GC/MS Analysis of Aromatics in Gasoline using ASTM D5769

Set-up, Optimization, and Automated Reporting

James McCurry
Agilent Technologies

GC/MS Analysis of Aromatics in Gasoline using ASTM D5769

ASTM D5769 Scope

- Measures benzene (0.1 to 4 vol%), toluene (1 to 13 vol%) and total aromatics (10 to 42 vol%) in finished motor gasolines
- Primary EPA regulatory method for reporting total aromatics
  - Alternative fluorescent indicator adsorption (FIA) method, D1319, no longer viable due to dye unavailability
  - D5769 now the only EPA approved method for total aromatics

Challenges for running D5769

- More complex instrumentation
- Must meet specific performance tests before running samples
  - Linearity, sensitivity, spectral fidelity, chromatographic resolution, QC check
  - Linearity specifications are particularly challenging and can lead to QC check failures
- More complex data analysis
- More costly to purchase and operate compared to D1319 FIA

GC/MS Analysis of Aromatics in Gasoline using ASTM D5769

- New Agilent 8860 GC bundle with 5977 Series MSD
  - Less expensive than similar 8890/5977 system
  - 5977 MSD with Stainless Steel source reduces costs
  - 8860 GC high performance design for routine yet critical applications
  - Compatible with hydrogen carrier gas for lower operational costs

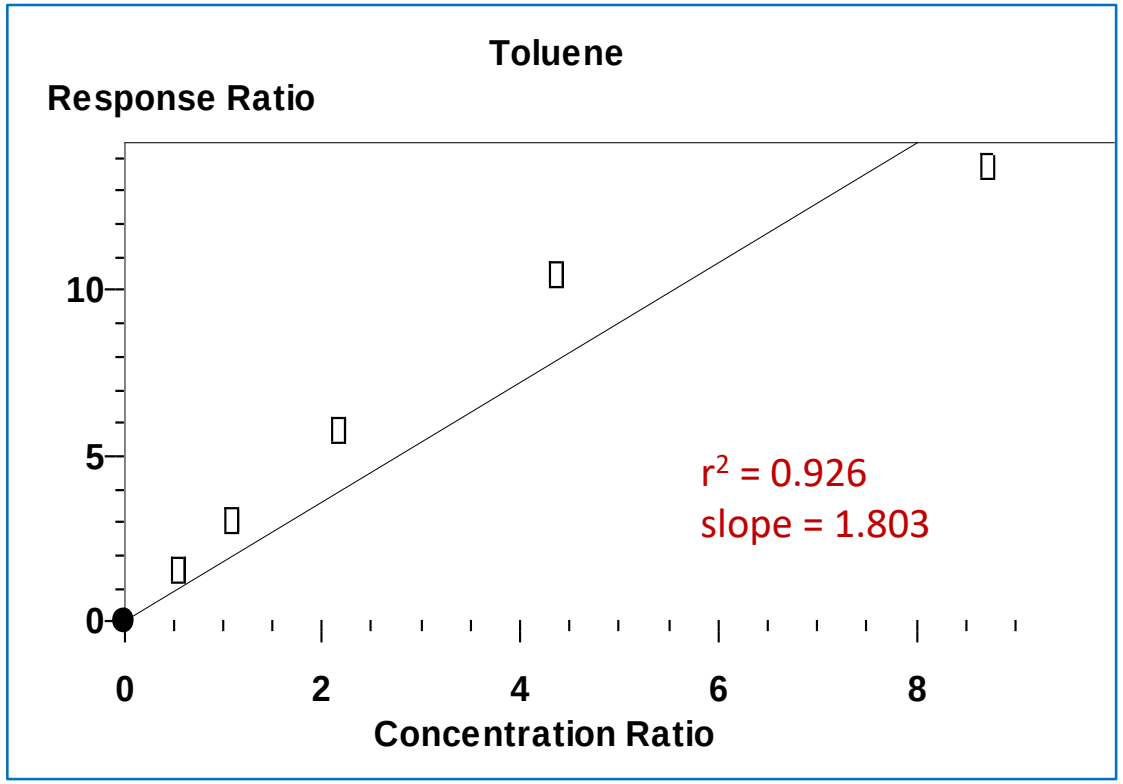
- Presentation Outline
  - Instrument configuration and operating conditions
  - Optimizing calibration linearity
  - Pre-analysis performance checks
  - Sample analysis performance
  - Conversion to hydrogen carrier gas
  - Method for faster analysis time

D5769 Operating Conditions for Agilent 8860/5977 GC/MS System

	GC Column 1	GC Column 2
ALS		
Syringe:	5 uL	5 uL
Injection volume:	0.1 uL	0.1 uL
Wash solvent:	isooctane	isooctane
Inlet		
Carrier gas:	helium	helium
Mode:	split, 250:1	split, 700:1
Temperature:	250 °C	250 °C
Liner:	Split (5190-2295)	Split (5190-2295)
Column		
Type:	DB-1, 60 m x 0.25 mm ID x 1.00 um	DB-1, 20 m x 0.18 mm ID x 0.4 um
Flow rate:	1.8 mL/min. constant flow (35 cm/s)	0.46 mL/min. constant flow (30 cm/s)
Initial temperature:	60 °C	35 °C
Initial hold time:	0 min.	1 min.
Ramp rate 1:	3 °C/min.	25 °C/min.
Temperature 1:	120 °C	210 °C
Hold time 1:	0 min.	1 min.
Ramp rate 2:	10 °C/min.	
Temperature 2:	250 °C	
Hold time 2:	2 min.	
Total run time:	35 min.	9 min.

	GC Column 1	GC Column 2
GC/MS Interface		
Type:	direct	direct
Temperature:	280 °C	250 °C
5977 MSD		
Ionization voltage:	70 eV	70 eV
Source temperature:	230 °C	230 °C
Quad temperature:	150 °C	150 °C
Scan range:	45 - 300	70 - 170
Scan rate:	3 scans/s	11 scans/s

D5769 - Optimizing Calibration Linearity



ASTM Calibration requirements

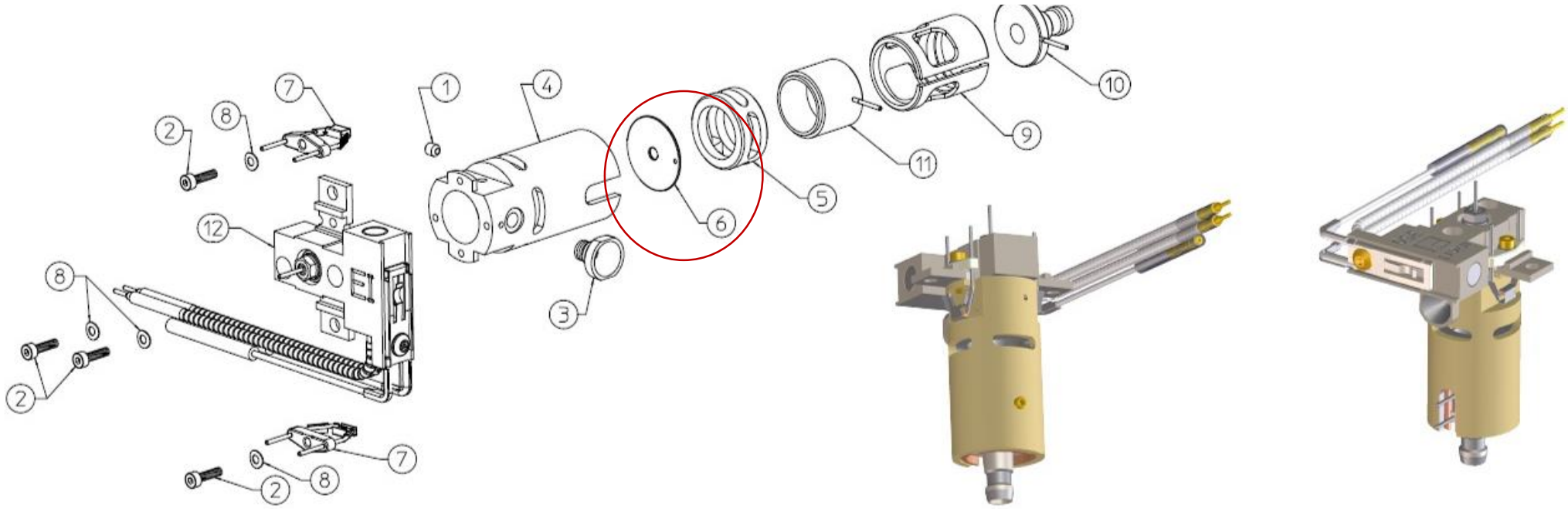
- Linear regression fit
- y-axis forced through 0
- Correlation (r^2) should be at least 0.99
- Non-linearity usually seen with toluene
  - highest calibration range: 0.5 to 20 vol%

Optimizing instrument and method conditions to obtain linear response

- Tools to use for linear response
  - Source hardware optimization
  - Injection size
  - Inlet split ratio

Optimizing Calibration Linearity with the Agilent 5977 Stainless Steel Source

Simple change of source component improves D5769 linearity



- Standard source has a 3 mm ID drawout plate (component #6)
  - Optimized for sensitivity
- Replace with optional 9 mm ID drawout plate (part # G3440-20022)
  - Improves linear response for higher concentration components
  - No response problems for lower level standards

Optimizing Calibration Linearity with the Agilent 5977 Stainless Steel Source

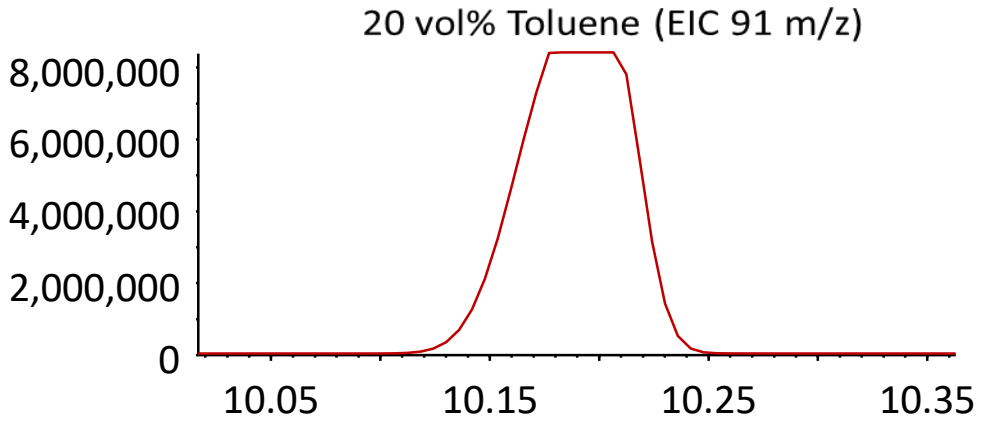
Simple change of source component improves D5769 linearity

Linearity check

- Run the highest concentration standard
- Extract Ion Chromatogram (EIC) with the quant ion
- Flat peak top indicates detector signal overload
- Maximum abundance should be below 5 x 10^6

