

# Simple Strategies for GC/MS Success

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# Time robbers in the GC/MS lab

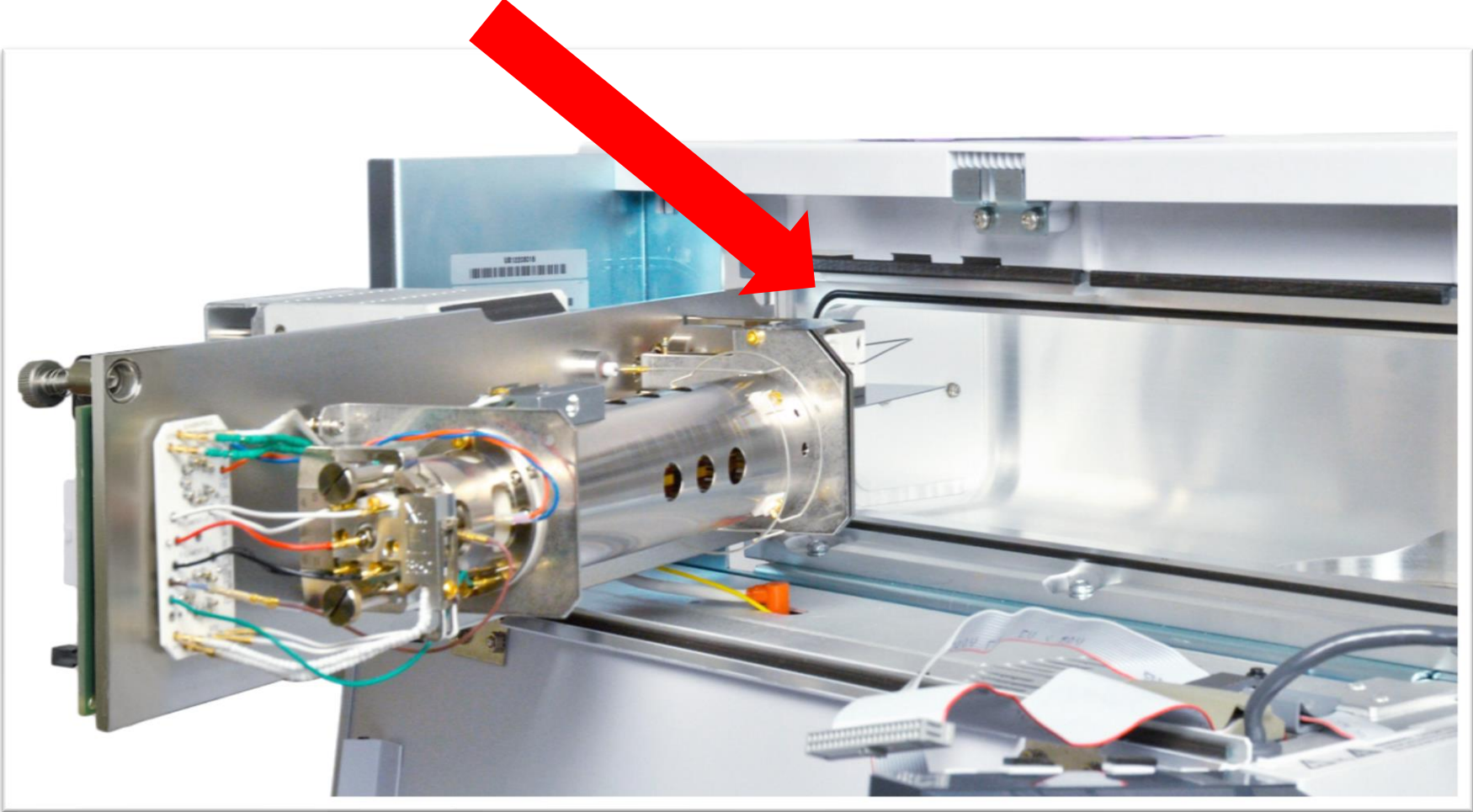
- **Looking for leaks**
  - Frequent leaks affect sensitivity, damage column, shift peak retention times
  - Locating leaks can be tedious
- **Unplanned maintenance**
  - Over time, deposits on MS source impair performance
  - Closer inspection of routine tune reports can proactively identify need for source maintenance
- **Sample reruns/reworks**
  - Enabling greater sensitivity helps prevent poor peak shape and contamination



