Petrochemical Applications

Extending the Power of Stabilized PLOT Column Technology to Process GC Analyzers

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Recent advances in PLOT column technology that were first developed in fused silica have now been transferred to metal MXT® PLOT columns. These new columns offer greater stability than conventional PLOT columns, making them a more reliable choice for continual process monitoring. Advantages include highly reproducible flow characteristics, improved layer stability, and excellent separation efficiencies.

Porous layer open tubular (PLOT) columns are useful for analyzing volatiles in petrochemical product streams, as the specialized adsorbents provide good resolution and fast analysis times. However, conventional PLOT columns suffer from poor mechanical stability, limiting their use in process analyzers which require robust columns for continual operation. Recently Restek developed new PLOT column bonding techniques that resulted in improved layer stability, consistent flow behavior, and more reproducible retention times. This technology, which was first developed for fused silica columns, is now being used with metal MXT® tubing, resulting in rugged columns that outperform typical metal PLOT columns. Exceptionally stable, new MXT® PLOT columns provide efficient resolution and reliable performance, making them ideal for process GC analyzers.

New Technology Increases Reliability and Reproducibility

Restek's PLOT columns are stabilized through a proprietary process that is based on concentric adsorption layers and improved particle bonding. The resulting columns are more stable than conventional PLOT columns and have much more reproducible flow behavior. To demonstrate the superior stability of MXT® PLOT columns, an MXT®-Q-BOND column and a competitor's Q type column were subjected to 240 pressure pulse cycles and the spiking observed in each analytical run was used as an indicator of particle generation or phase instability. Results demonstrate that particle generation on the vendor V column was significantly higher (Figure 1), resulting in restrictions in the column that caused a shift in retention time (Figure 2). In contrast, the MXT®-Q-BOND column showed little spiking. Greater phase stability resulted in consistent flow behavior and predictable retention times (Figure 3).

In addition to more consistent flows and reliable retention times, new MXT® PLOT columns show greater thermal stability and much less phase bleed than the comparable competitor product (Figure 4). Lower bleed improves sensitivity and ensures faster stabilization times. In addition, because less stationary phase is lost, retention times are more stable over the lifetime of the column.

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Key Phases Available for Optimized Separations

Metal MXT® columns are available for all major adsorbent types: porous polymer, molecular sieve, and alumina. Porous polymer MXT® columns are highly inert and effective at separating both polar and nonpolar compounds. Volatiles are strongly retained, making these columns extremely useful for separating many target analytes. As shown in Figure 5, MXT®-Q-BOND columns provide excellent chromatography for challenging solvents—even alcohols elute as sharp, symmetric peaks.

MXT®-Msieve 5A columns provide efficient separation of argon and oxygen, as well as other permanent gases (Figure 6). Special coating and deactivation procedures ensure chromatographic efficiency and the integrity of the porous layer coating. The unique immobilization process guarantees that particles remain adhered to the tubing, which is particularly valuable for flow and valve switching applications and allows these procedures to be run with greater confidence.

Metal alumina columns are recommended for light hydrocarbon analysis, as alumina is one of the most selective adsorbents available and allows all C1-C5 isomers to be separated with the highest degree of resolution. As shown in Figure 7, MXT®-Alumina PLOT columns provide excellent chromatographic separation of refinery gas components. Peaks are fully resolved and symmetric, showing no sign of degradation or reactivity with the metal tubing.

Summary

New MXT® PLOT columns from Restek offer greater stability than conventional PLOT columns, making them a better choice for process monitoring. New bonding techniques produce columns with highly reproducible flow characteristics, improved layer stability, and excellent separation efficiencies. These robust columns produce exceptionally reproducible chromatography, providing the reliable performance needed for process GC analyzer applications.