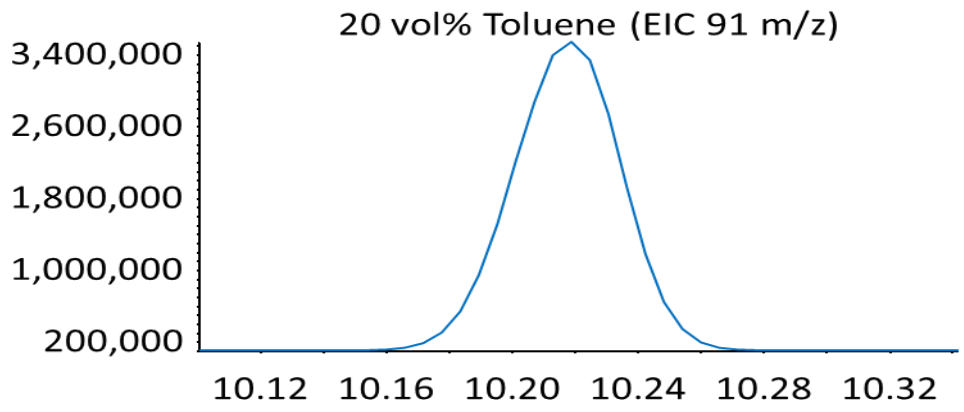
Instrument Conditions

- Standard 3 mm draw out plate
- 0.1 uL injection
- 250:1 split ratio

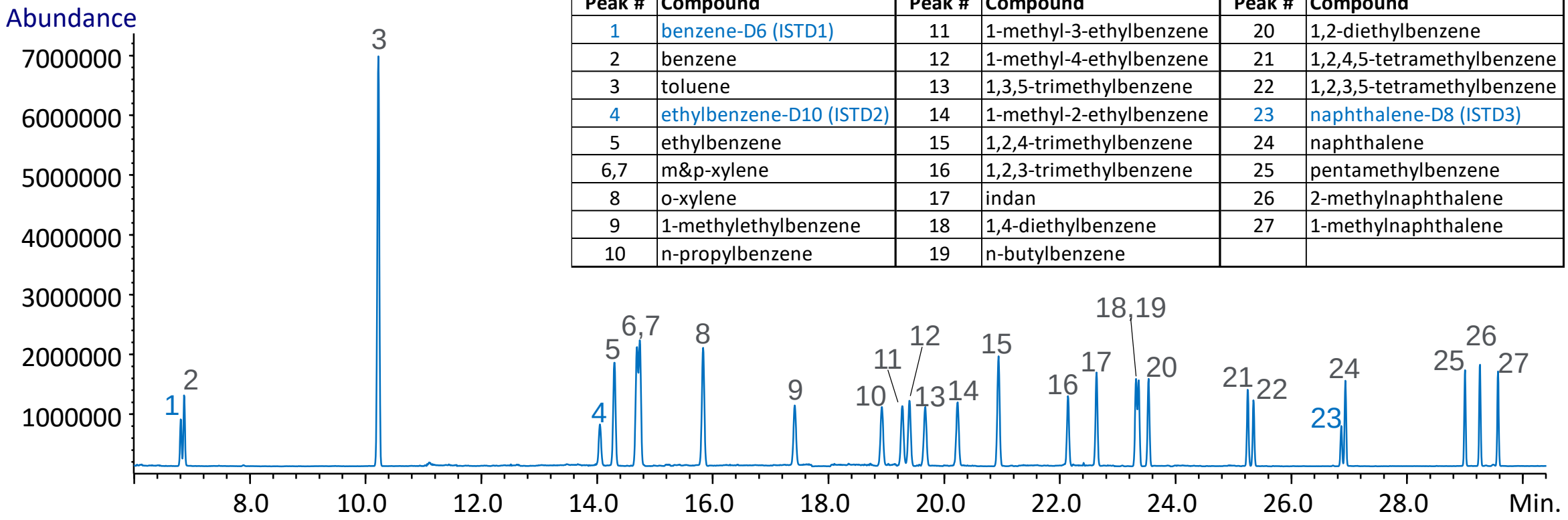


Instrument Conditions

- 9 mm draw out plate
- 0.1 uL injection
- 350:1 split ratio



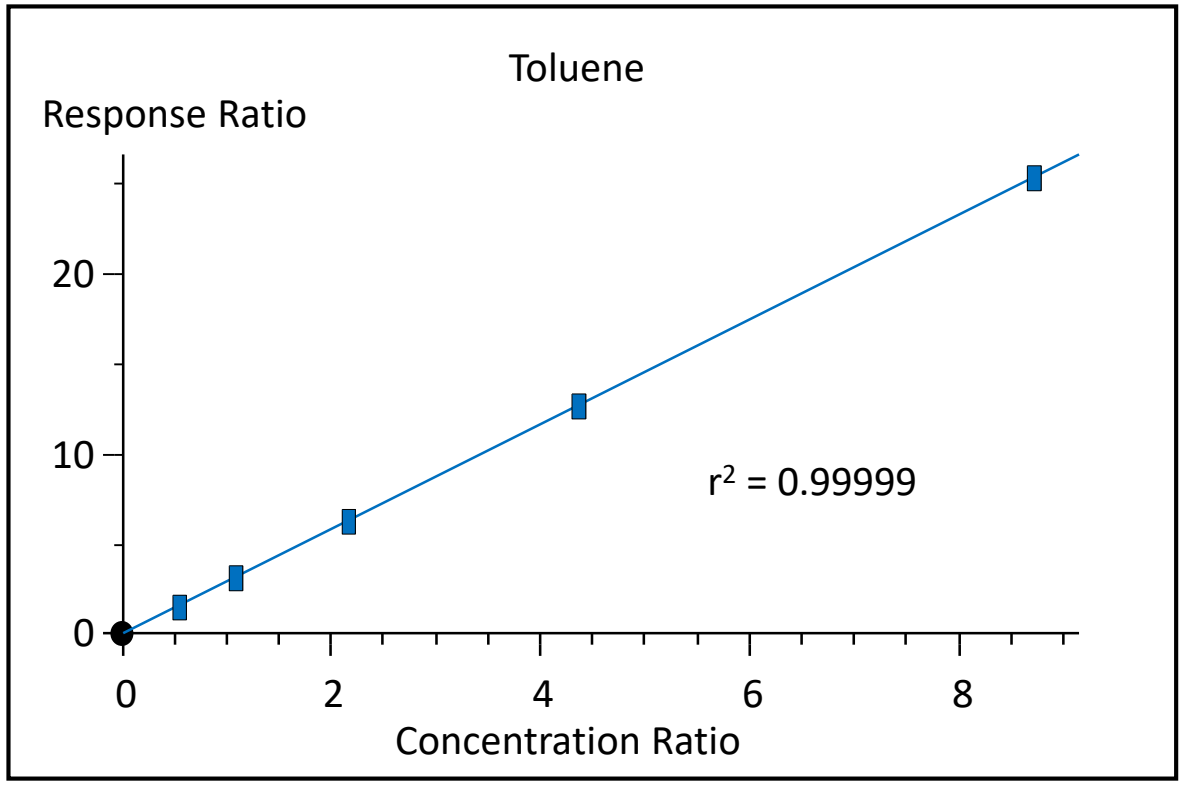
D5769 Calibration Compounds Using Column 1



Peak #	Compound	Peak #	Compound	Peak #	Compound
1	benzene-D6 (ISTD1)	11	1-methyl-3-ethylbenzene	20	1,2-diethylbenzene
2	benzene	12	1-methyl-4-ethylbenzene	21	1,2,4,5-tetramethylbenzene
3	toluene	13	1,3,5-trimethylbenzene	22	1,2,3,5-tetramethylbenzene
4	ethylbenzene-D10 (ISTD2)	14	1-methyl-2-ethylbenzene	23	naphthalene-D8 (ISTD3)
5	ethylbenzene	15	1,2,4-trimethylbenzene	24	naphthalene
6,7	m&p-xylene	16	1,2,3-trimethylbenzene	25	pentamethylbenzene
8	o-xylene	17	indan	26	2-methylnaphthalene
9	1-methylethylbenzene	18	1,4-diethylbenzene	27	1-methylnaphthalene
10	n-propylbenzene	19	n-butylbenzene		

- Three deuterated internal standards indicated in blue text
- m-Xylene and p-xylene isomers are combined as one compound
- 1,4-diethylbenzene and n-butyl benzene were sufficiently resolved on column 1
  - Method allows combining as a single compound

Simple Source Optimization Provides Required Calibration Linearity



Exceeds ASTM requirement of r^2 >= 0.99 for all compounds

Aromatics Analysis
Correlation Coefficient Results

Method : D5769_sstEI_Col1_He_DA.M
Calibration : Aromatics in Gasoline

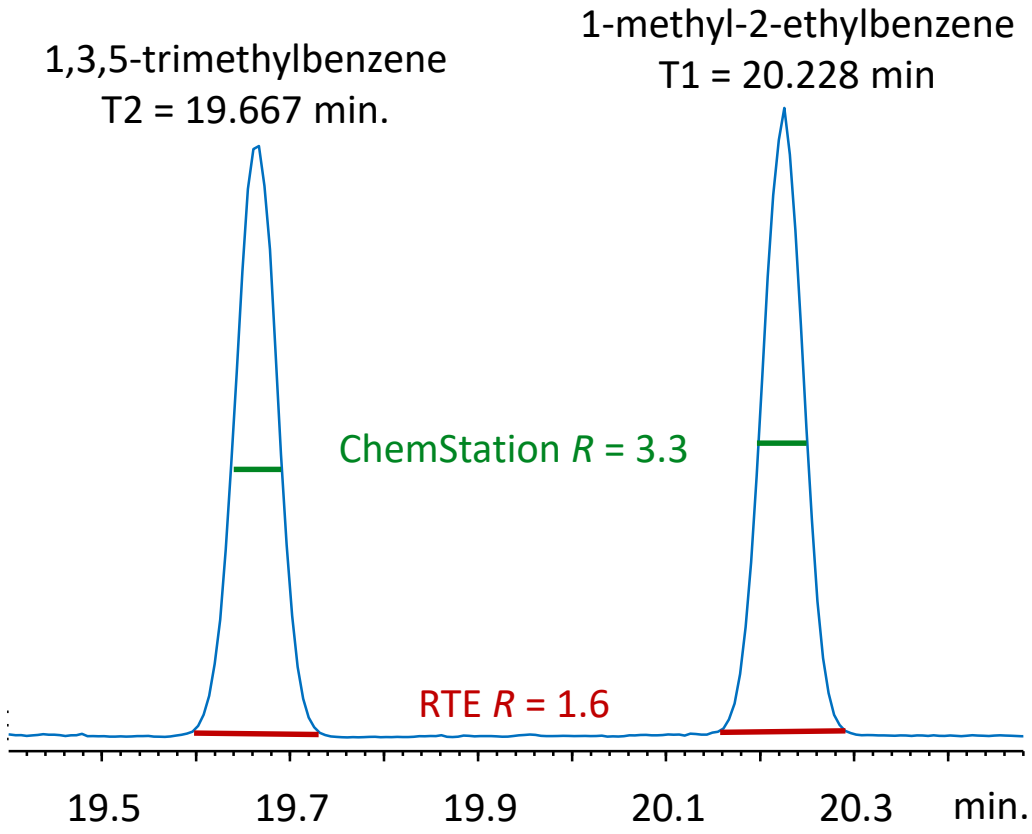
Cal Files A1 : C:\gcms\1\data\D5769_sstEI_Col1_190828\D5769_Std_01.D
A2 : C:\gcms\1\data\D5769_sstEI_Col1_190828\D5769_Std_02.D
A3 : C:\gcms\1\data\D5769_sstEI_Col1_190828\D5769_Std_03.D
A4 : C:\gcms\1\data\D5769_sstEI_Col1_190828\D5769_Std_04.D
A5 : C:\gcms\1\data\D5769_sstEI_Col1_190828\D5769_Std_05.D

Compound	Corr Coeff(r^2)	Y-Intercept Test
benzene	0.99992	0.00
Toluene	0.99999	0.00
ethylbenzene	0.99990	0.00
m&p xylene	0.99996	0.00
o-xylene	0.99999	0.00
1-methylethylbenzene	0.99986	0.00
n-propylbenzene	0.99997	0.00
1-methyl-3-ethylbenzene	0.99996	0.00
1-methyl-4-ethylbenzene	0.99993	0.00
1,3,5-trimethylbenzene	0.99999	0.00
1-methyl-2-ethylbenzene	0.99993	0.00
1,2,4-trimethylbenzene	0.99998	0.00
1,2,3-trimethylbenzene	0.99994	0.00
indan	0.99999	0.00
alkyl indans	0.99999	0.00
1,4-diethylbenzene	0.99996	0.00
n-butylbenzene	0.99940	0.00
1,2-diethylbenzene	0.99999	0.00
1,2,4,5-tetramethylbenzene	0.99993	0.00
1,2,3,5-tetramethylbenzene	0.99997	0.00
naphthalene	0.99991	0.00
pentamethylbenzene	0.99954	0.00
2-methylnaphthalene	0.99988	0.00
1-methylnaphthalene	0.99996	0.00
C10 benzenes	0.99999	0.00
C11 benzenes	0.99999	0.00
C12 benzenes	0.99999	0.00

D5769 Column 1 Resolution Test

Choosing the correct integrator

Column 1
DB-1, 60 m x 0.25 mm ID x 1.00 um



ASTM Resolution Calculation

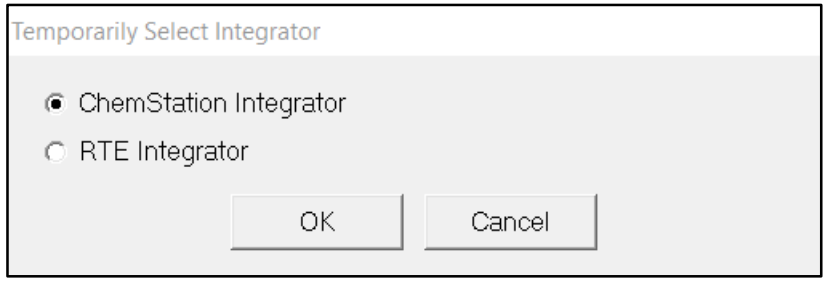
- Test mix containing 3 mass % of:
  - 1-methyl-2-ethylbenzene and 1,3,5-trimethylbenzene
- Resolution must be 2.0 or greater

ASTM D5769 Resolution Equation

$$R = \frac{2(RT1 - RT2)}{1.699(PW2_{0.5} - PW1_{0.5})}$$

Two data system integrator choices:

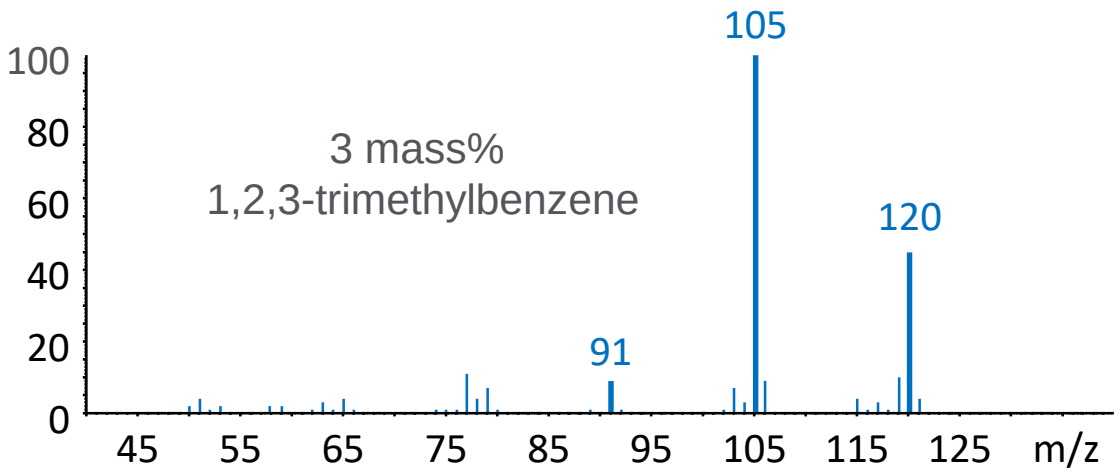
- Chemstation: reports peak width at half height ($PW_{0.5}$)
- RTE: reports peak width at baseline
- **TIP**: use the Chemstation Integrator for resolution test



D5769 Pre-Analysis Performance Checks

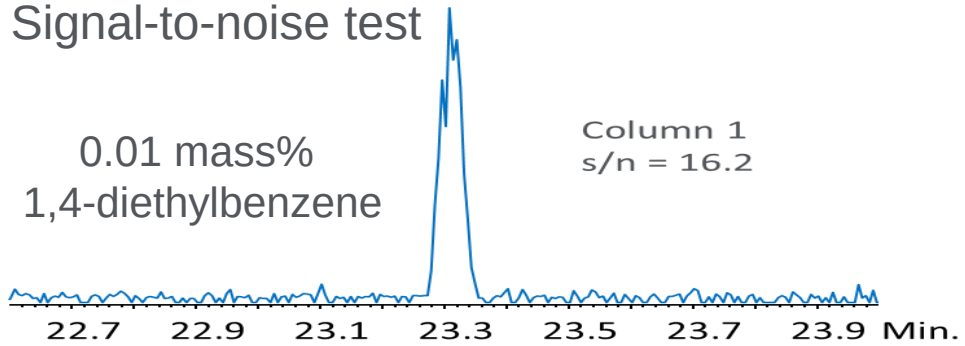
Fragmentation Pattern, Signal-to-Noise Tests and QC Check

Fragmentation pattern test



Ion (m/z)	Relative Intensity	
	D5769 Specification	Experimental Column 1
120	30 - 60	**40**
105	100	**100**
91	7 - 15	**9**

Signal-to-noise test



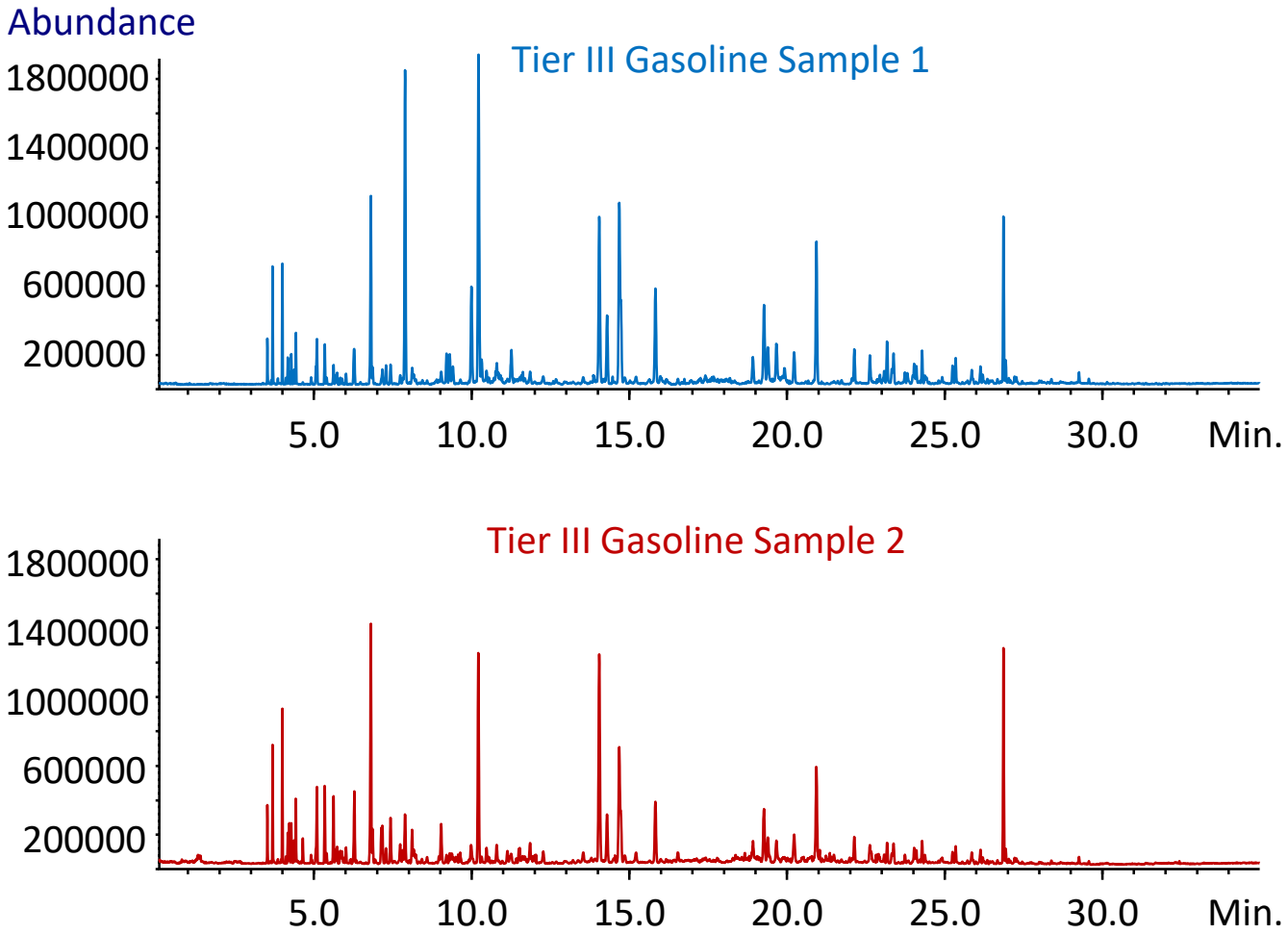
Meets ASTM D5769 of > 5:1 S/N

Pre-run QC check

	mass %		
Component	**Reference**	**Experimental**	**% difference**
benzene	0.99	0.95	4.04%
toluene	8.93	9.14	2.35%
m-xylene	2.98	3.03	1.68%
o-xylene	2.98	3.05	2.35%
ethylbenzene	2.98	3.00	0.67%
1,2,4-trimethylbenzene	2.98	3.07	3.02%
1,2,4,5-tetramethylbenzene	1.99	2.08	4.52%
naphthalene	1.00	0.97	3.00%