# GC/MS Time Robber #1: Leaks

# Where to look: common leak sites

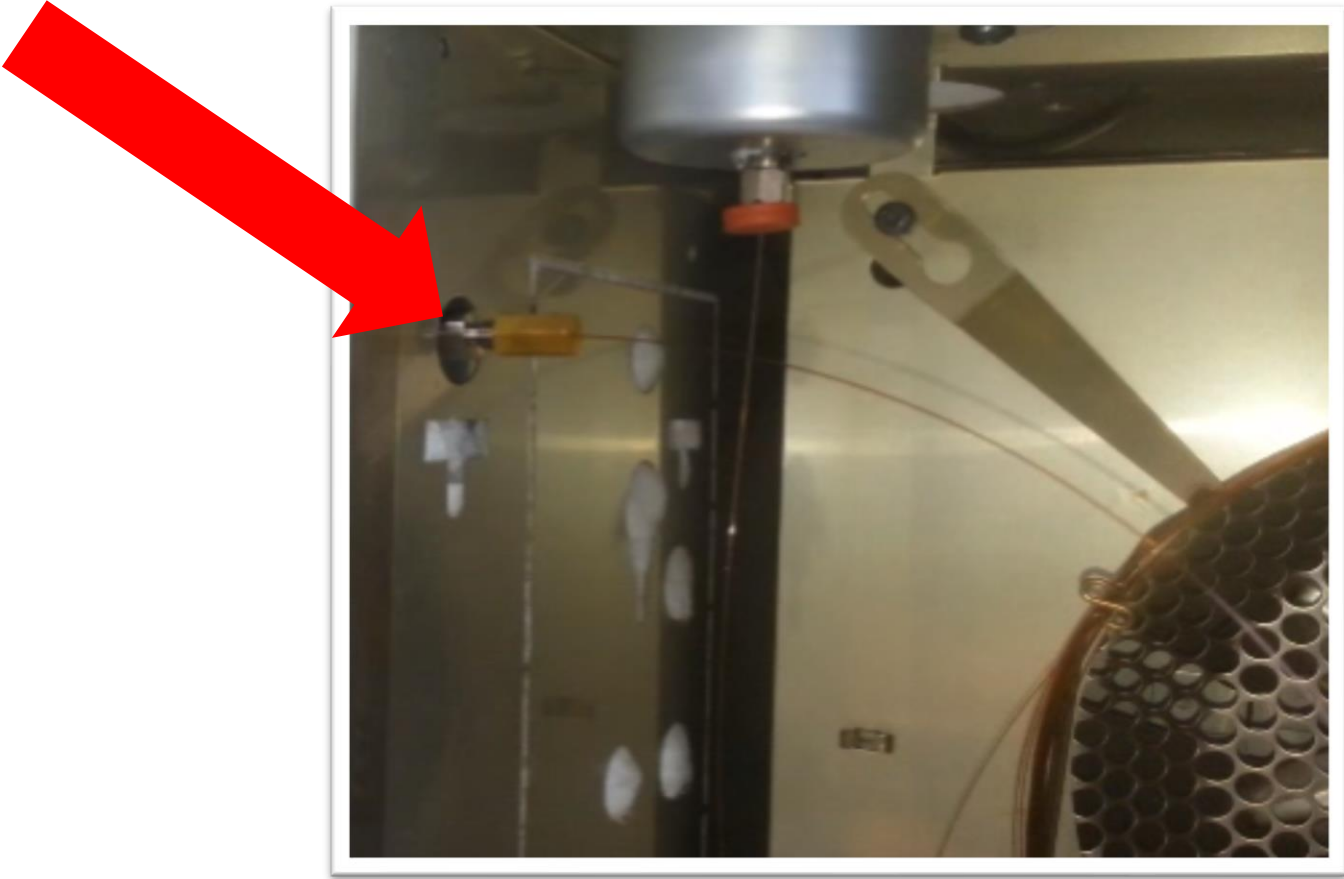
🔍 Where to look: common leak sites



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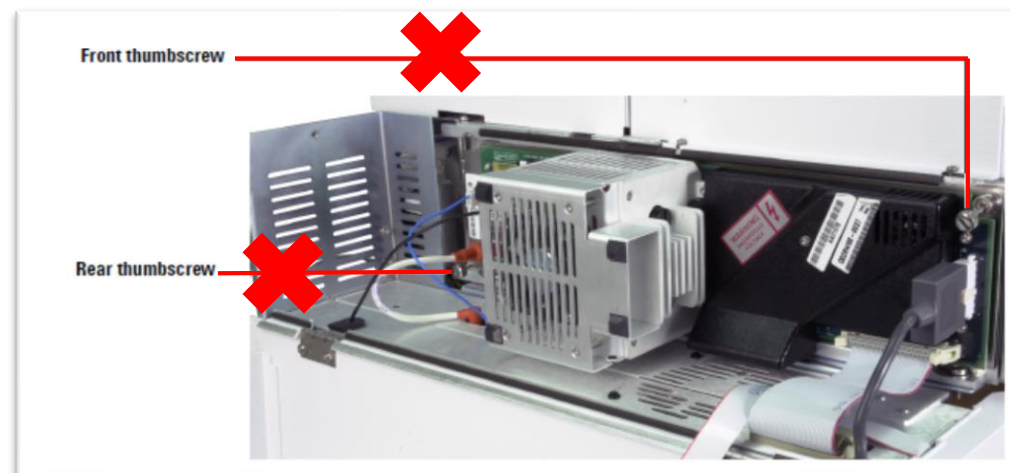
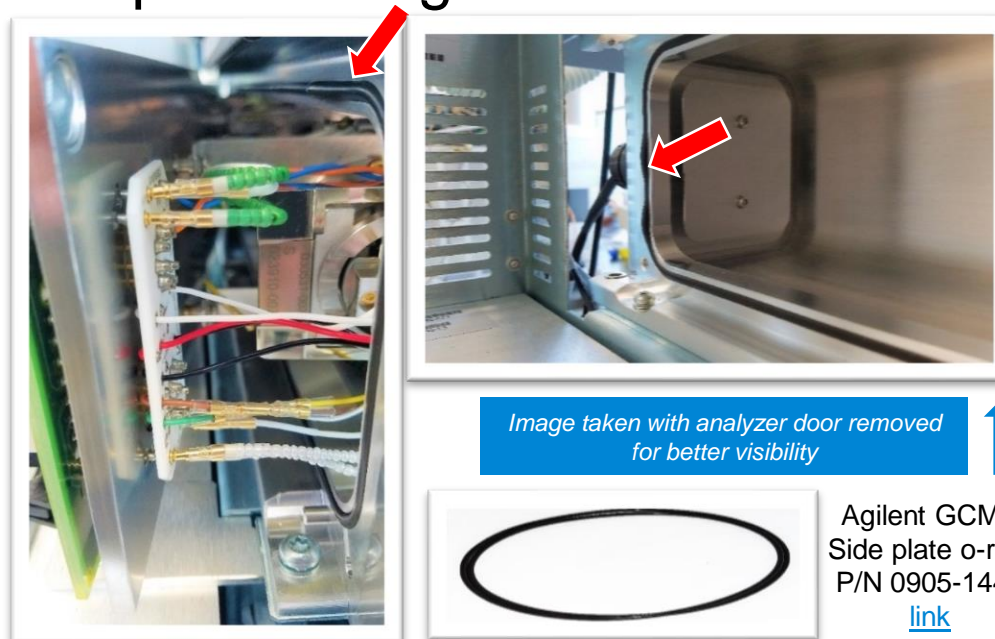




# Hunting for leaks: the analyzer side plate

## Tip 1: 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
  - Ensure MS is well-ventilated
  - Periodically vacuum beneath outer covers







# Hunting for leaks: the analyzer side plate

Don't let this happen to you!





# Hunting for leaks: the vent valve

## Tip 2: Forgetting to retighten- or overtightening- the vent valve

- How does this happen?
  - Easily overlooked
  - Urge to overtighten fittings
- Why is it bad?
  - Overtightening compresses o-ring
  - Prevents leak-free seal formation
- How is it fixed?
  - After venting, retighten vent valve before maintenance
  - Tighten gently to avoid cross-threading
  - If leaks are persistent, replace vent valve o-ring



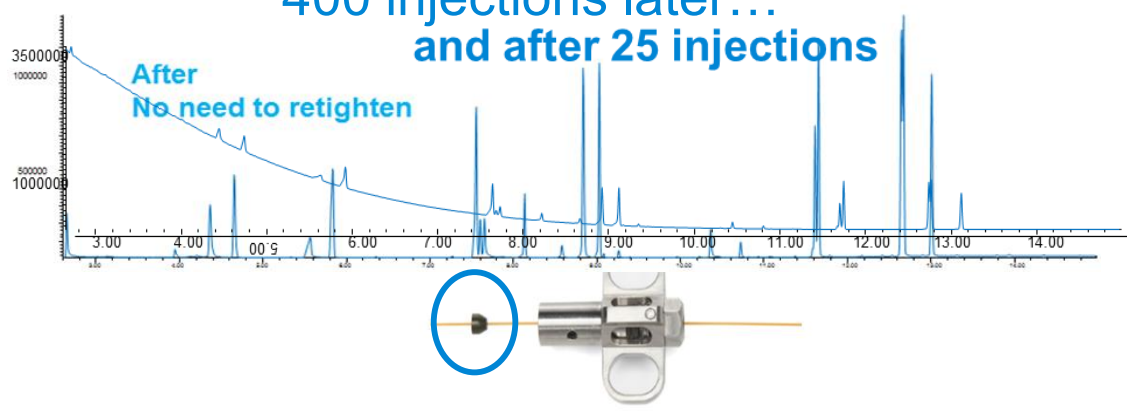
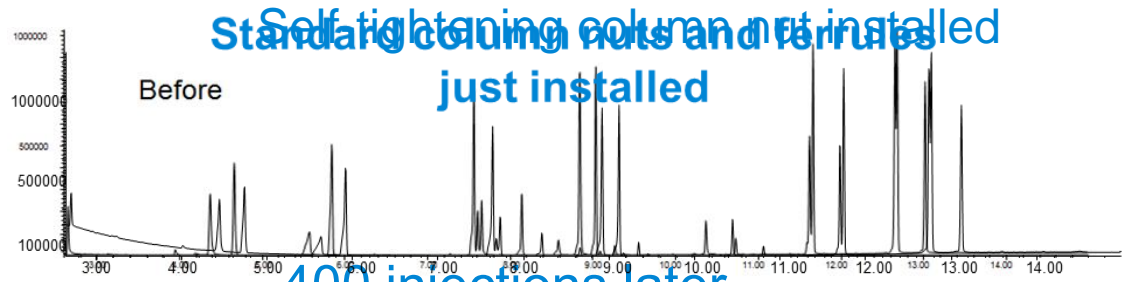
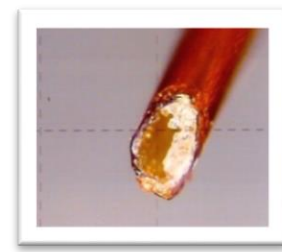
Agilent MSD Vent Valve o-ring  
P/N 0905-1014  
[link](#)





# Hunting for leaks: transfer line interface

## Tip 3: Tight, but not too tight...Better yet, self-tightening



For Agilent MS transfer line P/N 5190-5233

- Why is it bad?
  - Over tightening damages transfer line threads, column
  - Audible squealing → overtightening
- How is it fixed?
  - Stop overtightening
    - Stripped transfer line threads require replacement by service engineer
    - Just tight enough- use MS tune to check
  - Switch to self-tightening MS column nuts
    - Spring-driven piston **continuously** presses against ferrule
    - Easily installed, no tools
    - Benefits- **longer column lifetime, lower column bleed**
    - Available for Agilent, Perkin Elmer, Shimadzu, Thermo



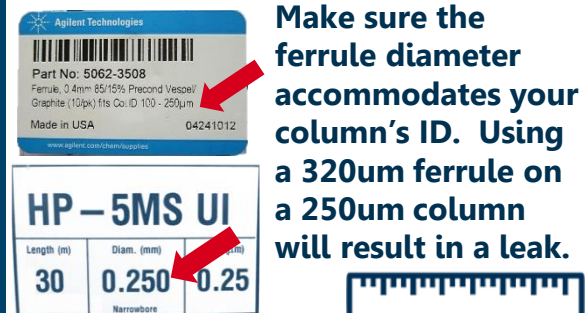
## A critical connection



## Focus on your ferrules



## Double check the diameter



### Just tight enough!

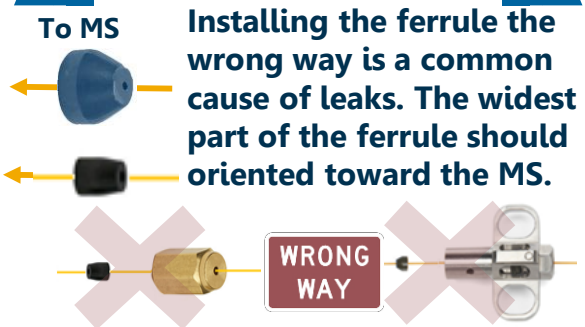
Overtightening damages fittings and your column. Periodically retighten brass column nuts, or switch to self-tightening.