Figure 1: New bonding technology in MXT® PLOT columns results in greater phase stability and reduced particle generation, compared to conventional PLOT columns.
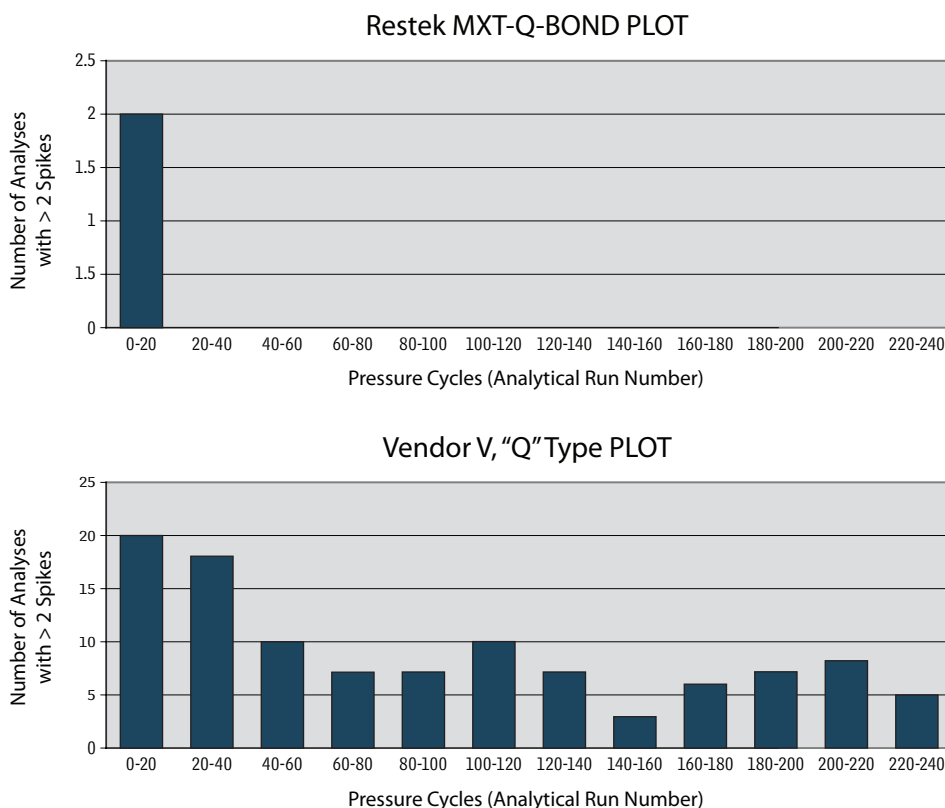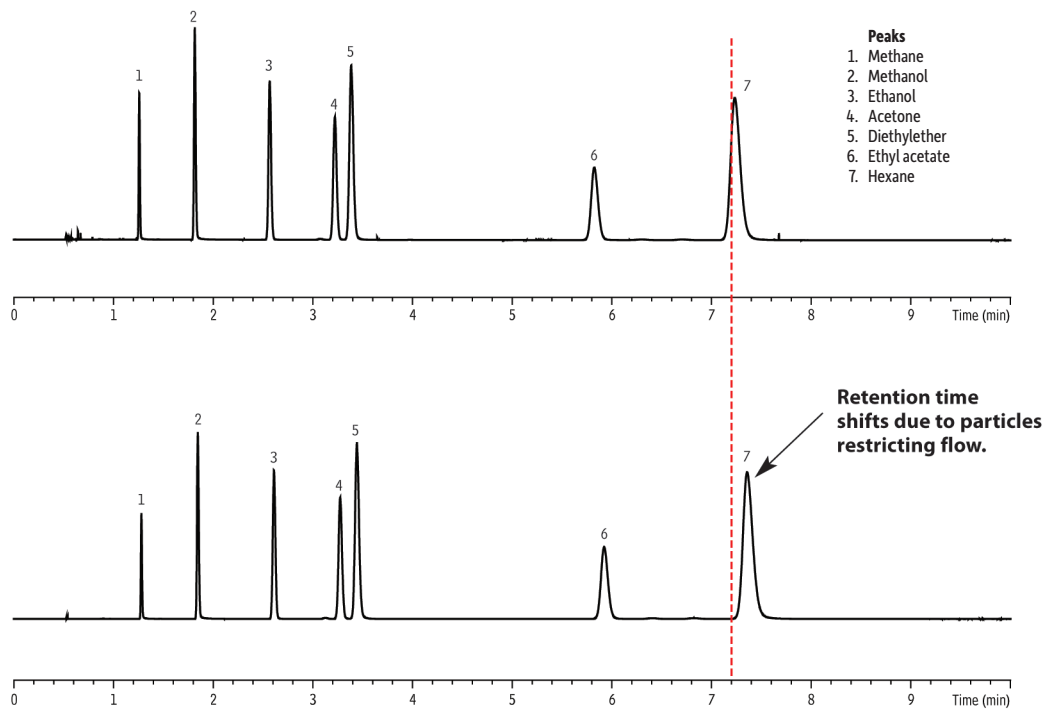
Figure 2: Vendor V PLOT columns release particles following pressure pulsing, forming restrictions in the column that affect flow behavior and change retention time.