Meets requirement of +/- 5%
(+/- 10% for 1,2,4,5-TMB and naphthalene)

D5769 – Performance Running Gasoline Samples



- Two samples of Tier III Reformulated Gasoline
  - Sample 1 is a “premium” gasoline with ethanol
  - Sample 2 is a “regular” gasoline with ethanol
- Each sample was used in a proficiency testing study
  - 61 laboratories used D5769 to report total aromatics (vol%) for each sample
- Ten replicates of each sample were prepared
  - One injection of each replicate was made on Agilent 8860/5977 GC/MS system

Performance Running Gasoline Samples Using 8860/5977 GC/MS with Column 1 Conditions

All results agree with the reported consensus values

	Tier III Gasoline Sample 1 - Volume Percent												
	Rep 1	**Rep 2**	**Rep 3**	**Rep 4**	**Rep 5**	**Rep 6**	**Rep 7**	**Rep 8**	**Rep 9**	**Rep 10**	**Average**	**Stddev**	**RSD**
benzene	0.24	0.23	0.23	0.24	0.23	0.23	0.23	0.23	0.23	0.23	0.23	0.0042	1.82%
toluene	3.98	3.84	3.95	4.00	3.91	3.91	3.88	3.75	3.84	3.78	3.88	0.0824	2.12%
total aromatics	19.9	19.3	19.9	20.0	19.5	19.9	19.5	19.4	19.8	19.5	**19.7**	**0.2555**	**1.30%**

Consensus value (total aromatics): 20.15 vol% (+- 1.78 vol%)

	Tier III Gasoline Sample 2 - Volume Percent												
	Rep 1	**Rep 2**	**Rep 3**	**Rep 4**	**Rep 5**	**Rep 6**	**Rep 7**	**Rep 8**	**Rep 9**	**Rep 10**	**Average**	**Stddev**	**RSD**
benzene	0.47	0.46	0.48	0.47	0.48	0.48	0.47	0.47	0.48	0.48	0.47	0.0070	1.48%
toluene	3.23	3.20	3.30	3.24	3.31	3.32	3.21	3.25	3.27	3.29	3.26	0.0424	1.30%
total aromatics	14.2	14.0	14.5	14.3	14.5	15.1	14.2	14.4	14.4	14.4	**14.4**	**0.2889**	**2.01%**

Consensus value (total aromatics): 14.82 vol% (+- 1.41 vol%)

D5769 - Conversion to Hydrogen Carrier Gas

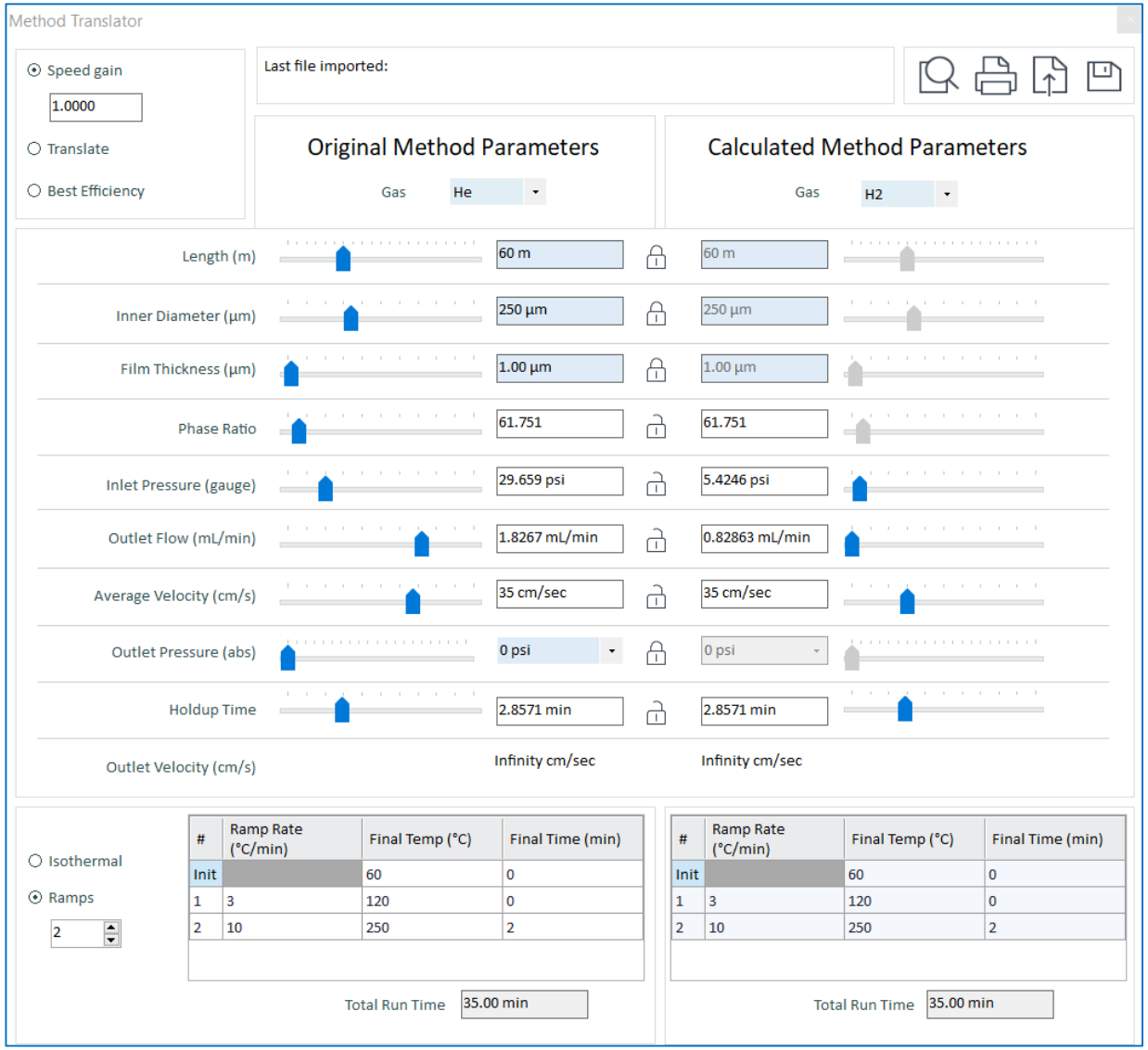
Method Translation Software eases transition to alternative carrier gases

D5769 Column 1 conversion to hydrogen carrier gas

- Method Translation Software simplifies transition to alternative carrier gases
- Enter “Original Method Parameters” for helium carrier gas
- Select “Speed Gain” of “1.000”
  - peak order maintained, minimal RT changes
- Change carrier gas to H_2 for “Calculated Method Parameters”
- Hydrogen linear velocity remains 35 cm/s to comply with ASTM D5769 operating parameters

Before running samples:

- Equilibration overnight with H_2 flow and filament 2 on
- Retune MSD
- Perform all D5769 performance checks
- Recalibrate



D5769 with H_2 Carrier Gas

All Checks and QC Passed

Pre-run QC Check Within +/- 5 mass %

	mass %		
Component	**Reference**	**Experimental**	**% difference**
benzene	0.99	0.97	2.02%
toluene	8.93	9.14	2.35%
m-xylene	2.98	3.02	1.34%
o-xylene	2.98	3.02	1.34%
ethylbenzene	2.98	2.99	0.34%
1,2,4-trimethylbenzene	2.98	3.02	1.34%
1,2,4,5-tetramethylbenzene	1.99	1.91	4.02%
naphthalene	1.00	0.96	4.00%

D5769 Test	ASTM Specification	H_2 Carrier Gas Result
Resolution	>= 2	5.5
Signal-to-Noise	>= 5	8.9
Peak Fragmentation		
91 m/z (rel abundance)	7 - 15	9
105 m/z (rel. abundance)	100	100
120 m/z (rel. abundance)	30 - 60	44

Aromatics Analysis
Correlation Coefficient Results

Method : D5769_sstEI_Col1_H2_DA.M
Calibration : Aromatics in Gasoline

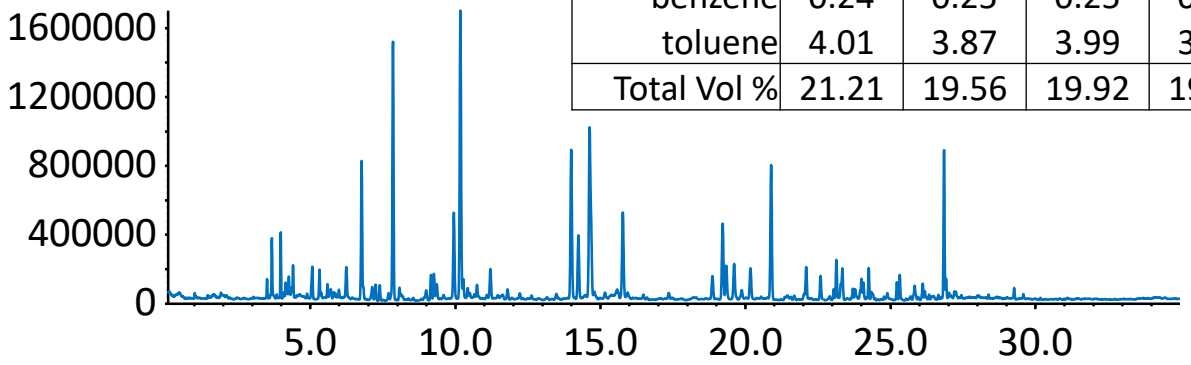
Cal Files
A1 : C:\gcms\1\data\D5769_sstEI_col1_H2_190905\D5769_Std_01.D
A2 : C:\gcms\1\data\D5769_sstEI_col1_H2_190905\D5769_Std_02.D
A3 : C:\gcms\1\data\D5769_sstEI_col1_H2_190905\D5769_Std_03.D
A4 : C:\gcms\1\data\D5769_sstEI_col1_H2_190905\D5769_Std_04.D
A5 : C:\gcms\1\data\D5769_sstEI_col1_H2_190905\D5769_Std_05.D

Exceeds ASTM requirement of r^2 >= 0.99 for all compounds

Compound	Corr Coeff(r^2)	Y-Intercept Test
benzene	0.99991	0.00
Toluene	0.99996	0.00
ethylbenzene	0.99999	0.00
m&p xylene	1.00000	0.00
o-xylene	0.99999	0.00
1-methylethylbenzene	0.99999	0.00
n-propylbenzene	0.99999	0.00
1-methyl-3-ethylbenzene	0.99999	0.00
1-methyl-4-ethylbenzene	0.99998	0.00
1,3,5-trimethylbenzene	0.99996	0.00
1-methyl-2-ethylbenzene	0.99998	0.00
1,2,4-trimethylbenzene	0.99997	0.00
1,2,3-trimethylbenzene	0.99996	0.00
indan	0.99998	0.00
alkyl indans	0.99998	0.00
1,4-diethylbenzene	0.99974	0.00
n-butylbenzene	0.99949	0.00
1,2-diethylbenzene	0.99998	0.00
1,2,4,5-tetramethylbenzene	0.99998	0.00
1,2,3,5-tetramethylbenzene	0.99994	0.00
naphthalene	0.99997	0.00
pentamethylbenzene	0.99995	0.00
2-methylnaphthalene	0.99975	0.00
1-methylnaphthalene	0.99990	0.00
C10 benzenes	0.99998	0.00
C11 benzenes	0.99998	0.00
C12 benzenes	0.99998	0.00

D5769 Tier III Gasoline Sample Results with H_2 Carrier Gas

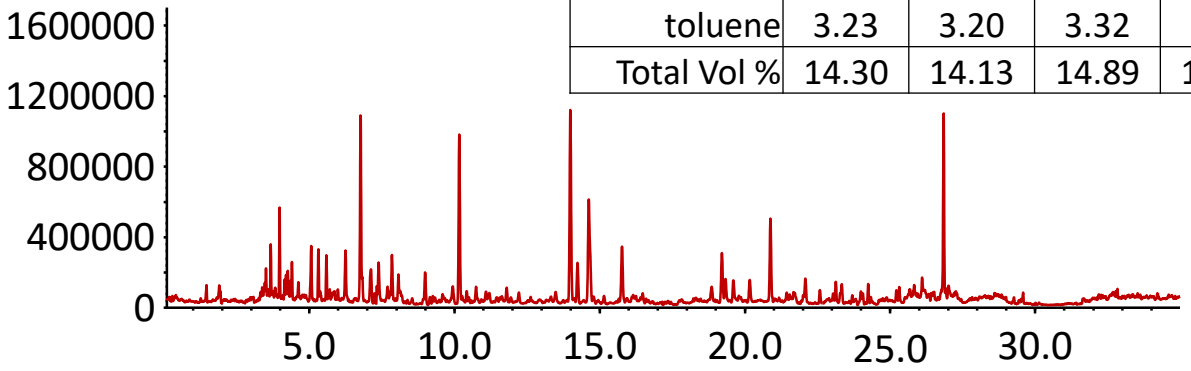
All results agree with He results and the reported consensus values



Tier III Gasoline Sample 1 - Volume Percent

	Rep 1	Rep 2	Rep 3	Rep 4	Rep 5	Rep 6	Rep 7	Rep 8	Rep 9	Rep 10	Avg	Stddev	RSD
benzene	0.24	0.25	0.25	0.25	0.24	0.24	0.23	0.23	0.24	0.23	0.24	0.0082	3.40%
toluene	4.01	3.87	3.99	3.94	3.88	3.96	3.91	3.81	3.89	3.80	3.91	0.0704	1.80%
Total Vol %	21.21	19.56	19.92	19.81	19.58	19.96	19.57	19.49	19.98	19.53	**19.86**	**0.5111**	**2.57%**

Consensus value (total aromatics): 20.15 vol% (+- 1.78 vol%)