## The Facts on Ferrules

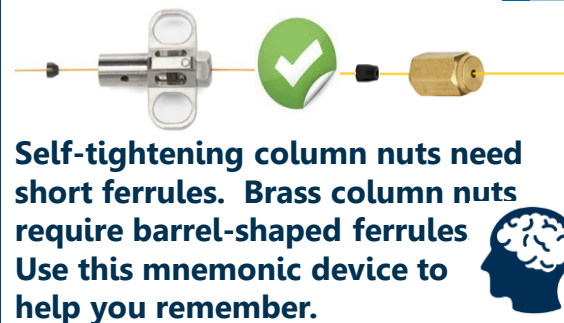


Recycling is great for the environment, but not so good for ferrules- their ability to make a leak free seal declines with age and wear. **Never reuse ferrules.**

## Right side up



## Short selfies and brass barrels



## Graphite doesn't go



Pure graphite ferrules are a no-go with GC/MS- it's too soft, permeable, and has a tendency to flake or crumble. **Always use Vespel®/graphite ferrules for GC/MS applications.**



# Hunting for leaks: weapon of choice

Tip: Arm yourself with the best...or in a pinch, what's nearby

- A good leak detector is a mass spectrometrists' best friend
  - High sensitivity
  - Recommended for leak detection in gas plumbing and fittings
- If you don't have a leak detector, use electronics duster instead
  - Hold can upright (don't spray liquid!)
  - Spray short bursts around likely leak suspects
  - Spray just enough
  - "Live" tune scanning for ions to pinpoint leak

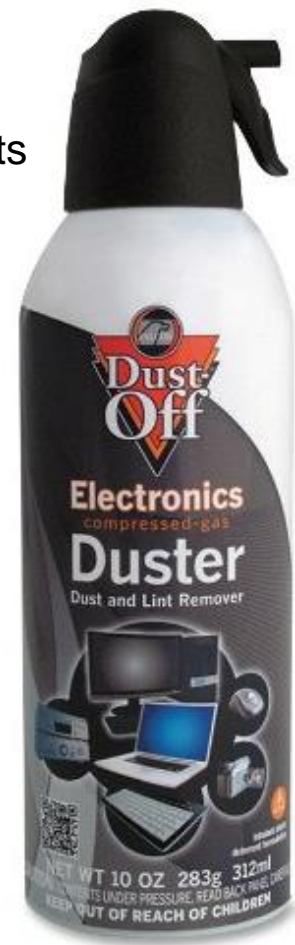


Agilent G338B Leak Detector

[link](#)

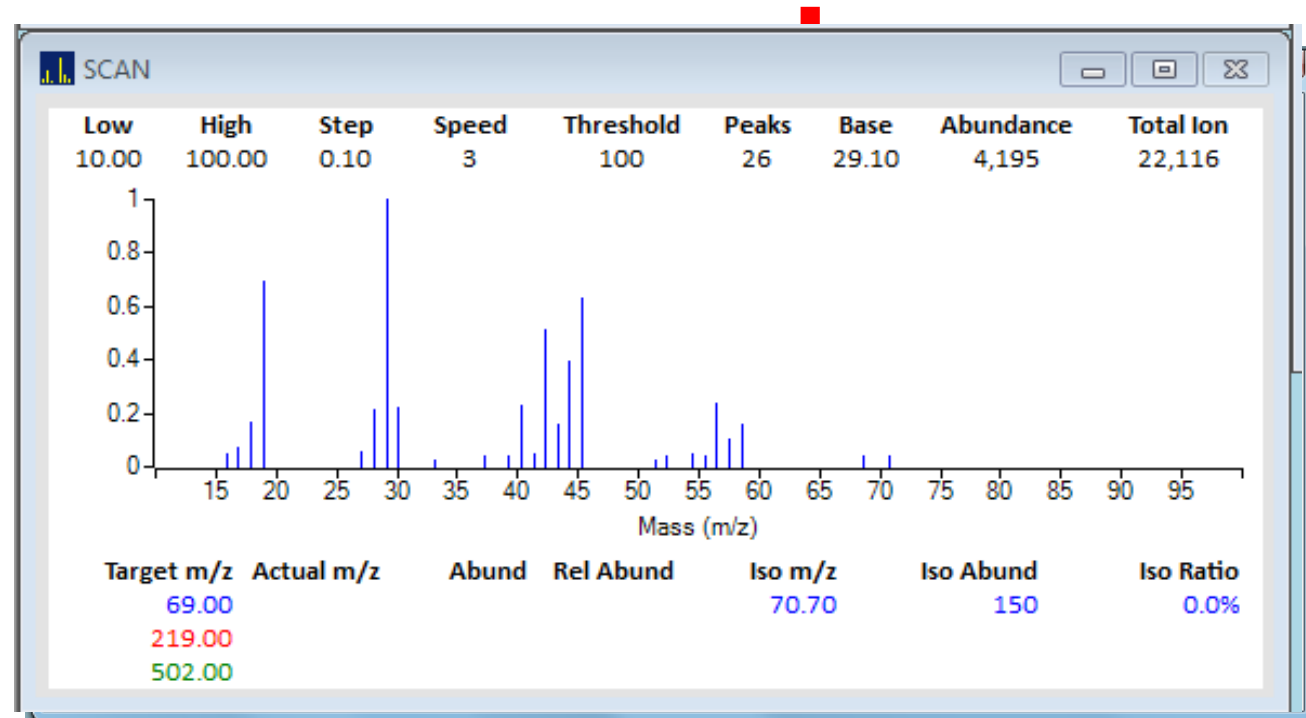
## Typical Electronic Duster Components and Ions

<chem>CC(F)F</chem>	1,1-difluoroethane	m/z 51,65
<chem>CC(F)(F)F</chem>	1,1,1-trifluoroethane	m/z 83
<chem>CC(F)(F)F(F)C</chem>	1,1,1,2-tetrafluoroethane	m/z 101



# Hunt for leaks in manual tune mode

- From MS tuning interface
- In Agilent's MassHunter Acquisition, Vacuum/Tune Control window
  1. Select Parameters > Manual Tune
  2. Click Scan tab on right-hand side
  3. Set low m/z = 10, high m/z = 100 amu
  4. Ensure PFTBA valve closed
  5. Click Scan
  6. Spray common leak sites, watch scan window for large duster ion spikes
  7. Exit manual tune screen, do not save parameters
  8. Return to acquisition



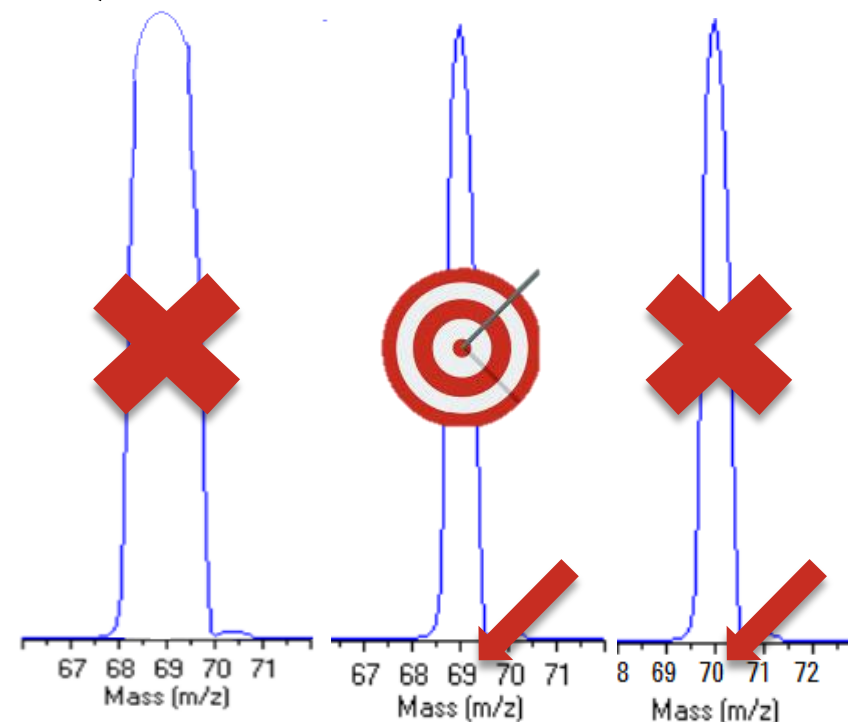
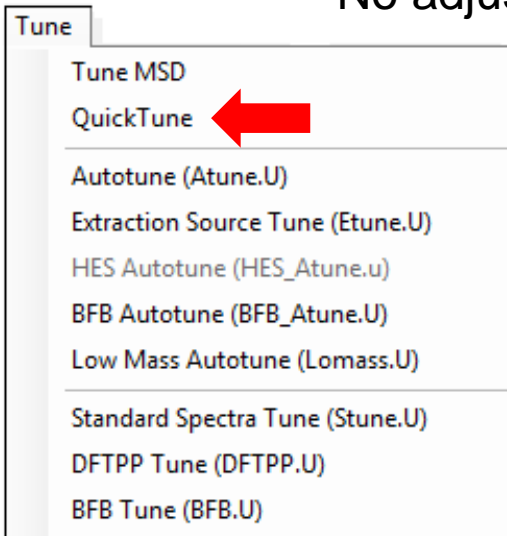
# GC/MS Time Robber #2:

Taking tune reports for granted

# «U» Tuning tip #1: Tune routinely to monitor MS performance



- Frequency depends on how often MS used
- Recommend at least weekly
- Provides comparison points over time
- If method calibration/response factors are a concern, use QuickTune
  - Adjusts mass axis, peak width, and EM voltage only
  - No adjustment of mass abundances







## Tuning tip #2:

### Tune before AND after changes to GCMS

- Provides reference point in case something goes wrong
- Compare tune pdf files over time and look for differences
- Use these to troubleshoot, **what changed** from one tune to the next?

