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EPA Method 8270 with Nitrogen Carrier Gas

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Method 8270 with Nitrogen Carrier Gas

A work in progress

This is progress Report Number 1

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Method 8270 with Nitrogen Carrier Gas

- At this point we are concentrating on 2 items:
  - Chromatographic separation
  - Detection limits

- If we are not able to generate acceptable results in either area, there is no reason to continue the study

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Why Nitrogen?

- **The helium shortage is <u>real</u>**
  - Rationing is already in place
  - High per tank cost
    - As high as $1000 per tank

- **Hydrogen does not work for many 8270 targets**
  - Works well for some neutrals
  - Not so well for acids, bases, other neutrals
  - In-source reactions (e. g. nitrobenzene)
  - High background from contamination

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Results with Hydrogen Carrier

8270 Compounds that work well with H_2 Carrier

1,3-Dichlorobenzene
1,4-Dichlorobenzene
1,2-Dichlorobenzene
Bis(2-Chloroisopropyl) ether
N-Nitrosodi-n-propylamine
1,2,4-Trichlorobenzene
Naphthalene
2-Methlynaphthalene
4-Chloroaniline
2-Chloronaphthalene
Acenaphthene
Dibenzofuran
4-Chlorophenyl phenyl ether
Fluorene
N-Nitrosodiphenylamine
Hexachlorobenzene
Phenanthrene
Anthracene
Fluoranthene
Pyrene
Benzo[a]anthracene
Chrysene
Benzo[b]fluoranthene
Benzo[kfluoranthene
Benzo[a]pyrene

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Results with Hydrogen Carrier

8270 compounds produce poor results with H_2 carrier

N-Nitrosodimethylamine

Phenol

2-Chlorophenol

Benzyl alcohol

3&4-Methylphenol

2-Methylphenol

Hexachloroethane

2,4-Dimethylphenol

Bis(2-chloroethoxy)methane

2,4-Dichlorophenol

Isophorone

Hexachlorobutadiene

4-Chloro-3-methylphenol

Hexachlorocyclopentadiene

2,4,6-Trichlorophenol,

2,4,5-Trichlorophenol,

Indeno[1,2,3-cd]pyrene

Dibenzo(a,h)anthracene

Pentachlorophenol

Carbazole

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Results with Hydrogen Carrier

8270 compounds produce **very** poor results with H_2 carrier

2-Nitrophenol
2-Nitroaniline
Dimethyl phthalate
2,6-Dinitrotoluene
3-Nitroaniline
2,4-Dinitrophenol
4-Nitrophenol
2,4-Dinitrotoluene
Diethyl phthalate
4-Nitroaniline
2-Methyl-4,6-dinitrophenol
Di-n-butyl phthalate
Butylbenzyl phthalate
3,3'-Dichlorobenzidine
Bis(2-ethylhexyl) phthalate
Di-n-octyl phthalate

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Can a GC/MS Pump Nitrogen?

- **Most cannot – Especially older units**
- **Newest instruments can if equipped with the latest pump**
  - Differential pumping helps too
- **Shimadzu GCMS QP-2020NX is equipped to pump nitrogen**
  - **Edwards nEXT-200/200D**
  - Differential pumping

Further noise reduction for H2 and N2 with the new TMP

Dual inlet differential evacuation

+

High efficient TMP

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Shimadzu GCMS QP-2020

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What negative effects did we expect to see?

- **Longer Chromatographic Runs**
  - Van Deemter Plot
- **Reduced sensitivity**
  - Caused by higher source pressure
  - 7X reduction in sensitivity expected
- **Band broadening on lighter compounds caused by low flow through the injection port**

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What positive effects did we expect to see?

- **May be able to use smaller ID columns**
  - Optimum linear velocity increases as column ID decreases
  - Lower flow minimizes effect of nitrogen on sensitivity
- **Less chromatographic impact on active compounds than H_2 carrier**
- **Less impact from contamination than with H_2 carrier**
- **No in-source reactions expected**