Tier III Gasoline Sample 2 - Volume Percent

	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8	Run 9	Run 10	Avg	Stddev	RSD
benzene	0.47	0.46	0.48	0.48	0.49	0.48	0.48	0.48	0.48	0.48	0.48	0.0079	1.65%
toluene	3.23	3.20	3.32	3.24	3.33	3.34	3.27	3.27	3.31	3.30	3.28	0.0468	1.43%
Total Vol %	14.30	14.13	14.89	14.53	14.81	14.91	14.63	14.42	15.00	14.69	**14.63**	**0.2852**	**1.95%**

Consensus value (total aromatics): 14.82 vol% (+- 1.41 vol%)

D5769 – Faster Analysis Time

	GC Column 1	GC Column 2
ALS		
Syringe:	5 uL	**5 uL**
Injection volume:	0.1 uL	**0.1 uL**
Wash solvent:	isooctane	**isooctane**
Inlet		
Carrier gas:	helium	**helium**
Mode:	split, 350:1	**split, 700:1**
Temperature:	250 °C	**250 °C**
Liner:	Split (5190-2295)	**Split (5190-2295)**
Column		
Type:	DB-1, 60 m x 0.25 mm ID x 1.00 um	**DB-1, 20 m x 0.18 mm ID x 0.4 um**
Flow rate:	1.8 mL/min. constant flow (35 cm/s)	**0.46 mL/min. constant flow (30 cm/s)**
Initial temperature:	60 °C	**35 °C**
Initial hold time:	0 min.	**1 min.**
Ramp rate 1:	3 °C/min.	**25 °C/min.**
Temperature 1:	120 °C	**210 °C**
Hold time 1:	0 min.	**1 min.**
Ramp rate 2:	10 °C/min.	
Temperature 2:	250 °C	
Hold time 2:	2 min.	
Total run time:	35 min.	**9 min.**

	GC Column 1	GC Column 2
GC/MS Interface		
Type:	direct	**direct**
Temperature:	280 °C	**250 °C**
5977 MSD		
Ionization voltage:	70 eV	**70 eV**
Source temperature:	230 °C	**230 °C**
Quad temperature:	150 °C	**150 °C**
Scan range:	45 - 300	**70 - 170**
Scan rate:	3 scans/s	**11 scans/s**

ASTM D5769 Configuration and Operating Parameter for Faster Analysis Time

- Shorter, narrower column: 20 m x 0.18 mm ID x 0.4 um
- Avoids column overload with higher split ratio
- Faster oven program
- MSD conditions optimized for narrower chromatographic peaks
  - Faster scan rate

Run time reduced from 35 minutes to 9 minutes

D5769 Fast Analysis Method

Performance Checks and QC Passed

Pre-run QC Check Within +/- 5%

	mass %		
Component	**Reference**	**Experimental**	**% difference**
benzene	0.99	0.96	3.03%
toluene	8.93	8.88	0.56%
m-xylene	2.98	2.91	2.35%
o-xylene	2.98	2.92	2.01%
ethylbenzene	2.98	2.90	2.68%
1,2,4-trimethylbenzene	2.98	2.94	1.34%
1,2,4,5-tetramethylbenzene	1.99	2.08	4.52%
naphthalene	1.00	0.95	5.00%

D5769 Test	ASTM Specification	Fast Method Result
Resolution	>= 2	2.9
Signal-to-Noise	>= 5	6
Peak Fragmentation		
91 m/z (rel abundance)	7 - 15	9
105 m/z (rel. abundance)	100	100
120 m/z (rel. abundance)	30 - 60	46

Aromatics Analysis
Correlation Coefficient Results

Method : D5769_sstEI_Col3_DA.M
Calibration : Aromatics in Gasoline

Cal Files
A1 : D:\MassHunter\GCMS\1\data\D5769_sstEI_Col3_190821\D5769_Std_01.D
A2 : D:\MassHunter\GCMS\1\data\D5769_sstEI_Col3_190821\D5769_Std_02.D
A3 : D:\MassHunter\GCMS\1\data\D5769_sstEI_Col3_190821\D5769_Std_03.D
A4 : D:\MassHunter\GCMS\1\data\D5769_sstEI_Col3_190821\D5769_Std_04.D
A5 : D:\MassHunter\GCMS\1\data\D5769_sstEI_Col3_190821\D5769_Std_05.D

Exceeds ASTM requirement of r^2 >= 0.99 for all compounds

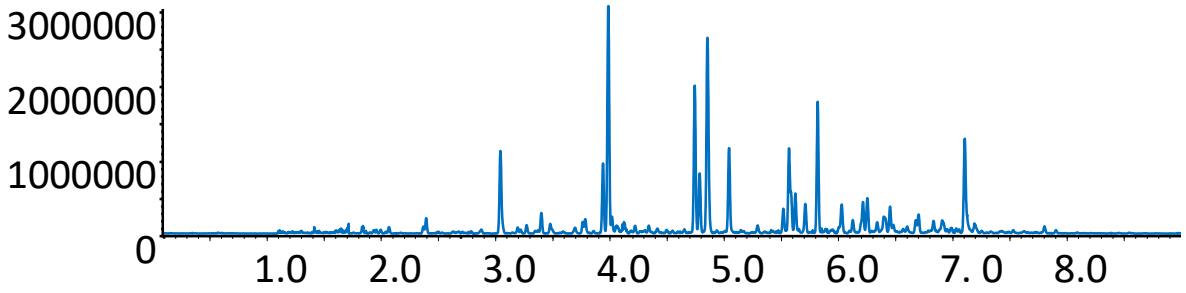
Compound	Corr Coeff(r^2)	Y-Intercept Test
benzene	0.99993	0.00
Toluene	1.00000	0.00
ethylbenzene	0.99989	0.00
m&p xylene	0.99996	0.00
o-xylene	0.99994	0.00
1-methylethylbenzene	0.99977	0.00
n-propylbenzene	0.99982	0.00
1-methyl-3-ethylbenzene	0.99962	0.00
1-methyl-4-ethylbenzene	0.99984	0.00
1,3,5-trimethylbenzene	0.99993	0.00
1-methyl-2-ethylbenzene	0.99996	0.00
1,2,4-trimethylbenzene	0.99998	0.00
1,2,3-trimethylbenzene	0.99995	0.00
indan	0.99994	0.00
alkyl indans	0.99994	0.00
1,4-diethylbenzene & n-butylbenzene	0.99998	0.00
1,2-diethylbenzene	0.99995	0.00
1,2,4,5-tetramethylbenzene	0.99996	0.00
1,2,3,5-tetramethylbenzene	0.99996	0.00
naphthalene	0.99997	0.00
pentamethylbenzene	0.99993	0.00
2-methylnaphthalene	0.99996	0.00
1-methylnaphthalene	0.99997	0.00
C10 benzenes	0.99995	0.00
C11 benzenes	0.99995	0.00
C12 benzenes	0.99995	0.00

Fast D5769 Tier III Gasoline Sample Results

All results agree with Column 1 method and are within the reported consensus values

Tier III Gasoline Sample 1 - Volume Percent

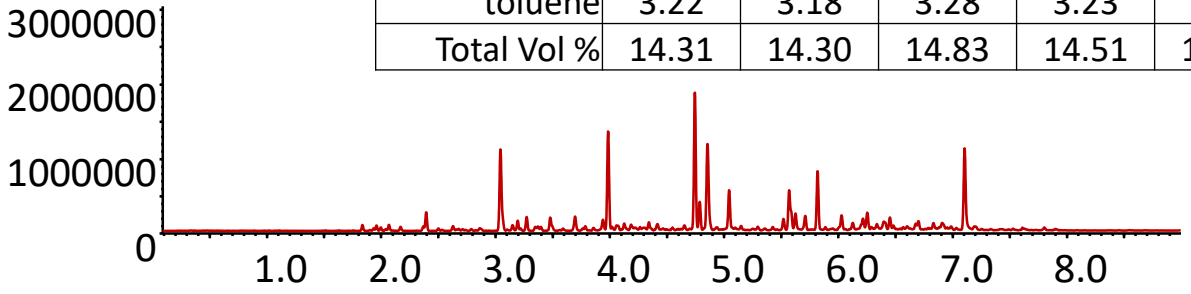
	Rep 1	Rep 2	Rep 3	Rep 4	Rep 5	Rep 6	Rep 7	Rep 8	Rep 9	Rep 10	Avg	SD	RSD
benzene	0.26	0.25	0.25	0.25	0.25	0.25	0.25	0.24	0.25	0.24	0.25	0.0057	2.28%
toluene	4.02	3.89	4.01	3.98	3.92	3.98	3.91	3.90	4.01	3.86	3.95	0.0583	1.48%
Total Vol %	20.39	19.65	20.33	20.05	19.78	20.21	19.92	19.81	20.31	19.72	**20.02**	**0.2774**	**1.39%**



Consensus value (total aromatics): 20.15 vol% (+- 1.78 vol%)

Tier III Gasoline Sample 2 - Volume Percent

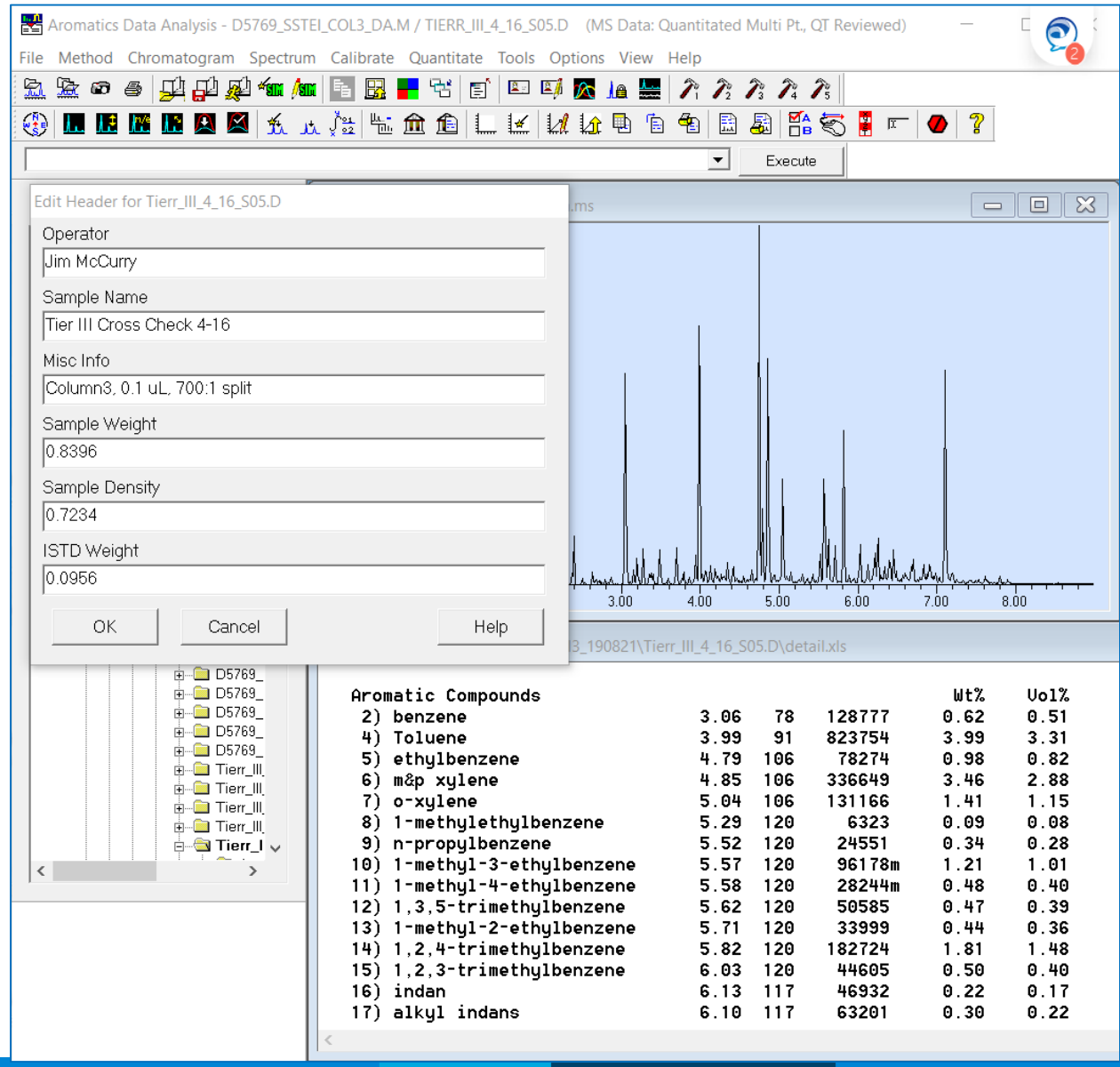
	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8	Run 9	Run 10	Avg	SD	RSD
benzene	0.49	0.49	0.51	0.49	0.51	0.51	0.50	0.50	0.51	0.52	0.50	0.0106	2.11%
toluene	3.22	3.18	3.28	3.23	3.31	3.31	3.23	3.25	3.31	3.37	3.27	0.0569	1.74%
Total Vol %	14.31	14.30	14.83	14.51	14.85	14.92	14.46	14.61	14.87	15.20	**14.69**	**0.2941**	**2.00%**



Consensus value (total aromatics): 14.82 vol% (+- 1.41 vol%)

Aromatics in Gasoline Software Solution

- Special Mass Hunter Configuration designed for D5769
- Sequencer provides sample input fields specific to D5769 calculation
  - Sample weight
  - Sample density
  - ISTD weight
- MS Chemstation macros automates report calculation and format to report
  - Individual aromatic amounts
  - Total aromatic contents
  - Both in mass percent and volume percent



Summary

- A new Agilent 8860/5977 GC/MS system bundle configured to run ASTM D5769
- Value price with high performance
- Simple MS source configuration provides linear response for higher concentration compounds
- High performance using published ASTM system configuration and operating parameter
- Operational costs reduced using hydrogen carrier gas
- Optional fast GC configuration completes analysis in 9 minutes
- Meets all ASTM performance measures
- Data acquisition and analysis software designed for D5769 Analysis
  - Mass Hunter Software Aromatics in Gasoline Mode

Considerations for Improving Analytical Productivity

Changing the approach to build on your success

Craig Marvin
Business and Product Marketing Manager
GC, MS and Sample Containment Supplies