- Examples:



- Repair or preventative maintenance
  - After cleaning MS source (changed abundance)
  - Inlet maintenance (ensure no leaks)
  - New column installation/column trim



- Change gas filter or cylinders
  - Quickly catch contaminated gas tank
- Filament switch
- Vacation or prolonged period of downtime
- On Agilent 5977 and newer models, pdf copies are automatically created
  - Default pathway: D:\MassHunter\GCMS\1\5977\PDF



## Tuning tip #3:

Create a maintenance GC method and cool MS tune file

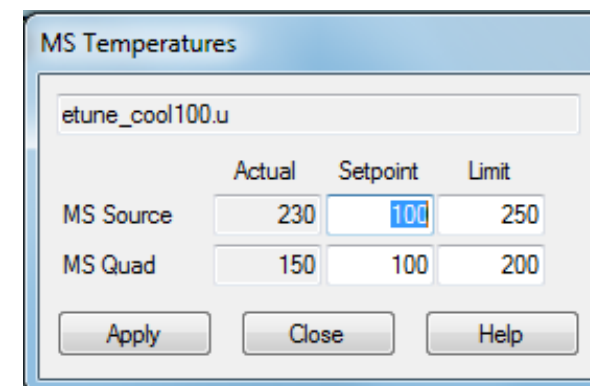
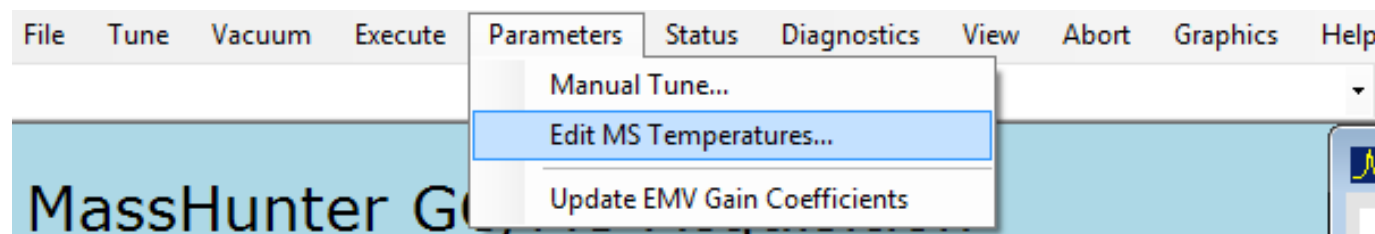
- Create cool.u tune file

- Load your normal tune file
- Adjust quad and source temps  $\leq 100^{\circ}\text{C}$
- Save as cool.u

- Create a Maintenance.m GC method

- Lower heated zones (set points  $\leq 100^{\circ}\text{C}$ , ideally cool enough to enable handling)
  - Oven, inlets, mass spec transfer line, etc.
- Do NOT turn off carrier gas flows
- Specify cool.u tune file in MS section of method

- Load Maintenance.m GC method before venting MS, or even program into end of sequence for convenient cool down



# «U» Tuning tip #4: 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?

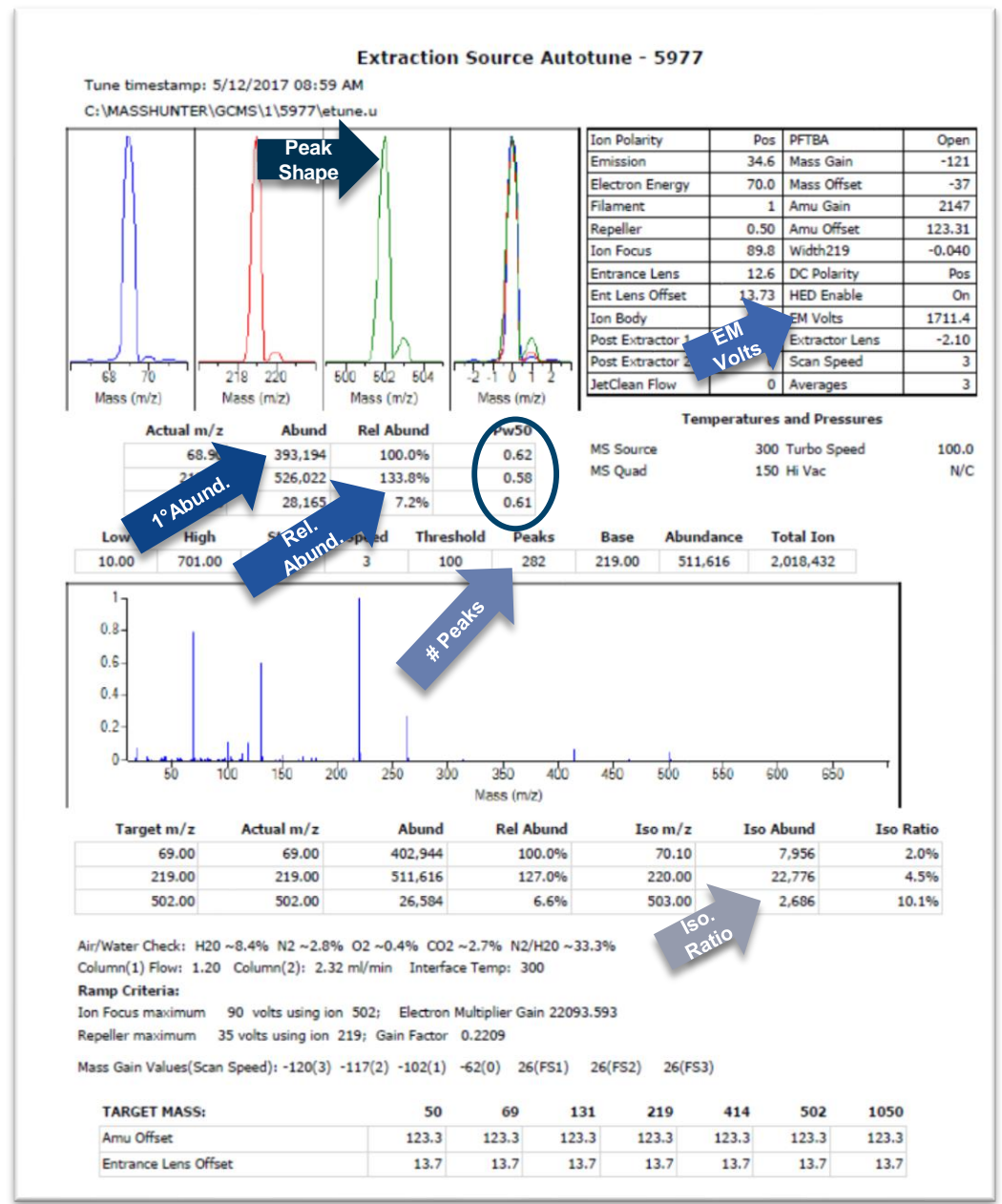
- As source grows dirtier, EM voltage increases
- Max voltage is 3000V
- **Consistency** is key

## ✓ Is background free from excessive peaks?

- Excessive peaks can indicate source contamination

## ✓ Isotopic ratios within expected values?

- 502 isotopic ratio ~ 10.1% (±20%)