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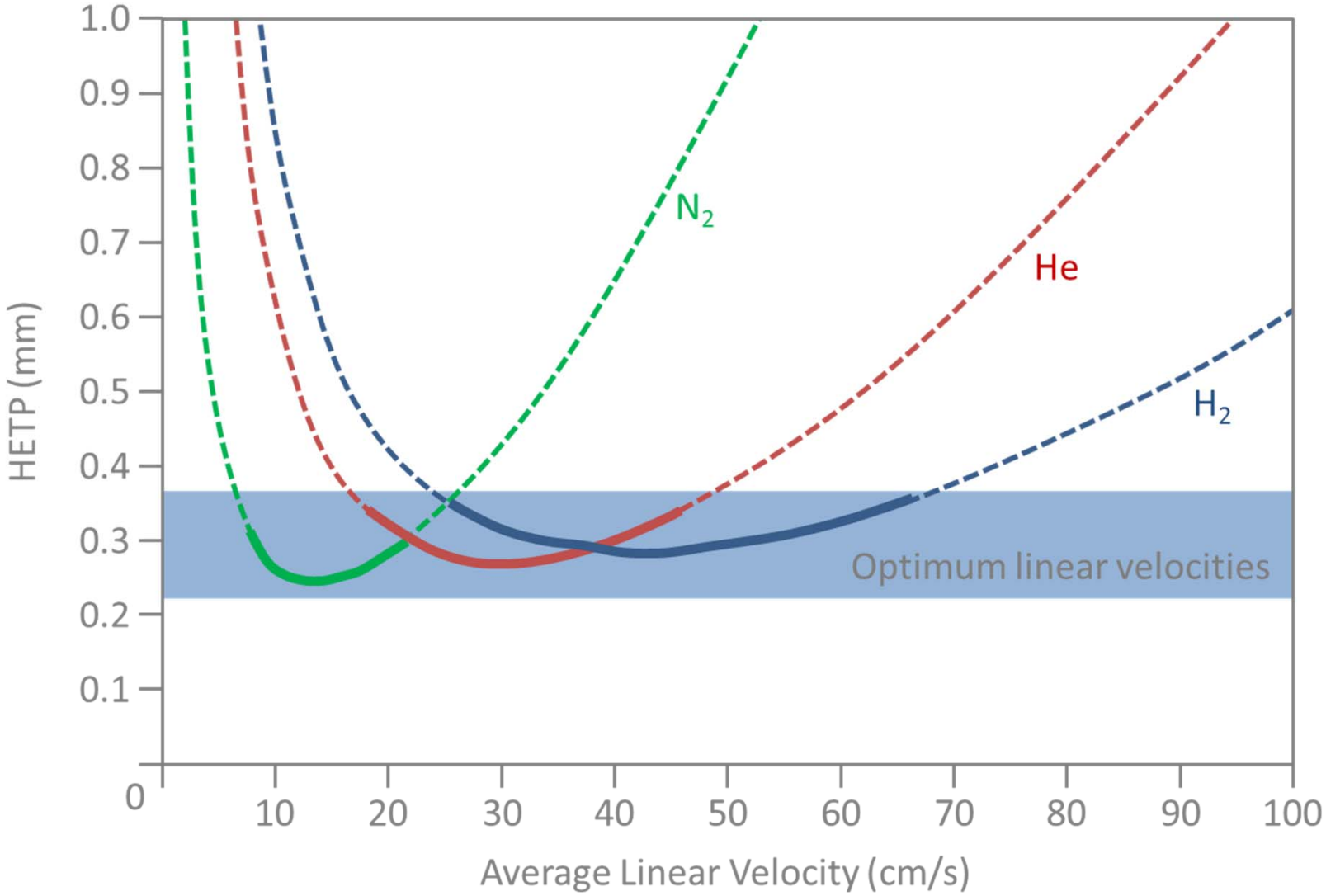
Van Deemter Plot