January 2020

Agilent
Trusted Answers

Challenges Facing Today's Analytical Laboratory

Expecting More from Less

Business Challenges

- Lower price per sample
- Increasing cost of operation

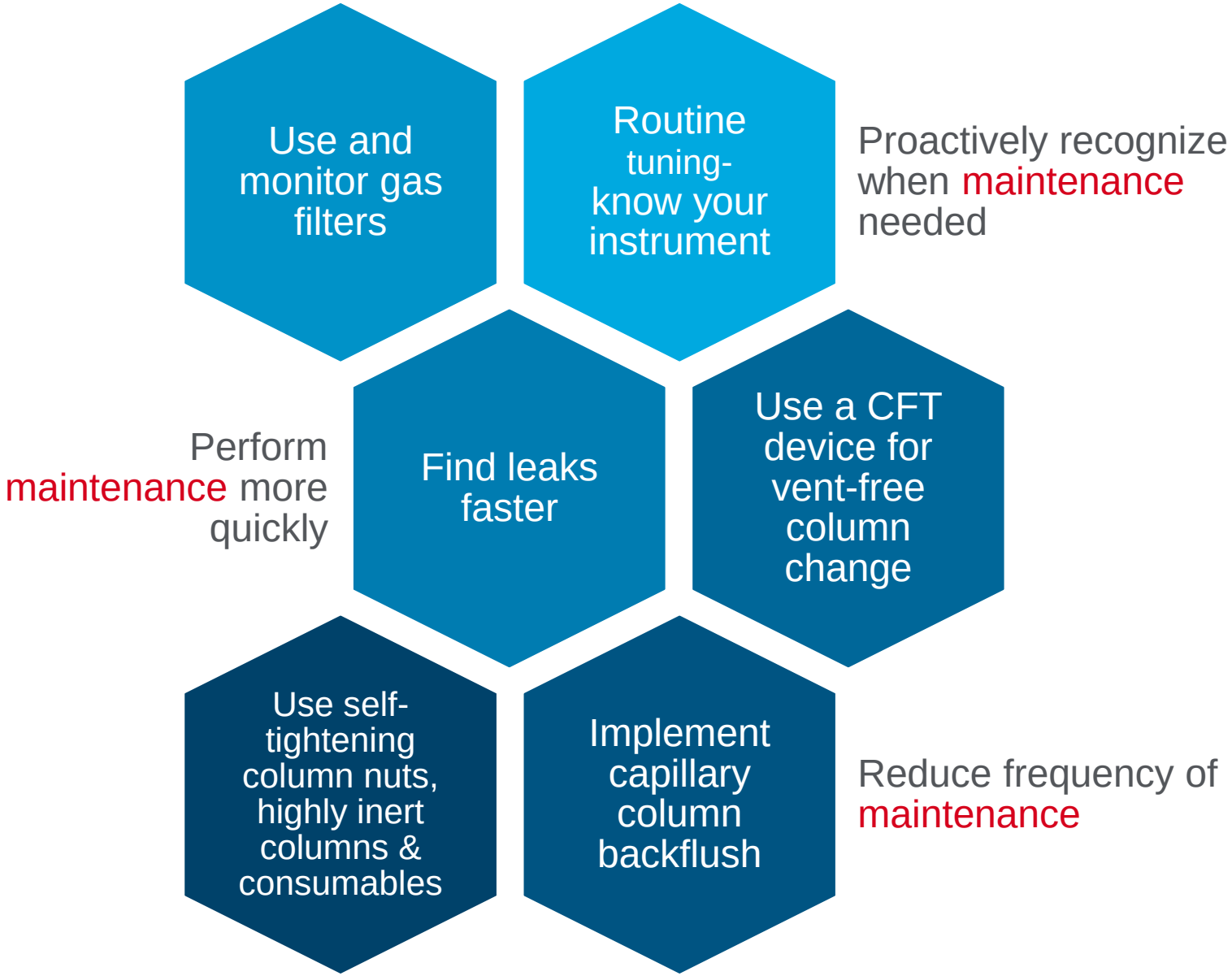
Resource Allocation

- Increasing cost of labor
- Personnel retention, loss of expertise

Optimizing Efficiency

- Eliminating non-value add activities
- Reducing reruns
- Reducing unscheduled down time

Strategies for improving sample throughput- it's all about maintenance



Recognize when it’s time for maintenance

Use (and change) gas filters, and tune your MS often

Recognizing when you need maintenance

Oxygen in carrier gas is detrimental to GC

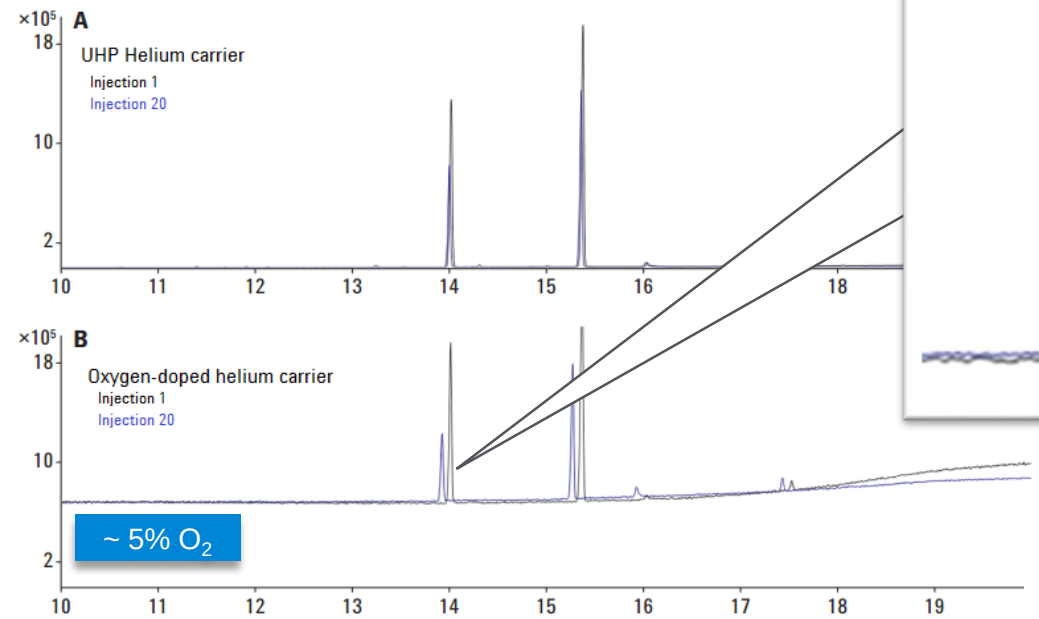
- Reduced response
- Elevated background
- Irreversible column damage
- Impaired electron multiplier function
- Premature filament, liner lifetime
- Excessive source maintenance

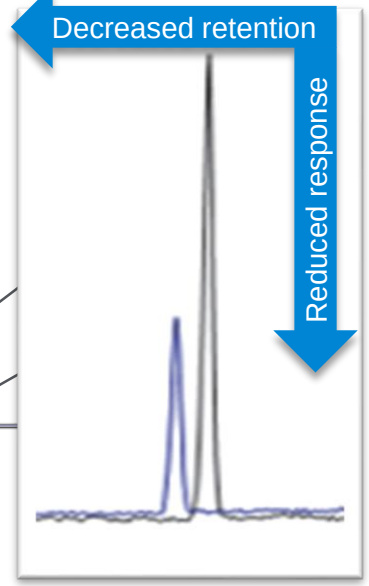
Use UHP carrier gases

- 99.9995% or greater

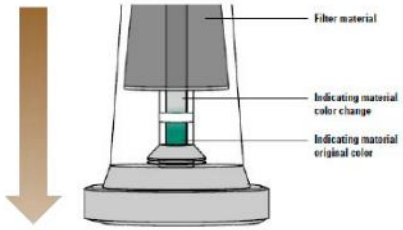
Use high quality, GC/MS gas filters

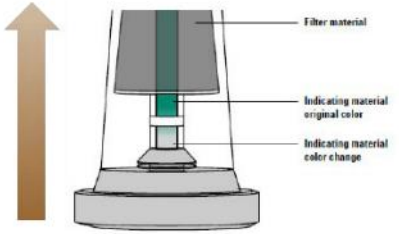
- GasClean gas filters remove oxygen and water
- Monitor gas filter indicators
  - Replace when needed
  - Correct any leaks present
- Monitor nitrogen percentage in tune files





Indicator changes color from the top down
If the indicating material changed color from the top down there is a leak upstream of the filter in your gas line, or your gas quality is poor. Check for leaks at the cylinder, regulator, and fittings, and check your gas quality.

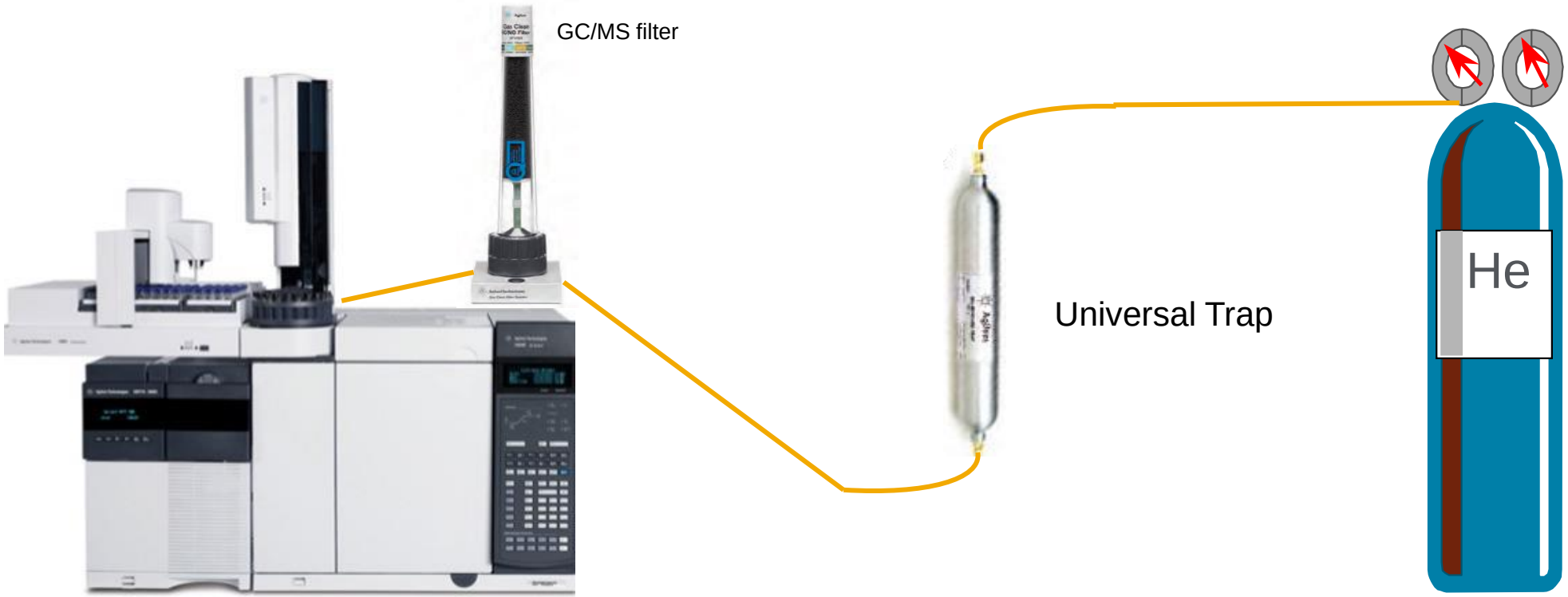




Indicator changes color from the bottom up
If your filter's indicator changes color from the bottom up shortly after installation this indicates a leak downstream of the filter in your gas line. Check for leaks between the filter and your instrument.

Gas Quality and Filters

Using lower quality gases: Concerns about background removal



- Install the Universal trap vertically
- Extend the lifetime of your Gas Clean (indicating) filter AND (most importantly) your column!

Agilent Gas Clean Sensor for 8890 and 8860 GC

Automatically monitors the chemical indicators alerting operator via the LUI and software when a filter requires replacement.

Ships standard on all GC/MS Ready Systems

- Replacing the filters when at capacity protects GC column and analytical hardware.
- The sensitive indicators change color, alerting you that the filter needs to be replaced.

Tuning tip

Monitor tunes for signs of a dirty source

Tune ion peaks sharp and symmetric?

- 502 ion mass usually declines first
- Peak widths (Pk50) are usually ~ 0.6 amu

Consistent primary tune ion abundances?

- Atune, HES Atune: m/z 69 ~450,000 – 600,000
- Etune: m/z 219 ~450,000 – 600,000
- Consistency is key

Relative abundances within accepted values?

- 502 ion relative to m/z 69 > 3%
- Consistency is key

EM voltage consistent from last tune?

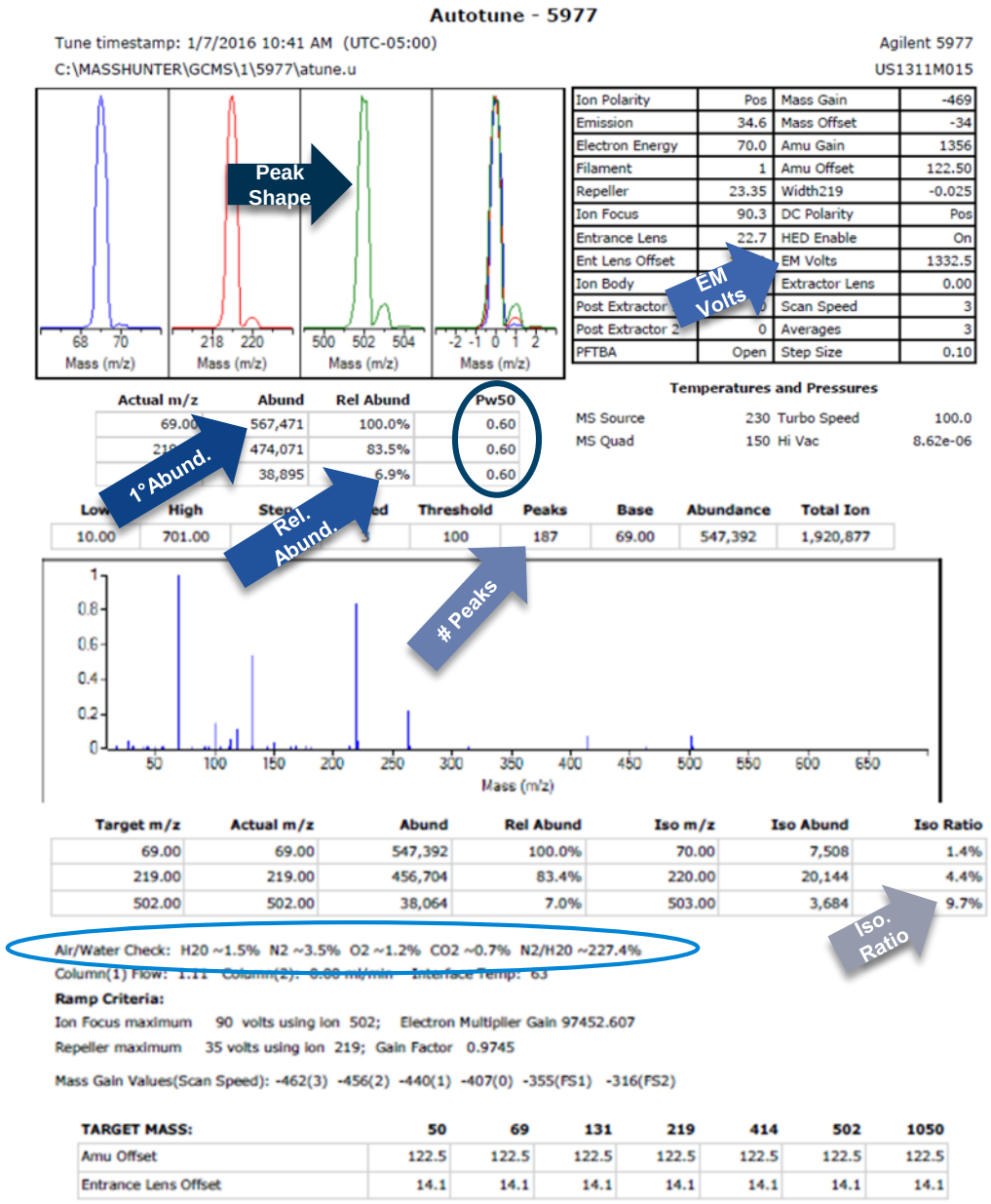
- As source grows dirtier, EM voltage increases
- Max voltage is 3000V
- Consistency is key

Is background free from excessive peaks?