Peaks
1. Methane
2. Methanol
3. Ethanol
4. Acetone
5. Diethylether
6. Ethyl acetate
7. Hexane

Retention time shifts due to particles restricting flow.

GC_PC1185

Column	Vendor V Metal Q PLOT, 25 m, 0.53 mm ID
Sample	Solvent mix
Injection	
Inj. Vol.:	1.0 µL split
Inj. Temp.:	250 °C
Split Vent Flow Rate:	150 mL/min.
Oven	
Oven Temp:	150 °C
Carrier Gas	H_2, constant pressure (4 psi, 27.6 kPa)
Detector	FID @ 250 °C
Instrument	Agilent/HP6890 GC
Notes	Pressure pulse test = 240 cycles

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Figure 3: MXT® PLOT columns are exceptionally stable; flow characteristics and retention times are highly consistent and not affected by pressure pulses.
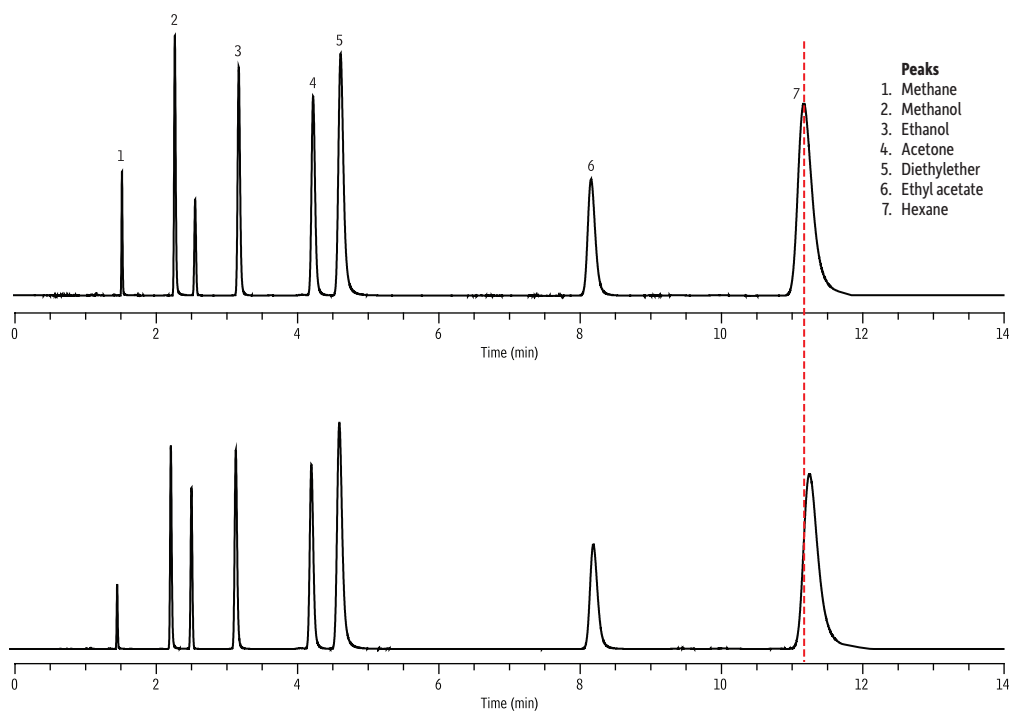

Peaks
1. Methane
2. Methanol
3. Ethanol
4. Acetone
5. Diethylether
6. Ethyl acetate
7. Hexane

GC_PC1186

Column	MXT®-Q-BOND, 30 m, 0.53 mm ID, 20 µm (cat.# 79716)
Sample	Solvent mix
Injection	
Inj. Vol.:	1.0 µL split
Inj. Temp.:	250 °C
Split Vent Flow Rate:	150 mL/min.
Oven	
Oven Temp:	150 °C
Carrier Gas	H_2, constant pressure (4 psi, 27.6 kPa)
Detector	FID @ 250 °C
Instrument	Agilent/HP6890 GC
Notes	Pressure pulse test = 240 cycles