4) LCGC's CHROMacademy

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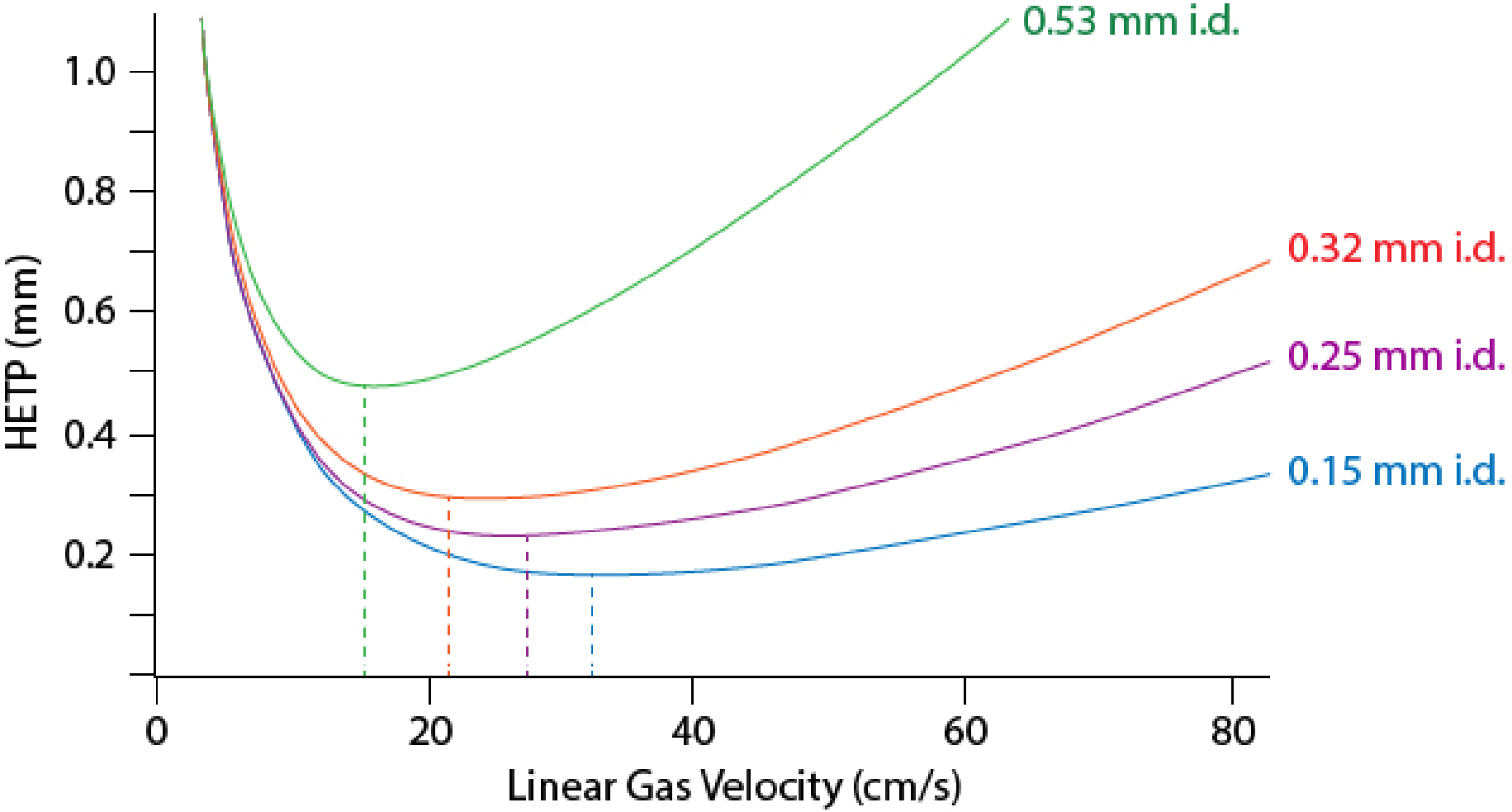
Efficiency Dependence on Column ID