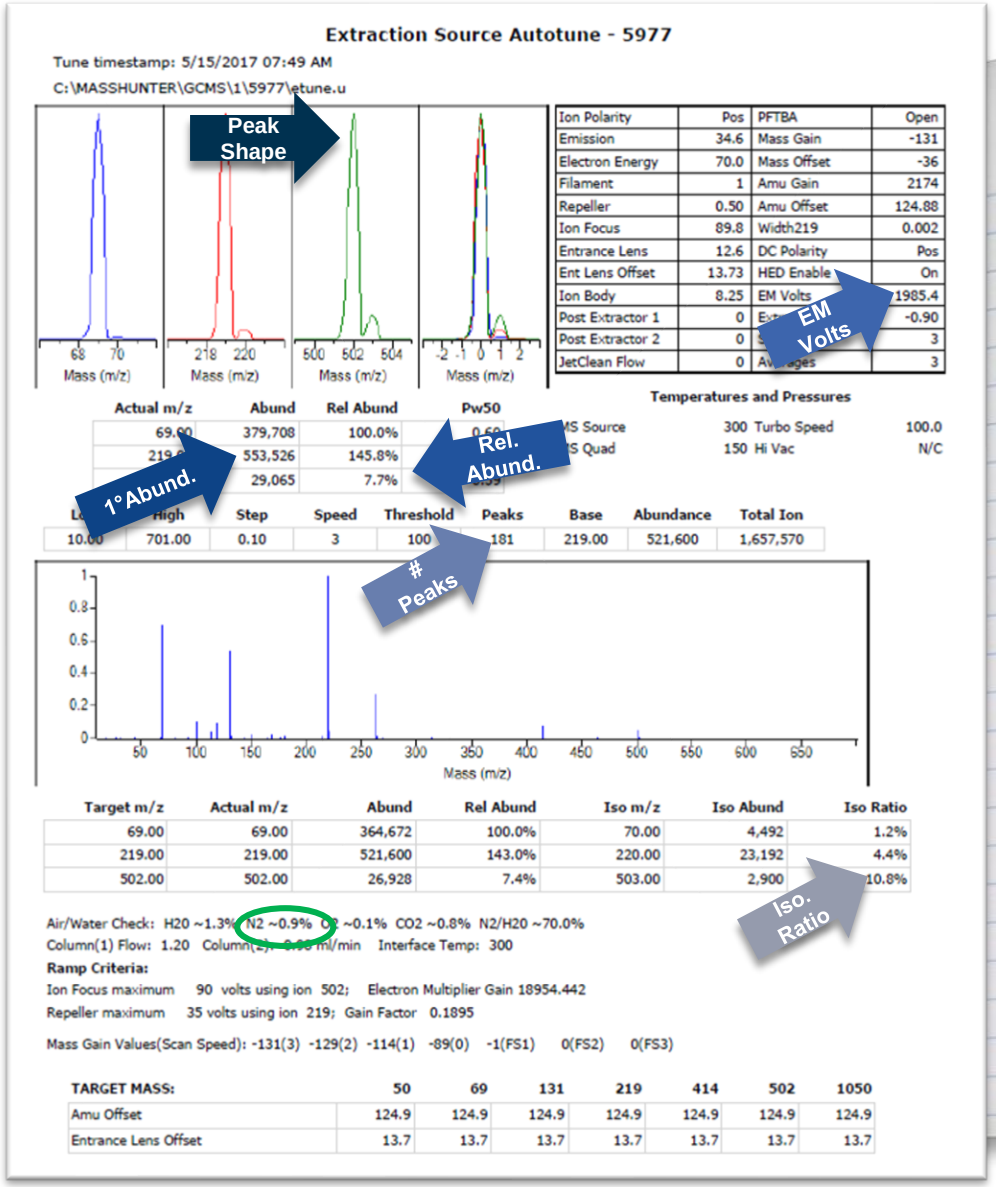
- Excessive peaks can indicate source contamination

Isotopic ratios within expected values?

- 502 isotopic ratio ~ 10.1% (±20%)



Case study
Monitoring tune reports over time



Extraction Source Autotune - 5977

Tune timestamp: 5/15/2017 07:49 AM

C:\MASSHUNTER\GCMS\1\5977\etune.u

Peak Shape

Ion Polarity	Pos	PFTBA	Open
Emission	34.6	Mass Gain	-131
Electron Energy	70.0	Mass Offset	-36
Filament	1	Amu Gain	2174
Repeller	0.50	Amu Offset	124.88
Ion Focus	89.8	Width219	0.002
Entrance Lens	12.6	DC Polarity	Pos
Ent Lens Offset	13.73	HED Enable	On
Ion Body	8.25	EM Volts	1985.4
Post Extractor 1	0	Ext	-0.90
Post Extractor 2	0	S	3
JetClean Flow	0	Averages	3

EM Volts

Actual m/z	Abund	Rel Abund	Pw50
69.00	379,708	100.0%	0.60
219.00	553,526	145.8%	
	29,065	7.7%	

1° Abund.

Rel. Abund.

Temperatures and Pressures

MS Source	300	Turbo Speed	100.0
MS Quad	150	Hi Vac	N/C

Low	High	Step	Speed	Threshold	Peaks	Base	Abundance	Total Ion
10.00	701.00	0.10	3	100	181	219.00	521,600	1,657,570

Peaks

Target m/z	Actual m/z	Abund	Rel Abund	Iso m/z	Iso Abund	Iso Ratio
69.00	69.00	364,672	100.0%	70.00	4,492	1.2%
219.00	219.00	521,600	143.0%	220.00	23,192	4.4%
502.00	502.00	26,928	7.4%	503.00	2,900	10.8%

Iso. Ratio

Air/Water Check: H20 ~1.3% N2 ~0.9% O2 ~0.1% CO2 ~0.8% N2/H20 ~70.0%

Column(1) Flow: 1.20 Column(2) 0.00 ml/min Interface Temp: 300

Ramp Criteria:

Ion Focus maximum 90 volts using ion 502; Electron Multiplier Gain 18954.442

Repeller maximum 35 volts using ion 219; Gain Factor 0.1895

Mass Gain Values(Scan Speed): -131(3) -129(2) -114(1) -89(0) -1(FS1) 0(FS2) 0(FS3)

TARGET MASS:	50	69	131	219	414	502	1050
Amu Offset	124.9	124.9	124.9	124.9	124.9	124.9	124.9
Entrance Lens Offset	13.7	13.7	13.7	13.7	13.7	13.7	13.7

5/15/17 Set up run for Alex's next 10 samples-
Observed extra particulate in samples before prep.
Tune results:

Peak shape: smooth and symmetric

Etune ion abundance: m/z 219, **553K**

Relative ion abundance: m/z 502, **7.7%**

EM voltage: 1985

Background peaks: **181**

Isotopic ratio: m/z 502, **10.8%**

Agilent

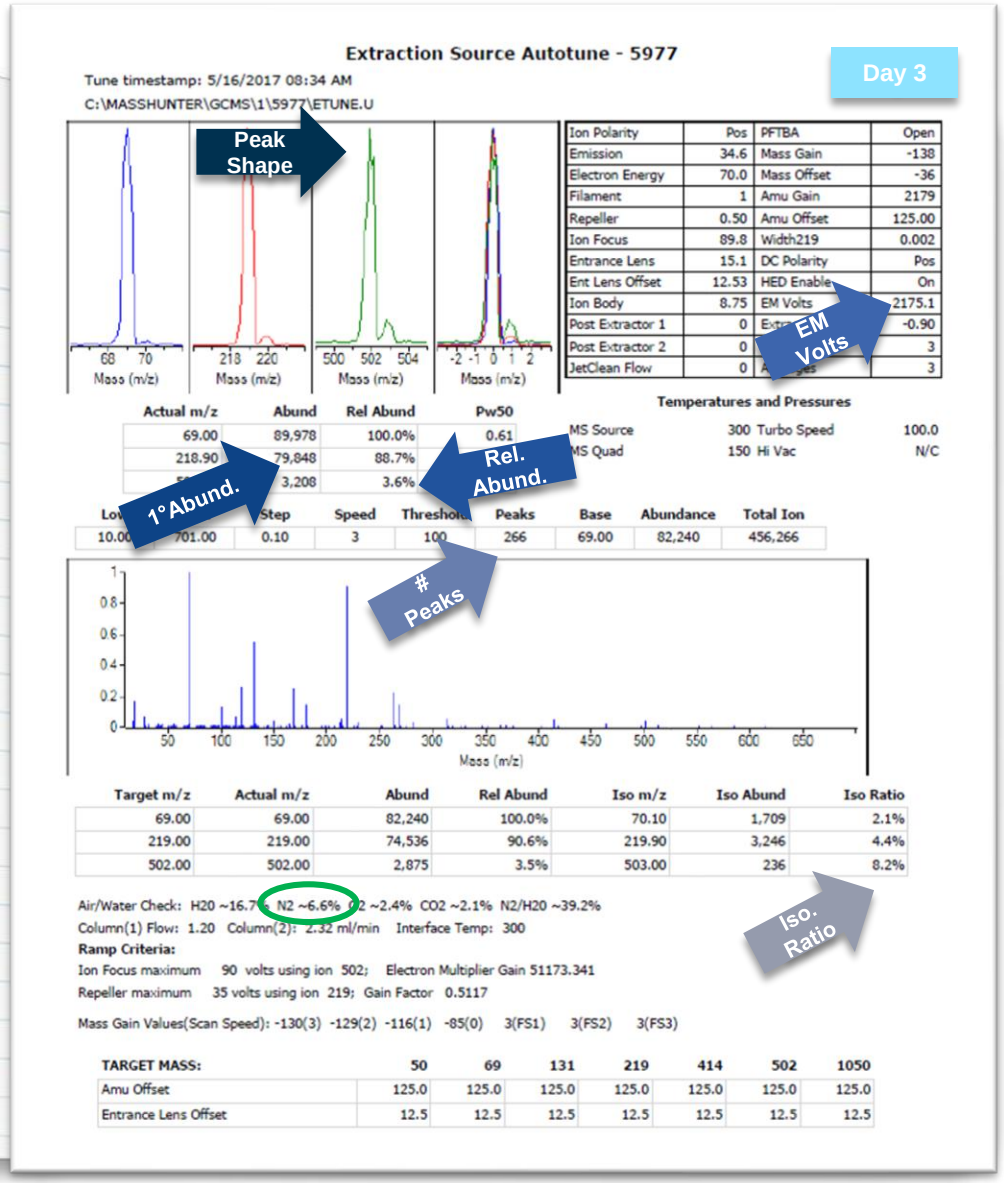
Case study

Monitoring tune reports over time

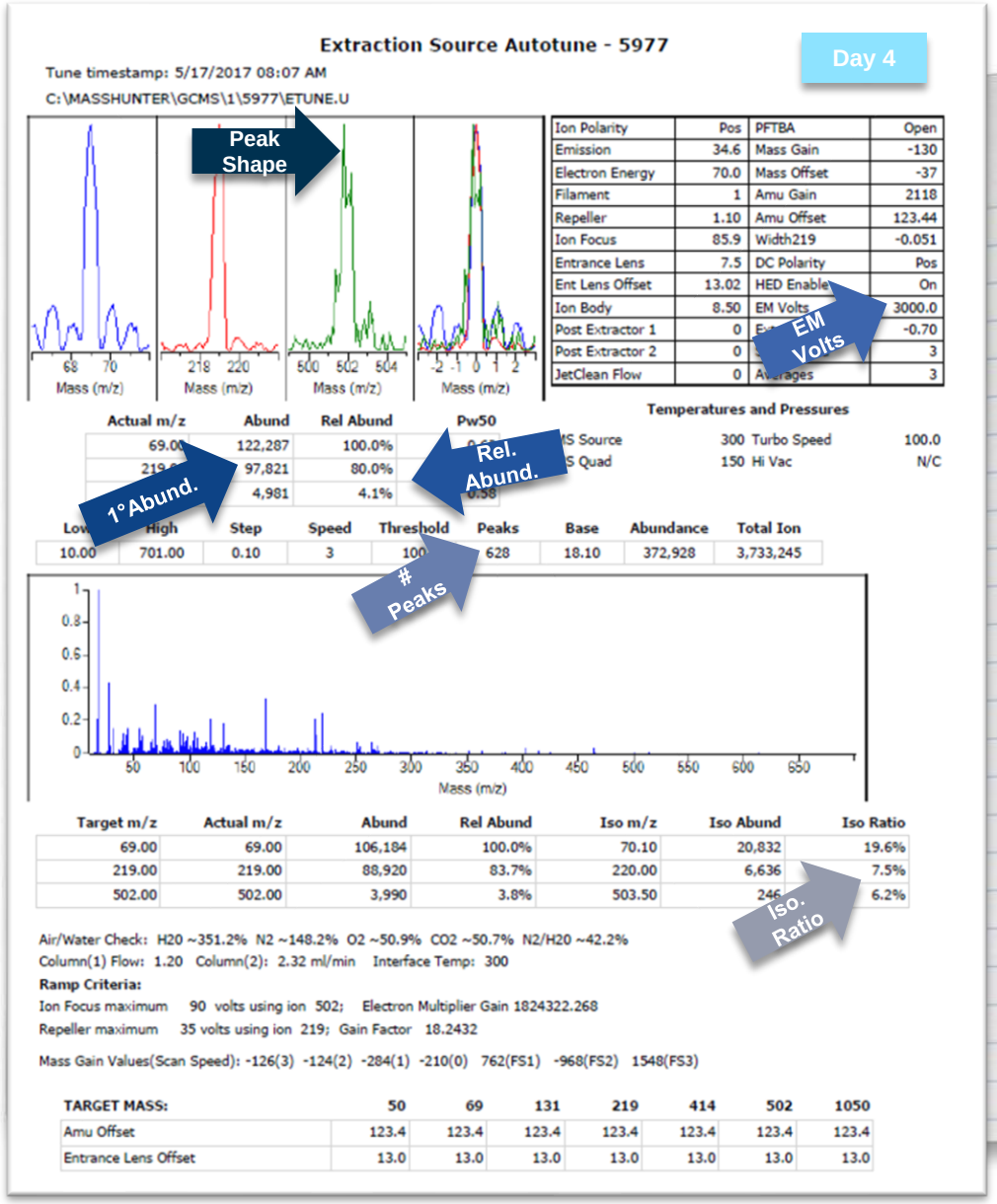
5/16/17 Set up test run for method development.
Tune results:

- Peak shape: 502 slightly jagged
- Etune ion abundance: m/z 219, **79K**
- Relative ion abundance: m/z 502, **3.6%**
- EM voltage: 2175
- # Background peaks: **266**
- Isotopic ratio: m/z 502, **8.2%**

Monday's Tune
219 Abund.- 553K
Rel. Abund.- 7.7%
EM Volts- 1985
#Bkgrd.- 181
Iso Ratio- 10.8%



What could have happened



Extraction Source Autotune - 5977

Day 4

Tune timestamp: 5/17/2017 08:07 AM

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Peak Shape

Ion Polarity	Pos	PFTBA	Open
Emission	34.6	Mass Gain	-130
Electron Energy	70.0	Mass Offset	-37
Filament	1	Amu Gain	2118
Repeller	1.10	Amu Offset	123.44
Ion Focus	85.9	Width219	-0.051
Entrance Lens	7.5	DC Polarity	Pos
Ent Lens Offset	13.02	HED Enable	On
Ion Body	8.50	EM Volts	3000.0
Post Extractor 1	0		-0.70
Post Extractor 2	0		3
JetClean Flow	0	Averages	3

EM Volts

Mass (m/z)

Actual m/z	Abund	Rel Abund	Pw50
69.00	122,287	100.0%	
219.00	97,821	80.0%	
502.00	4,981	4.1%	

1° Abund.

Rel. Abund.

