, K. A. *et al.* Modified Ion Source Triple Quadrupole Mass Spectrometer Gas Chromatograph for Poly Cyclic Aromatic Hydrocarbon Analysis. *J. Chromatog. A* **2015**, *1419*, 89–98. Doi:10.1016/j. chroma 2015.09.054
4. Walker, D. EPA Method 8270 for SVOC Analysis on the 5977A Series GC/MSD. *Agilent Technologies application note*, publication number 5991-2153EN, **2013**.
5. Churley, M. *et al.* EPA 8270 Re-optimized for Widest Calibration Range on the 5977 Inert Plus GC/MSD, *Agilent Technologies application brief*, publication number 5994-0350EN, **2018**.
6. Prest, H. *et al.* A Quick Start to Optimizing Detector Gain for GC/MSD, *Agilent Technologies*, publication number 5991-2105EN, **2013**.
7. Fausett, E. *et al.* Analysis of Semivolatile Orgainic Compounds with US EPA 8270E Using the Agilent 7000E Triple Quadrupole GC/MS. *Agilent Technologies application note*, publication number 5994-4964EN, **2022**.

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.

Table 3. Agilent consumables list.

Consumable	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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