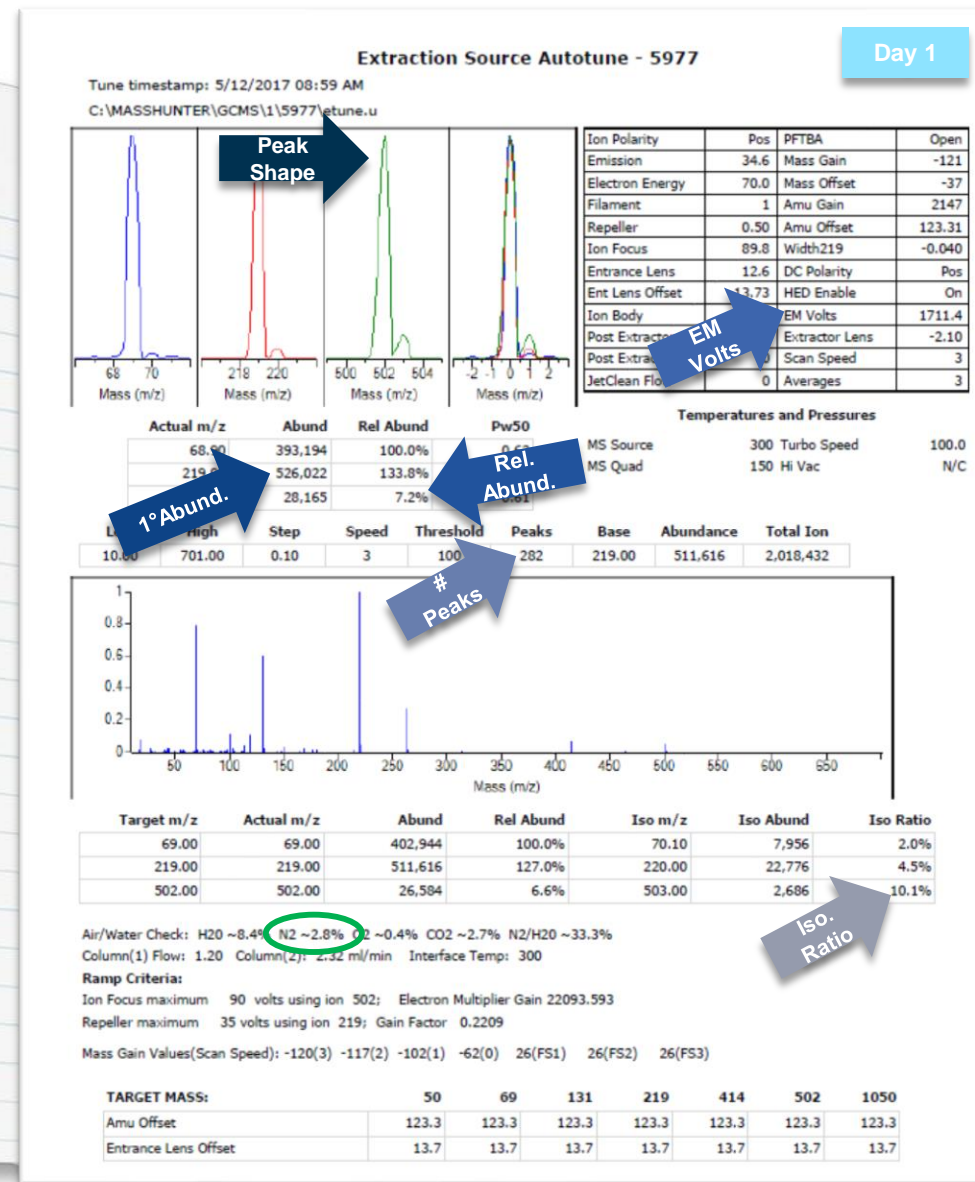


# Case Study

## Monitoring tune reports over time

5/12/17 Set up run for Alex's 15 samples.  
 Alex thinks samples are very concentrated.  
 Tune results:

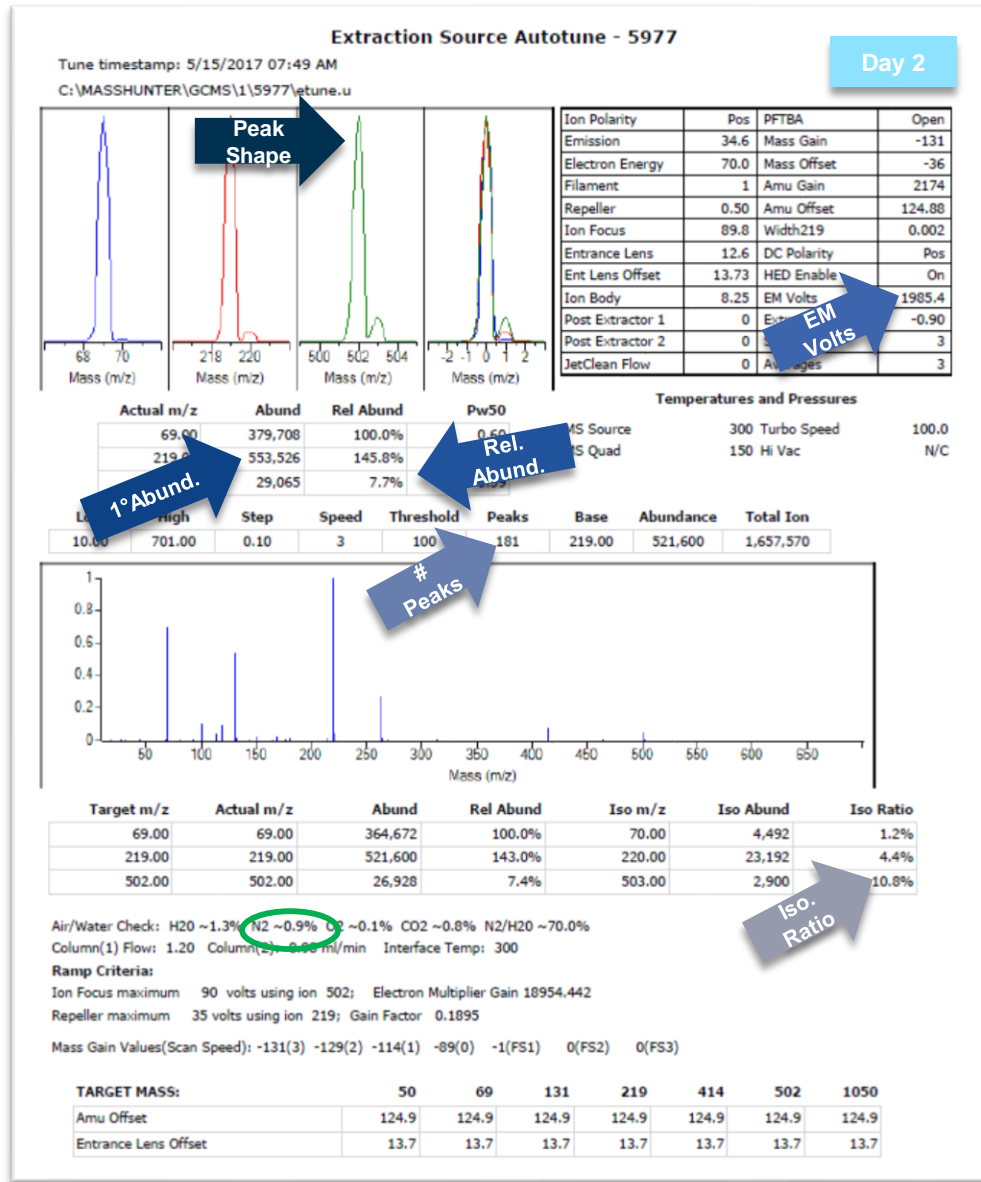
- Peak shape: smooth and symmetric
- Etune ion abundance: m/z 219,526K
- Relative ion abundance: m/z 502, 7.2%
- EM voltage: 1711
- # Background peaks: 282
- Isotopic ratio: m/z 502, 10.1%





# Case study

## Monitoring tune reports over time



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%**

Friday's Tune  
219 Abund.- 526K  
Rel. Abund.- 7.2%  
EM Volts- 1711  
#Bkgrd.- 282  
Iso Ratio- 10.1%