Figure 4: The bonding technology used in new MXT® PLOT columns increases thermal tolerance, resulting in lower bleed, faster stabilization times, and higher sensitivity.
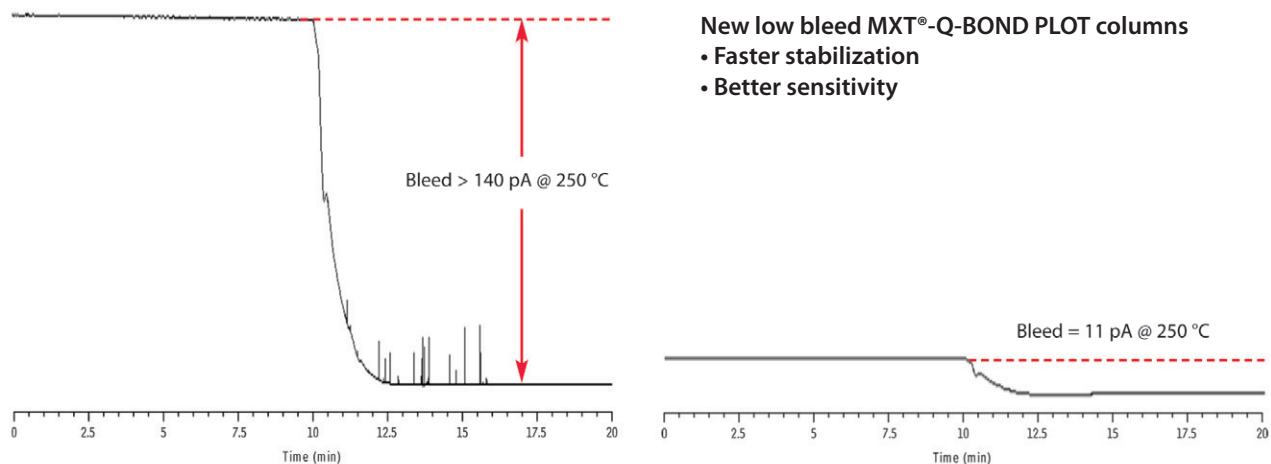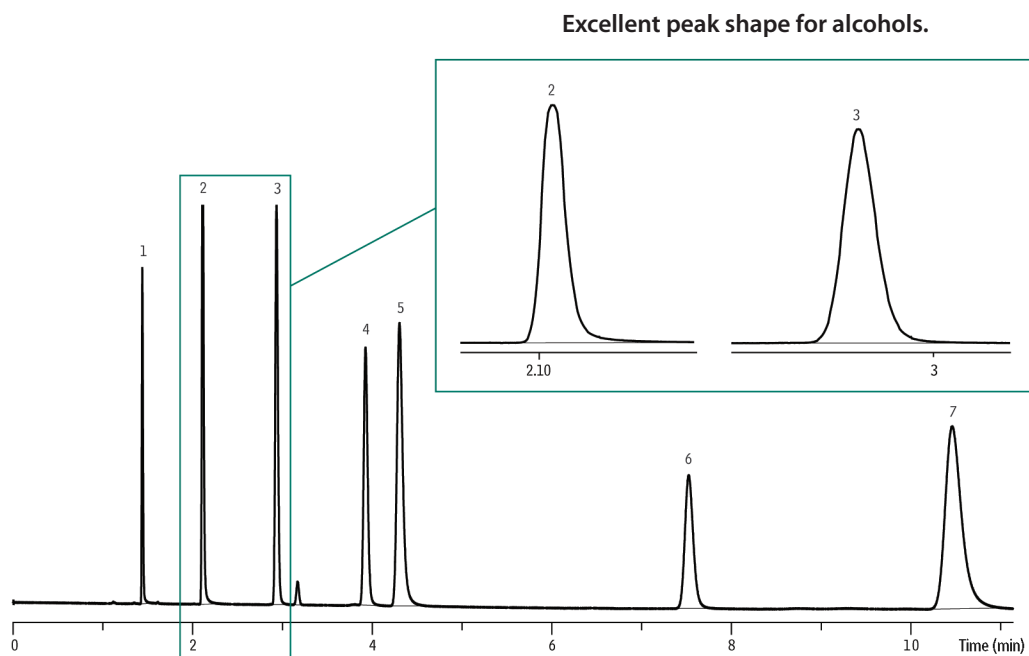