Temperatures and Pressures

MS Source	300	Turbo Speed	100.0
MS Quad	150	Hi Vac	N/C

Low	High	Step	Speed	Threshold	Peaks	Base	Abundance	Total Ion
10.00	701.00	0.10	3	100	628	18.10	372,928	3,733,245

Peaks

Mass (m/z)

Target m/z	Actual m/z	Abund	Rel Abund	Iso m/z	Iso Abund	Iso Ratio
69.00	69.00	106,184	100.0%	70.10	20,832	19.6%
219.00	219.00	88,920	83.7%	220.00	6,636	7.5%
502.00	502.00	3,990	3.8%	503.50	246	6.2%

Iso. Ratio

Air/Water Check: H20 ~351.2% N2 ~148.2% O2 ~50.9% CO2 ~50.7% N2/H20 ~42.2%

Column(1) Flow: 1.20 Column(2): 2.32 ml/min Interface Temp: 300

Ramp Criteria:

Ion Focus maximum 90 volts using ion 502; Electron Multiplier Gain 1824322.268

Repeller maximum 35 volts using ion 219; Gain Factor 18.2432

Mass Gain Values(Scan Speed): -126(3) -124(2) -284(1) -210(0) 762(FS1) -968(FS2) 1548(FS3)

TARGET MASS:	50	69	131	219	414	502	1050
Amu Offset	123.4	123.4	123.4	123.4	123.4	123.4	123.4
Entrance Lens Offset	13.0	13.0	13.0	13.0	13.0	13.0	13.0

5/17/17 Received samples for rush turnaround.
Tune results:

Peak shape: really jagged

Etune ion abundance: m/z 219, **97K**

Relative ion abundance: m/z 502, **4.1%**

EM voltage: **3000**

Background peaks: **628**

Isotopic ratio: m/z 502, **6.2%**

Tuesday's Tune
219 Abund.- 79K
Rel. Abund.- 3.6%
EM Volts- 2175
#Bkgrd.- 266
Iso Ratio- 8.2%

Agilent

Improved Self-Tightening Column Nut

Enhancing ease of use for the analyst

Technology Innovation

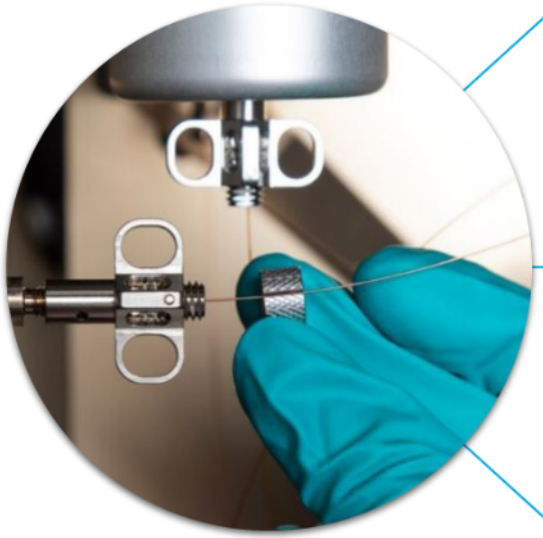
Spring-driven piston to help maintain a consistently tight seal, regardless of use and temperature

Sealing collar to help hold the column in place

Soft rubber to grip the column and prevent damage from over-tightening

Self-Tightening Column Nuts

No leaks, No downtime, No frustration



More Accurate Results

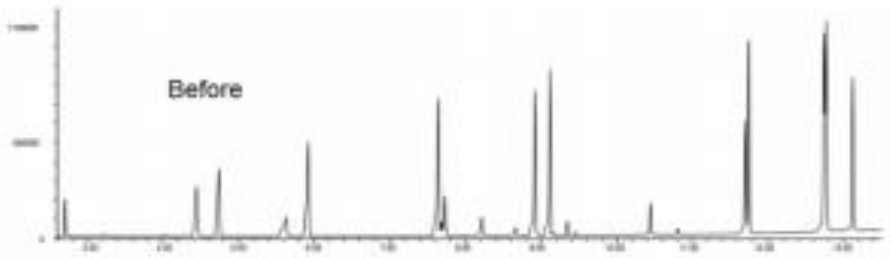
- Consistent column length
- Leak-free connection over 100s of cycles
- Unaffected by changes in temperature

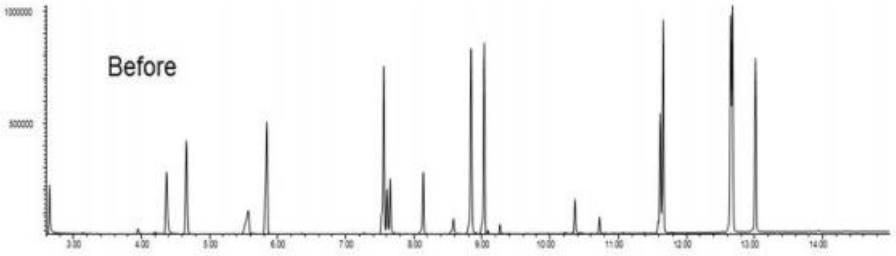
Reduced Installation Time

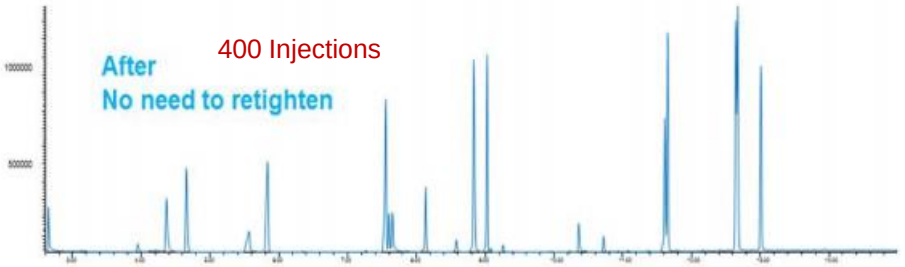
- Eliminates need to open MS port
- Easy finger-tightening mechanism
- Reduced maintenance requirements

Cost Savings

- Fewer reruns due to leaks
- Longer lasting
- Reduced downtime







Hunting for leaks: the analyzer side plate

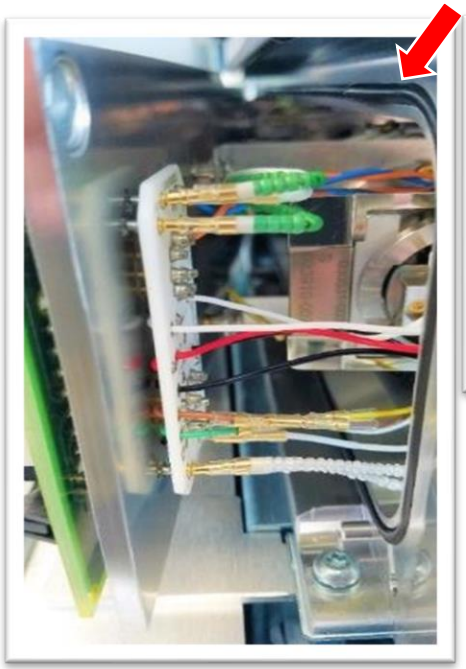
Ensure seal integrity at the side plate o-ring

Factors that disturb seal integrity

- Sticking/dislodging upon opening
- Aging and wear
- Physical obstructions: dust, lint, metal fines

How is it fixed and prevented?

- Using gloves, gently manipulate o-ring within groove to ensure uniform surface
- Visually inspect seal integrity prior to pump down
- Replace worn or damaged o-rings
- Wipe o-ring perimeter with lint-free tissue
- Stop using thumbscrews
  - Can create metal fines with excessive use
  - Only use during shipment/relocation



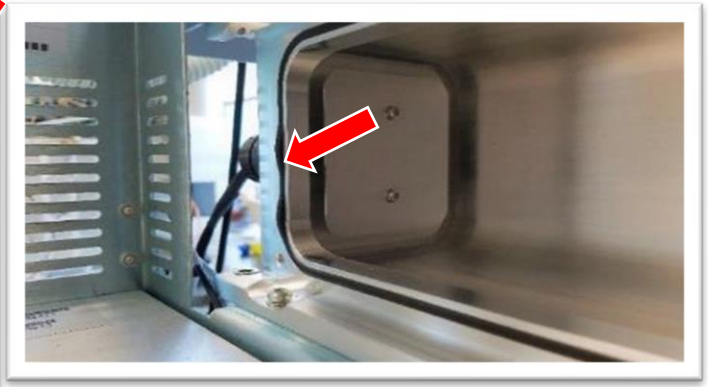
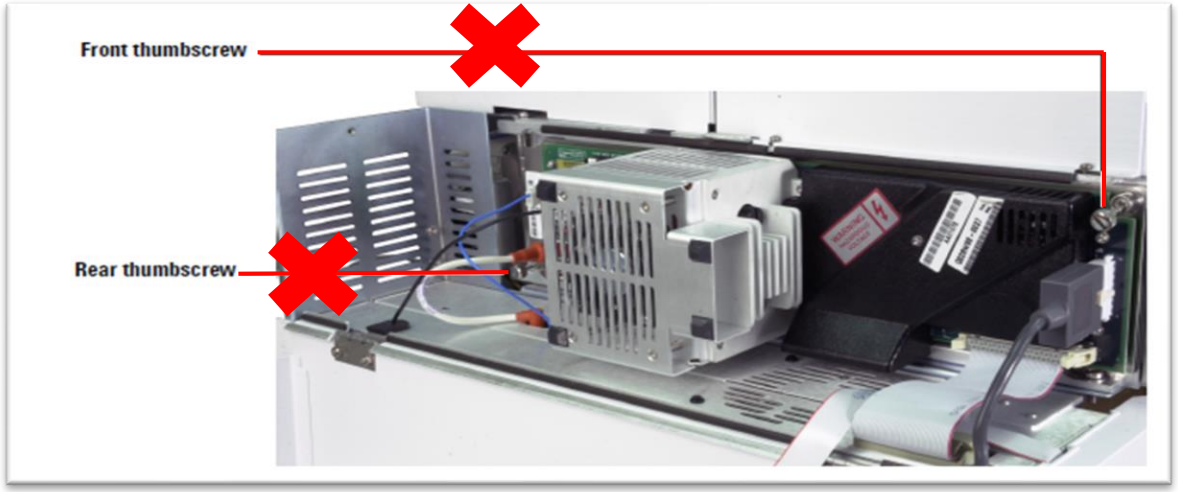


Image taken with analyzer door removed for better visibility

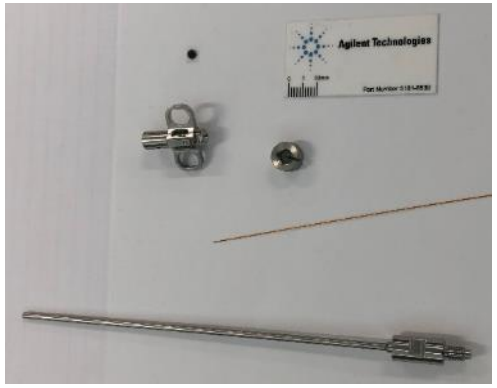
Agilent GCMS Side plate o-ring
P/N 0905-1442
link