# Case study

## Monitoring tune reports over time

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

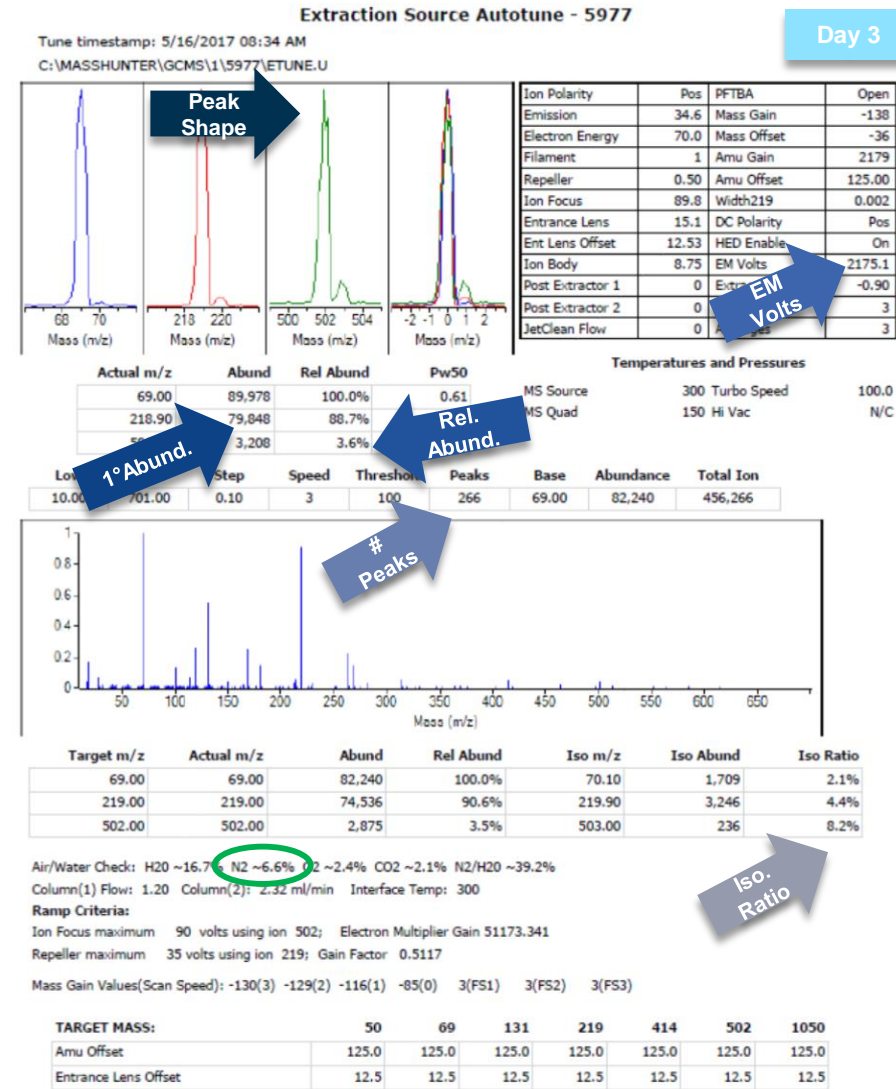
- ⚠ Peak shape: 502 slightly jagged
- ⚠ Etune ion abundance: m/z 219, **79K**
- ⚠ Relative ion abundance: m/z 502, **3.6%**
- EM voltage: 2175
- # Background peaks: **266**
- ⚠ Isotopic ratio: m/z 502, **8.2%**

### Friday's Tune

Abund- 152.6K  
Rel. Abund. and # looked good.  
EM Volts- 1711  
#Bkgrd.- 282  
Iso Ratio- 10.1%

### Monday's Tune

Abund- 79.1K  
Rel. Abund. started sequence.  
EM Volts- 1985  
#Bkgrd.- 181  
Iso Ratio- 10.8%



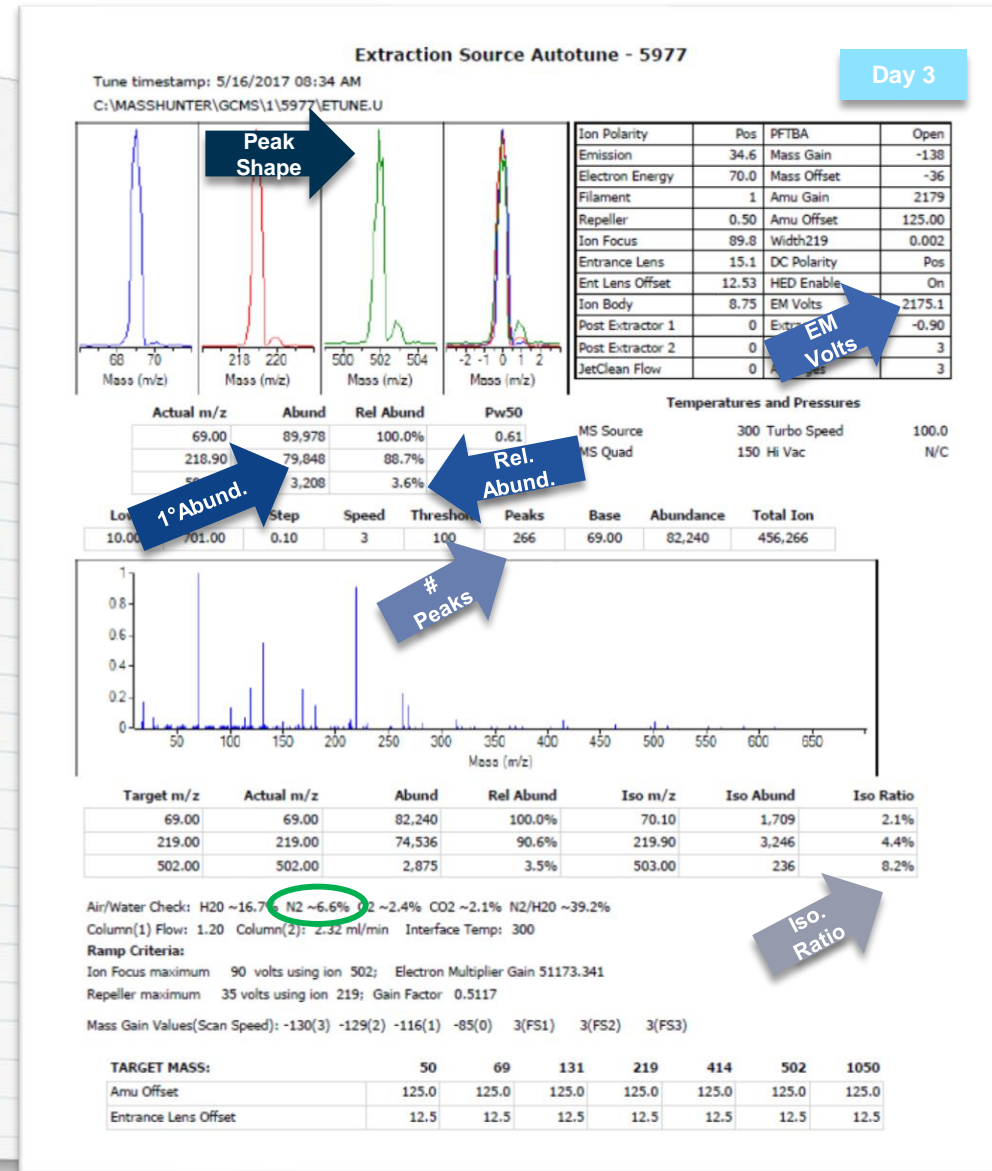
# Case study

## Monitoring tune reports over time

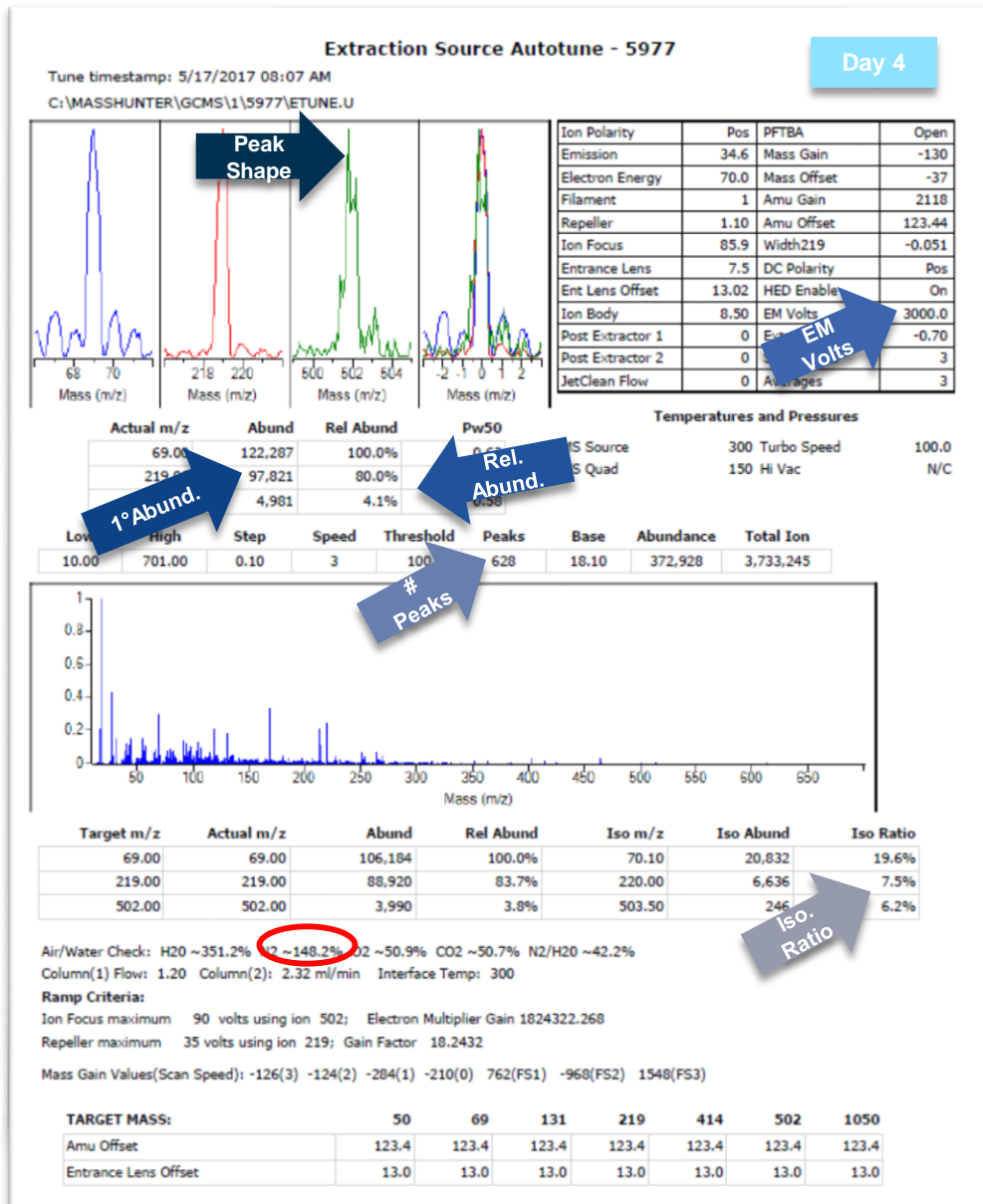
5/16/17 Set up test run for method development.  
Tune results:

- ⚠ 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%**

~~Tune not looking great. Cleaned source, reran tune and all looked good. Started sequence.~~  
Tune passed. Started sequence.



# What could have happened



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

Peak shape: really jagged

Etune

Relat

EM vo

# 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%



# GC/MS Time Robber #3: Poor Sensitivity

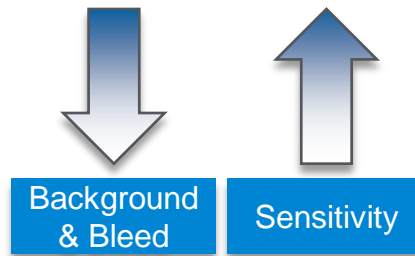


# Improving sensitivity tip #1

## Stop the bleeding

- Signal to noise relationship

- Excessive bleed → noise
- Reduces spectral strength and quality



- Potential sources of bleed or excessive background in GC/MS:

### Analytical column

- Leaks → bleed
- Look for bleed ions in mass spectral background

### Problematic consumables

- Poor quality
- Overtightening
- Not changing often enough

### Bad gases

- Poor quality
- Lack of filtration, or not changing filter often enough





# Improving sensitivity

## First aid and preventative medicine for column bleed

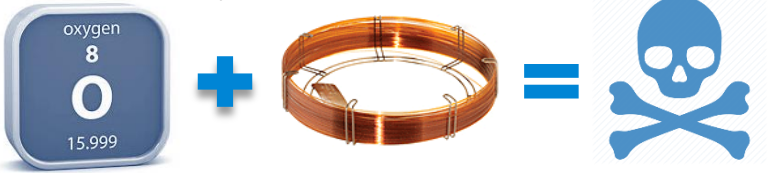
- Choose the right column
  - Inert columns and liners are essential for trace GC/MS
    - Better bleed levels
    - Greater sensitivity for active analytes
    - More runs before maintenance, source cleaning

Thick films + GC/MS →



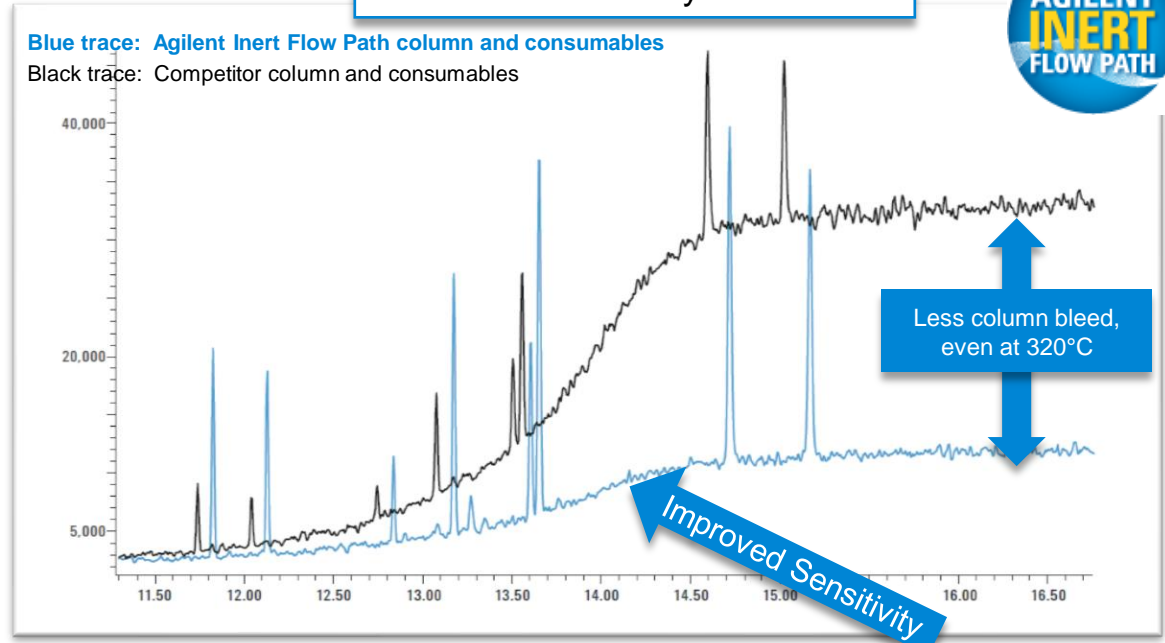
### Treat your column right

- Oxygen is toxic to your column

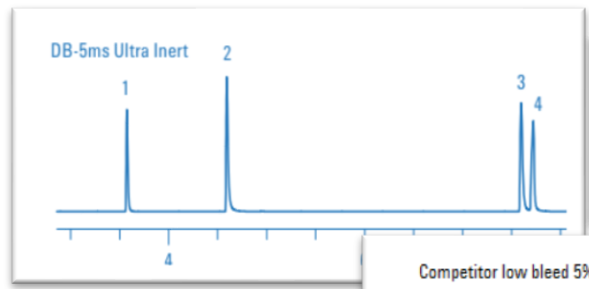


- Maintain gas flow when installed in GC
- Cap column when not in use
- Prevent leaks (self-tightening column nuts!)
- Use and filter high purity gases

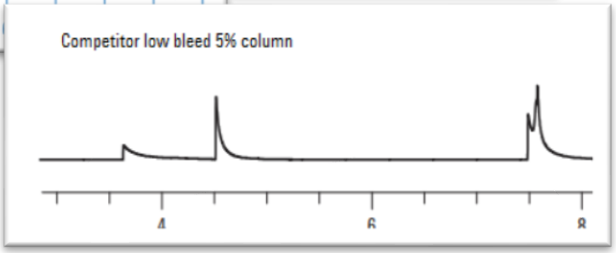
### Semivolatiles by GC/MS



Column: Agilent JW DB-UI 8270D, 20m x 0.18mm x 0.36µm, P/N 121-9723  
Liner: Agilent Ultra Inert single taper with wool, P/N 5190-2293  
For detailed information, see Agilent application note 5991-2745