New low bleed MXT®-Q-BOND PLOT columns
• **Faster stabilization**
• **Better sensitivity**

Bleed > 140 pA @ 250 °C

Bleed = 11 pA @ 250 °C

GC_PC1187

Column	See notes for column descriptions.
Injection	split
Inj. Temp.:	250 °C
Split Vent Flow Rate:	150 mL/min.
Oven	
Oven Temp:	250 °C (hold 10 min.) to 40 °C at 50 °C/min.
Carrier Gas	H$_2$, constant pressure (4 psi, 27.6 kPa)
Detector	FID @ 250 °C
Instrument	Agilent/HP6890 GC
Notes	Columns tested:
	Vendor V, metal Q type column
	Restek MXT®-Q-BOND

Columns were conditioned at 250 °C for the same length of time, and then bleed was compared to demonstrate the temperature stability of each column. Lower bleed columns allow higher sensitivities and faster stabilization times.

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Figure 5: Sharp, symmetric solvent peaks are obtained on an MXT®-Q-BOND PLOT column.

Excellent peak shape for alcohols.

GC_PC1184

Peaks	**Column**	MXT®-Q-BOND, 30 m, 0.53 mm ID, 20 µm (cat.# 79716)
1. Methane	**Sample**	Solvent mix
2. Methanol	**Injection**	split
3. Ethanol	Inj. Temp.:	250 °C
4. Acetone	Split Vent	
5. Diethylether	Flow Rate:	200 mL/min
6. Ethyl acetate	**Oven**	
7. Hexane	Oven Temp:	150 °C
	Carrier Gas	H$_2$, constant flow
	Linear Velocity:	40 cm/sec
	Detector	FID
	Instrument	Agilent/HP6890 GC

Figure 6: Permanent gases, including argon and oxygen, are fully separated on an MXT®-Msieve 5A column using a μ-TCD.
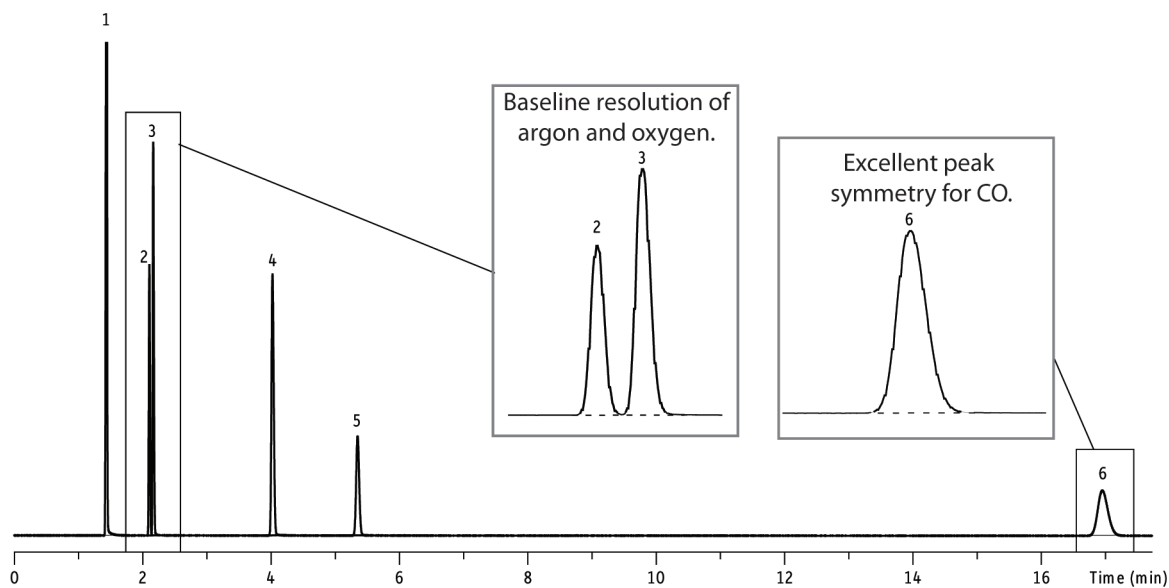
GC_PC1182