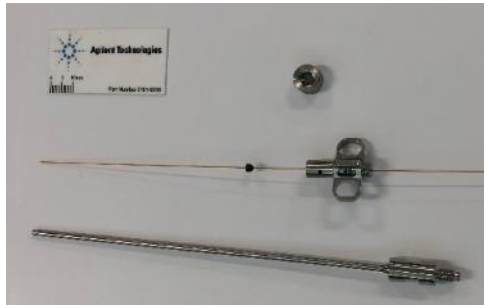


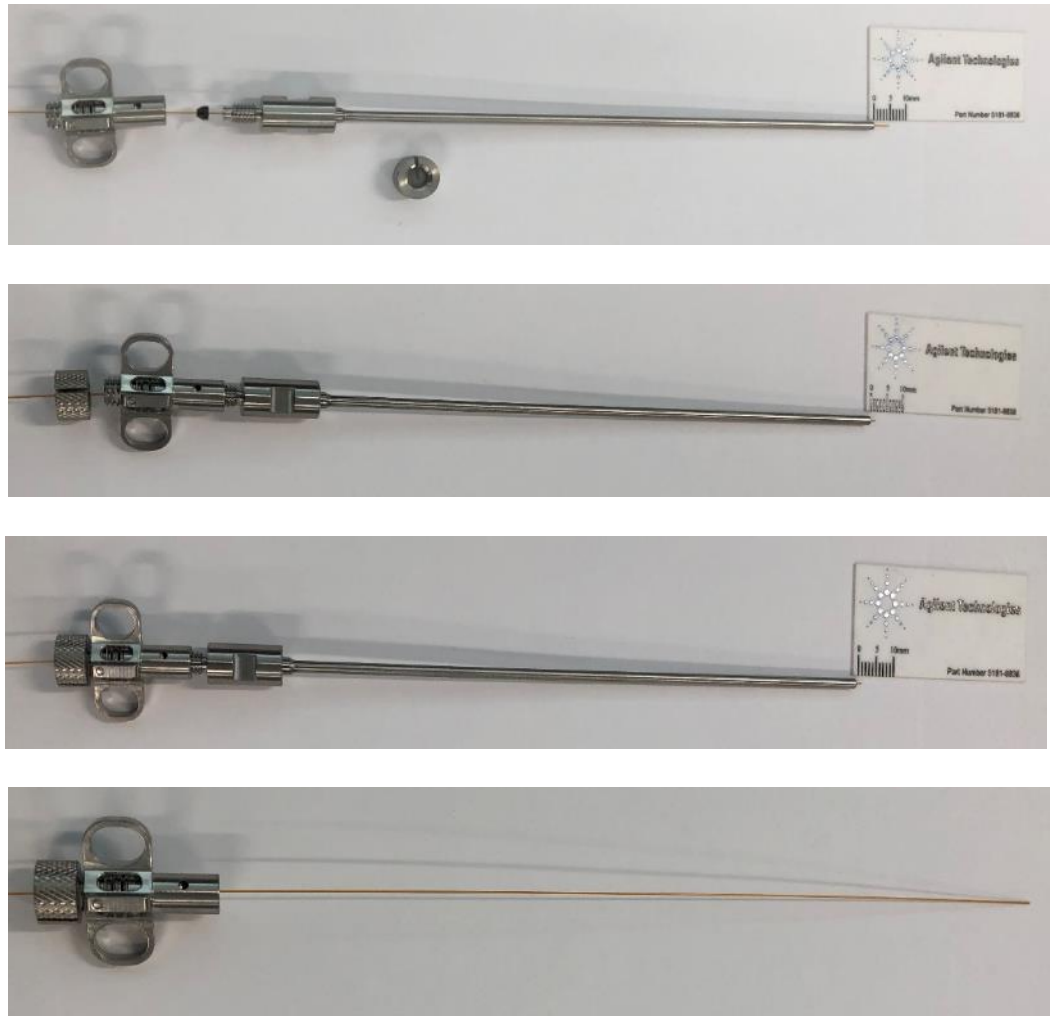
MS Configuration

Facilitates MS Column Installation

Redesigned
MS Transfer Line
Self Tightening Nut







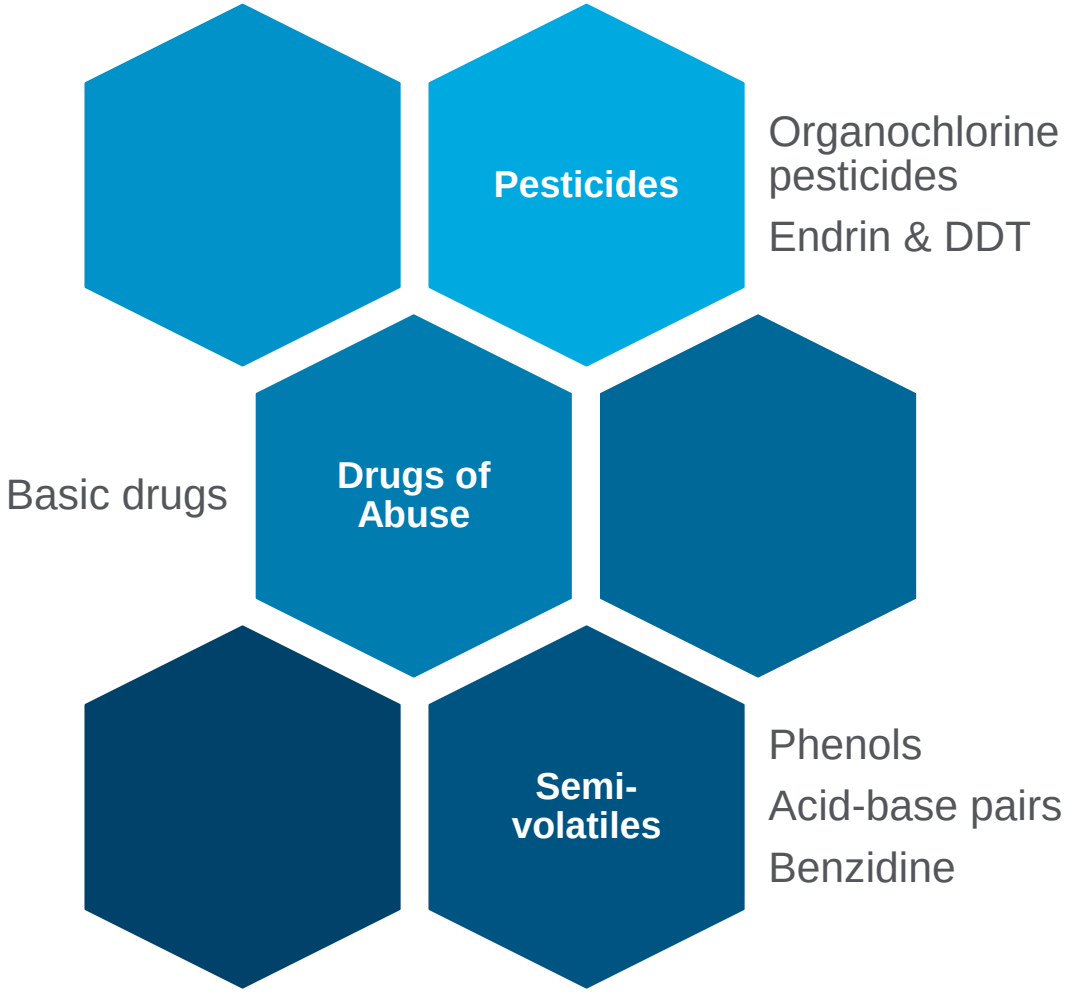
Glass-fritted Inlet Liners

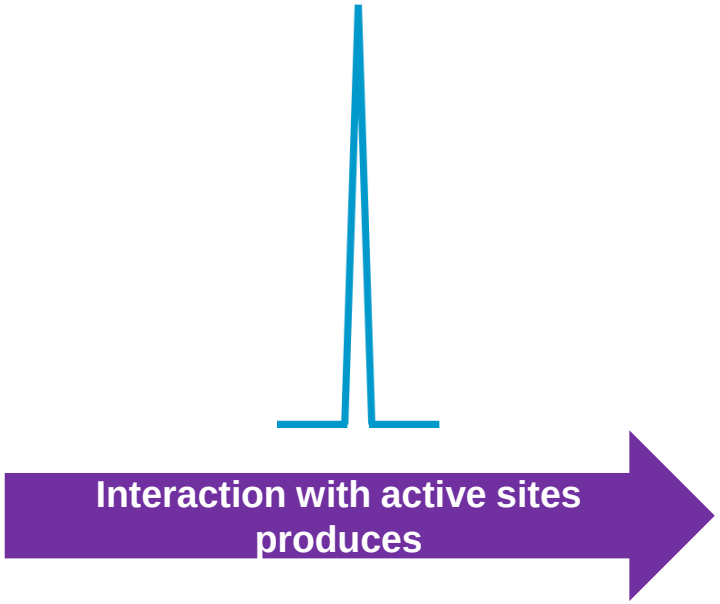
More consistent results coupled with longer lifetimes

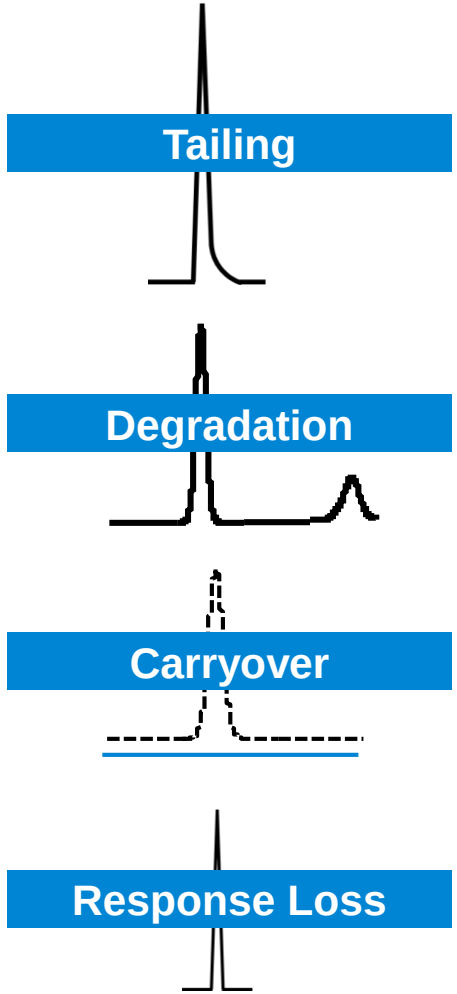
Agilent

Why should we do this?

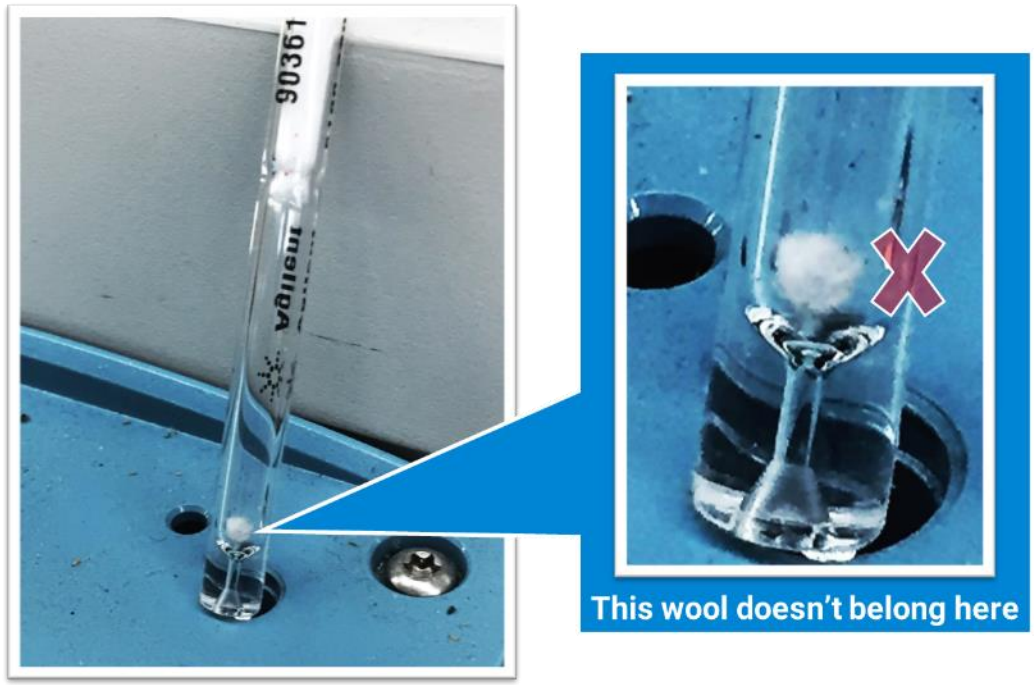
Dislodged glass wool fibers expose active sites that interact with sensitive analytes

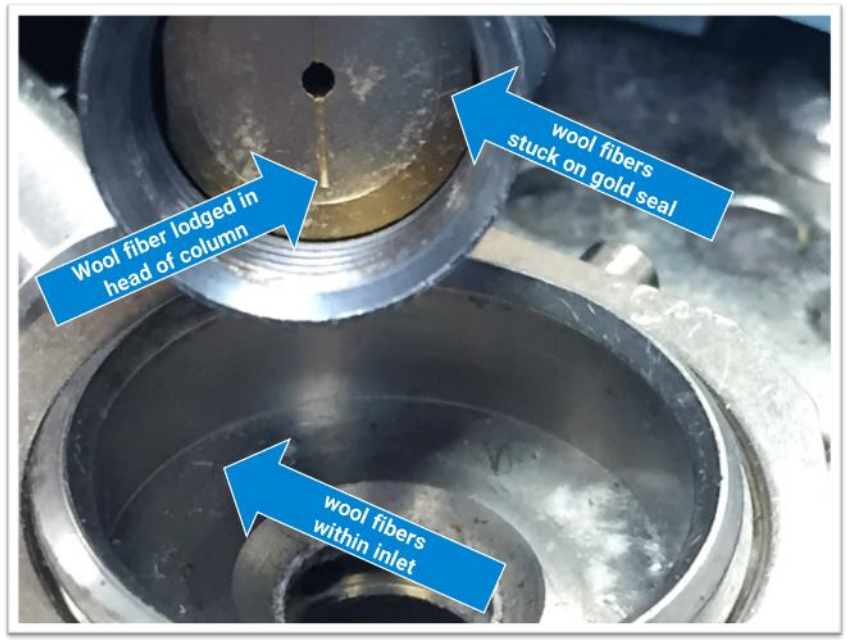






Reported Issues with Glass Wool

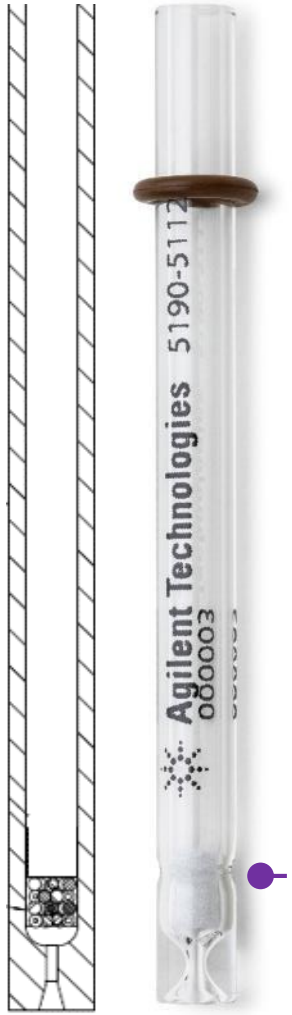




Once dislodged, glass wool fibers migrate through the flow path

What's new? Glass wool alternative liners

Ultra Inert liners with sintered glass frits



Low frit single taper liner
(new)

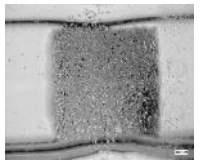
- Designed for dedicated splitless analyses
- Ideal for heavier MW compound analysis
- SVOCs, and OC/OP pesticides

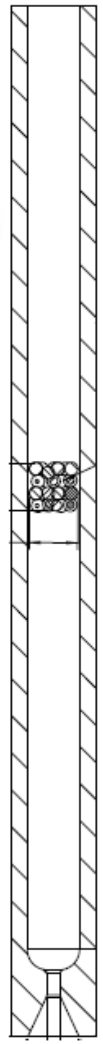
- General purpose split/splitless liner
- Ideal for basic lighter MW compound analysis

Mid frit single taper liner

- 2x Increase in Liner Lifetime

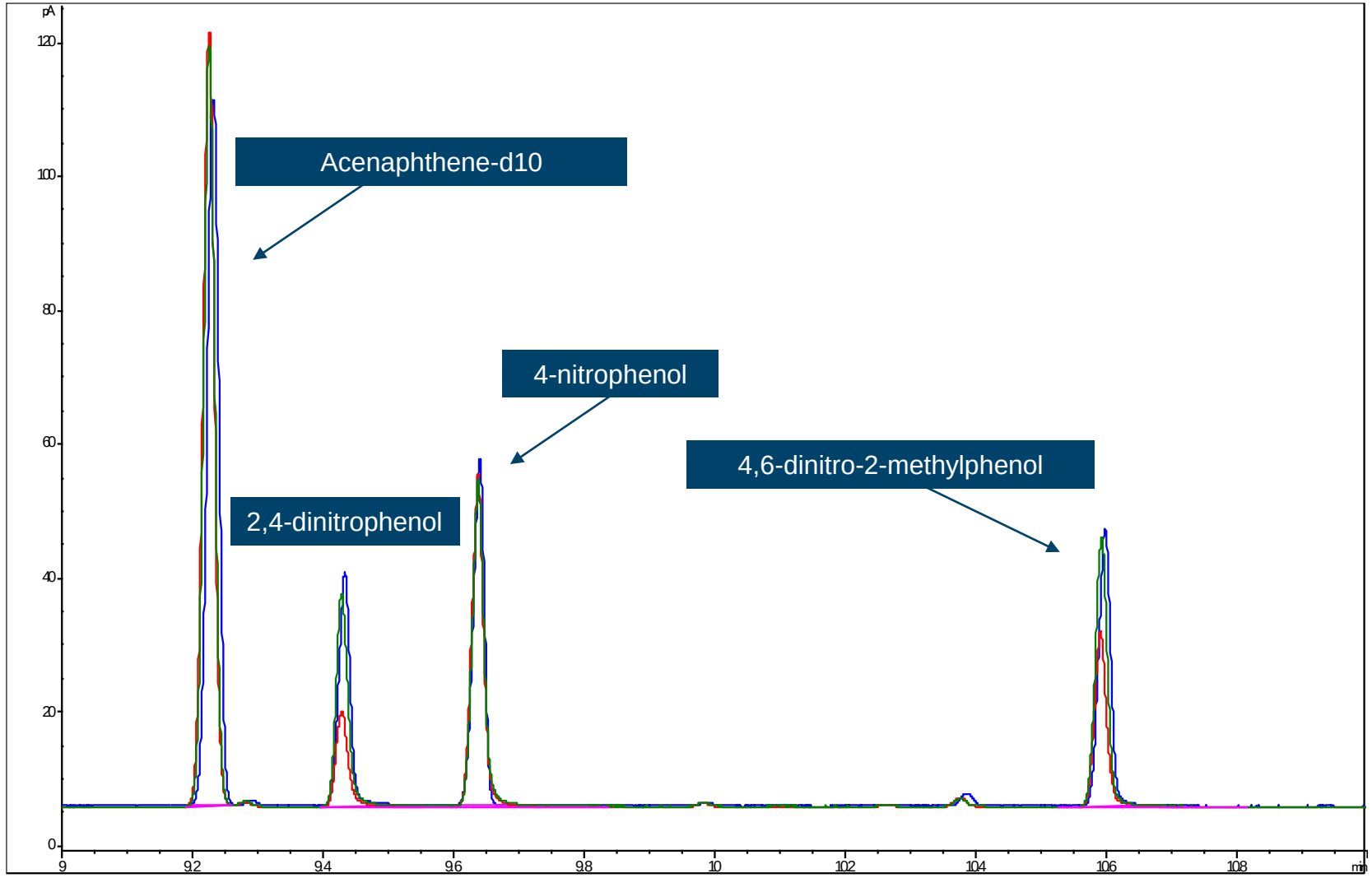
Porous glass frit





8270 Chromatogram Overlay- Phenols/Low Frit Liner

Low frit liner gives excellent response and peak shape for tricky analytes like phenols



Blue = initial injection
Red = after 100 matrix injections
Green = after liner replacement

5ppm, 1uL splitless injection
FID detector

Thank you for your attention!