1. Triethylamine
2. Pyridine
3. 4-Methylpyridine
4. N,N-dimethylacetamide

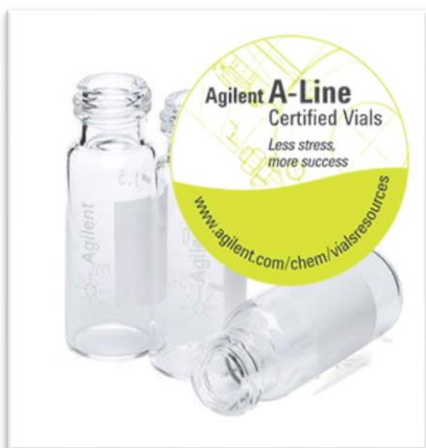
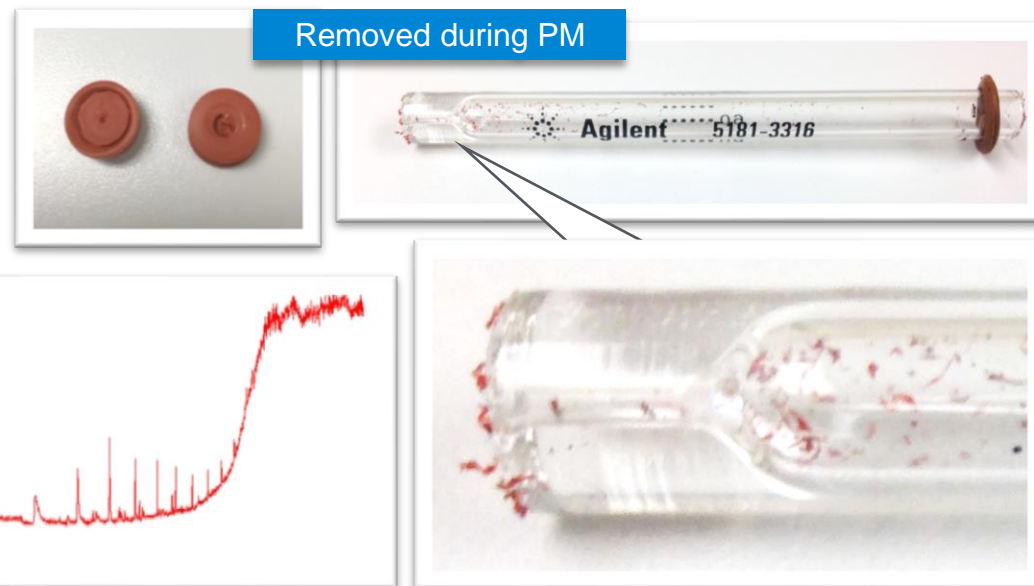




# Improving sensitivity tip #2

## Take care of your consumables

- Don't overtighten your septum nut
  - Compresses septa → chunks in flow path → “bonus” peaks
  - Replace routinely to prevent coring
- Choose high quality vials and caps
  - Poorly constructed vial septa → siloxanes → bleed peaks
  - Low quality vial → leach contaminants into sample
  - Choose the right cap/septa for your solvent



	High performance septa	Thin PTFE	PTFE/Silicone*	PTFE/Silicone/PTFE*	PTFE/Red rubber	Fluoroelastomer	Butyl
Temperature range	40 °C to 300 °C**	Up to 260 °C	-40 °C to 200 °C	-40 °C to 200 °C	-40 °C to 90 °C	-40 °C to 260 °C	-50 °C to 150 °C
Use for multiple injections	No	No	Yes	Yes	No	No	No
Price	More expensive	Very economical	Economical	Most expensive	Very economical	Economical	Economical
Resistance to coring	Excellent	None	Excellent	Excellent	None	None	None
Recommended for storage	No	No	Yes	Yes	No	No	No
Best for	High temperature headspace applications	Superior chemical inertness, short cycle times, and single injections	Most common HPLC and GC analyses, not as resistant to coring as P/S/P	Superior performance for ultra trace analysis, repeat injections, and internal standards	Chlorosilanes, more economical option for single injections	Chlorinated solvents, higher temperatures	Organic solvents, acetic acids, impermeable to gases

\* Agilent silicone is platinum cured (versus peroxide cured), making it more inert and less likely to interact with samples.

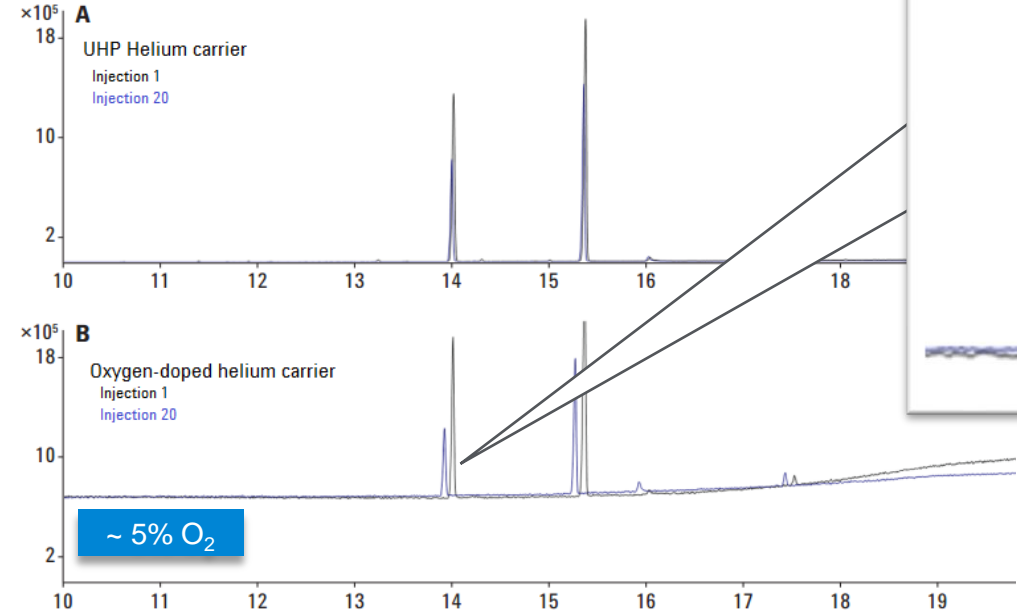
\*\* For up to 1 hour.



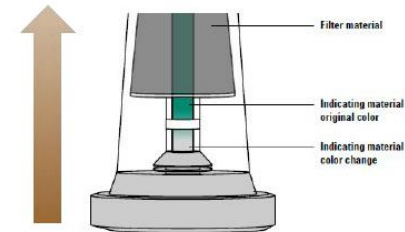
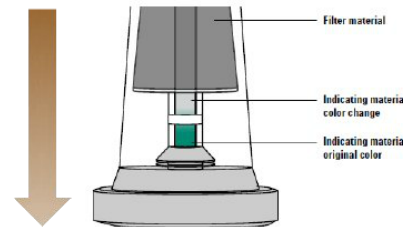
# Improving sensitivity tip #3

## Bad gas stinks

- Oxygen in carrier gas is detrimental to GC, resulting in:
  - 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



**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.



GC/MS filter  
Agilent P/N CP17973



# Improving sensitivity tip #4

## Check yourself before you wreck...your chromatography

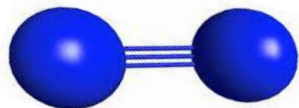
m/z 50

Lowest recommended ion to start a scan range

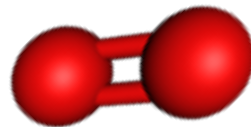
- Scanning masses <50 problematic due to common carrier gas contaminants:



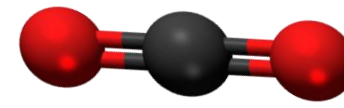
Water,  $m/z$  18



Nitrogen,  $m/z$  28



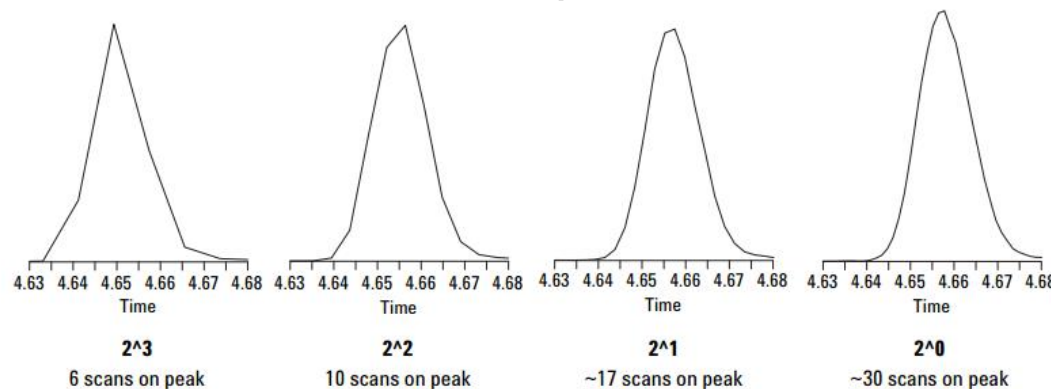
Oxygen,  $m/z$  32



Carbon dioxide,  $m/z$  44

10

Minimum recommended number of points, "scans" across a peak for quant



4

Recommended number of SIM ions searched for a given compound

# Thank you!

## Questions?

# Contact Agilent Chemistries and Supplies Technical Support



1-800-227-9770 Option 3, Option 3:

- Option 1 for GC/GCMS Columns and Supplies
- Option 2 for LC/LCMS Columns and Supplies
- Option 3 for Sample Preparation, Filtration and QuEChERS
- Option 4 for Spectroscopy Supplies



- [gc-column-support@Agilent.com](mailto:gc-column-support@Agilent.com)
- [lc-column-support@agilent.com](mailto:lc-column-support@agilent.com)
- [spp-support@agilent.com](mailto:spp-support@agilent.com)
- [spectro-supplies-support@agilent.com](mailto:spectro-supplies-support@agilent.com)