Peaks	**Column**	MXT®-Msieve 5A, 30 m, 0.53 mm ID, 50 µm (cat.# 79723)
1. Helium	**Sample**	
2. Argon	Conc.:	1% in hydrogen
3. Oxygen	**Injection**	split (split ratio 50:1)
4. Nitrogen	**Oven**	
5. Methane	Oven Temp:	30 °C
6. Carbon monoxide	**Carrier Gas**	H_2
	Detector	µ-TCD

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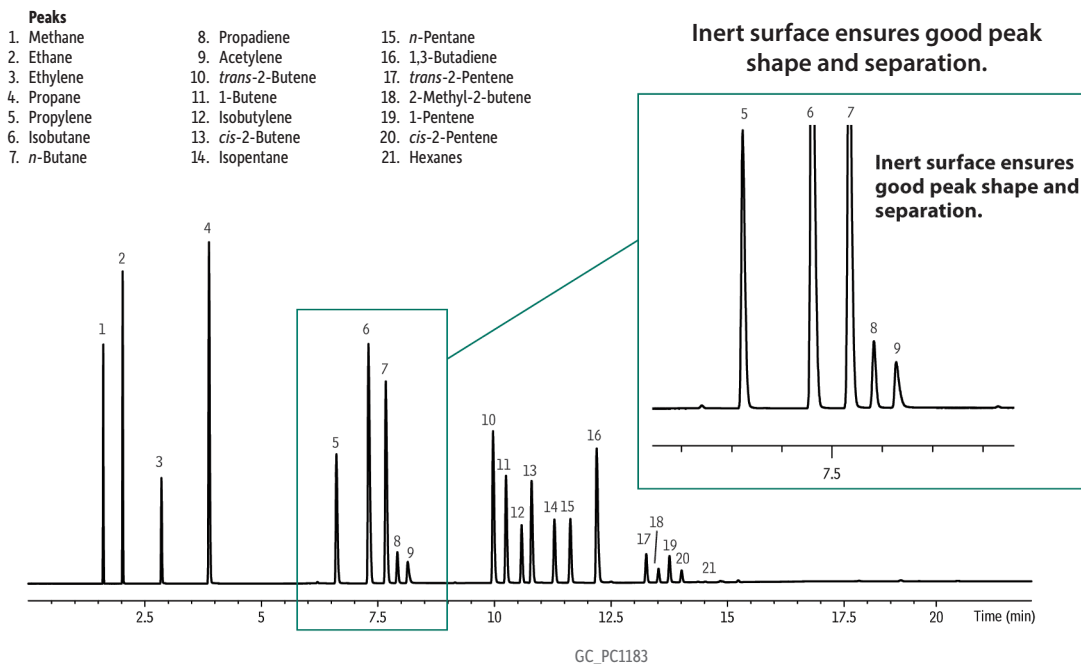
Figure 7: Highly inert MXT®-Alumina BOND columns provide reliable baseline separation of refinery gas components.

Peaks
1. Methane
2. Ethane
3. Ethylene
4. Propane
5. Propylene
6. Isobutane
7. *n*-Butane
8. Propadiene
9. Acetylene
10. *trans*-2-Butene
11. 1-Butene
12. Isobutylene
13. *cis*-2-Butene
14. Isopentane
15. *n*-Pentane
16. 1,3-Butadiene
17. *trans*-2-Pentene
18. 2-Methyl-2-butene
19. 1-Pentene
20. *cis*-2-Pentene
21. Hexanes

Inert surface ensures good peak shape and separation.

GC_PC1183

Column	MXT®-Alumina BOND/Na$_2$SO$_4$, 30 m, 0.53 mm ID, 10 µm (cat.# 79714)
Sample	Refinery ga
Injection	
Inj. Vol.:	10 µL split
Liner:	2mm split
Inj. Temp.:	45 °C
Split Vent	
Flow Rate:	80 mL/min
Oven	
Oven Temp:	45 °C (hold 1 min) to 200 °C at 10 °C/min (hold 8.5 min)
Carrier Gas	He, constant pressure (10 psi, 68.9 kPa)
Linear Velocity:	31 cm/sec @ 45 °C
Detector	FID @ 200 °C

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