4) LCGC's CHROMacademy

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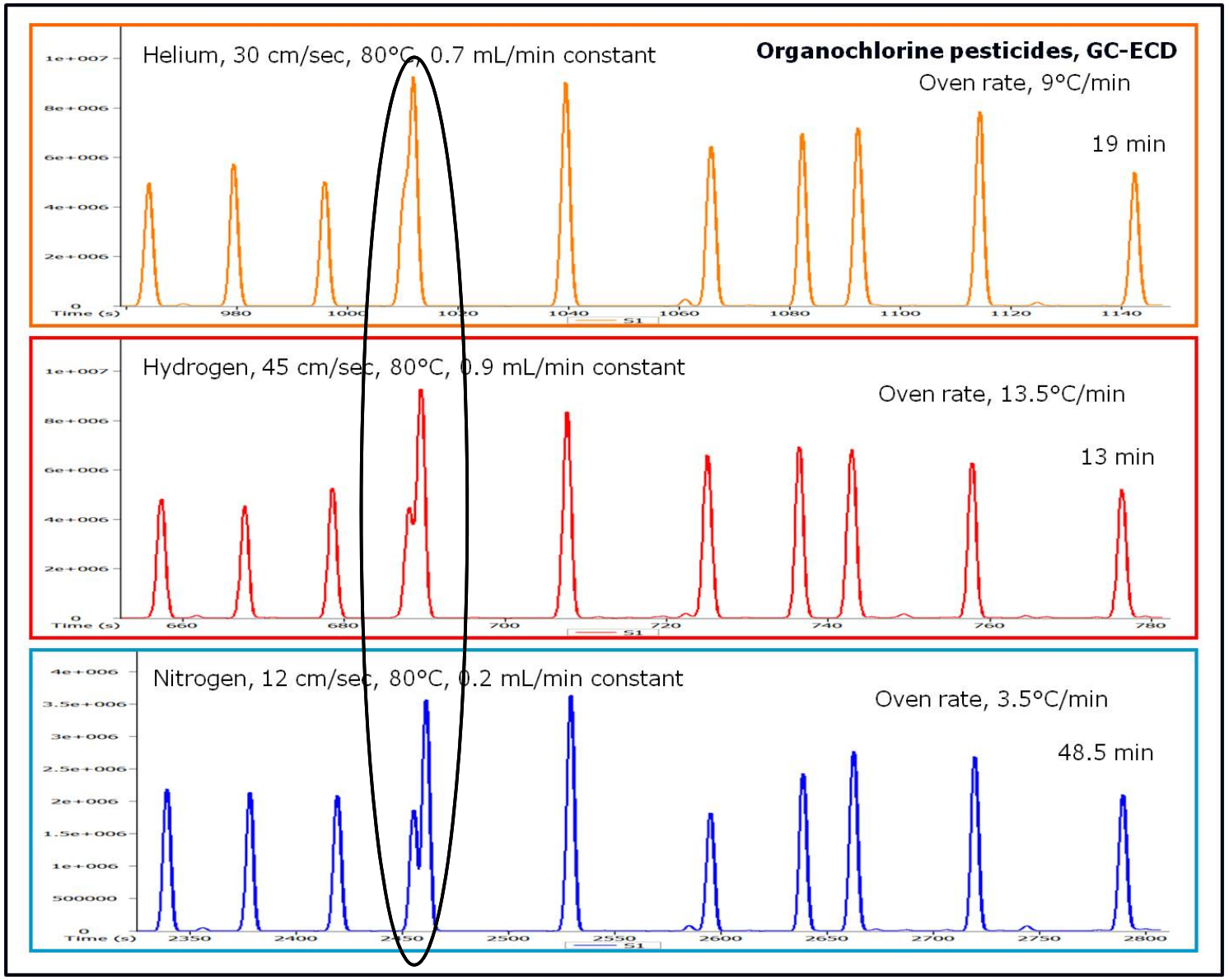
OC Pesticides with different carrier gasses



3) Restek

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Plan of Action

- **Goal: Minimize nitrogen in the source**
  - Helps reduce loss of sensitivity
  - Minimize linear velocity
    - Improves the position on the efficiency curve

- **Minimize nitrogen presence in the manifold**
  - Narrow bore columns
  - Lower linear velocities

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Columns

- **Narrow bore columns**
  - 0.18 mm ID Column
    - 20M, 0.18 mm ID Rxi-5ms, 0.18 µM film
  - 0.15 mm ID column
    - 20M, 0.15 mm ID SH- Rxi-5ms, 0.15 µM film
- **Low flow through IP causes band broadening**
    - Liner volume is ~870 uL
    - At 0.3 mL/Min that is an issue
    - Did not try low volume liner
      - Concerns about vaporization volume / flashover

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Flow through the Injection Port

- **High pressure injection**
  - Works, but has disadvantages
  - Time
  - Leaks

- **High split ratio / larger injection volume**
  - On a 20M, 0.15 mm ID column flow is 0.33 mL/min @60°C and 27 cm/sec
  - Used large volume injection
  - Seems to work the best
  - Can be used in combination with high pressure if necessary

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Surprises

- **Chromatography best at higher than typical linear velocity**
  - Most labs run helium at 35-45 cm/sec
  - Helium - 60 cm/sec on 0.18 mm ID Columns
  - Nitrogen - 45 cm/sec on 0.18 mm ID Columns

- **Temperature program is critical to PNA peak shape**
  - Run too high and you loose separation on the isobars – we all know that
  - Programming too fast is also a problem – we know that too
  - These effects are MUCH more pronounced with nitrogen – did not expect that

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Work with 0.18 mm ID column

- **Bottom line: Did not work well.**
  - PNA peak shapes were problematic at low linear velocity
  - Was not able to compensate with temperature
  - Tried various injection techniques and liner types
- **Tried higher linear velocity**
  - Peak shape improved
  - Separation on the last few PNAs was not good enough
  - Signal was significantly attenuated on the late eluting PNAs
  - Signal was attenuated on the rest of the compounds too
  - Manifold pressure was well within specs ~6.5 x 10^{-6} Torr, but still high compared to helium (typically ~ 8x10^{-7} Torr @ 1 mL/min) on that instrument

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MS Conditions for 0.18 mm Columns with Helium Carrier

GCMS-QP Series

Ion Source Temp. : 200 ℃

Interface Temp. : 280 ℃

Solvent Cut Time : 1.45 min

Detector Voltage : (•) Relative to the Tuning Result ( ) Absolute

Micro Scan Width : 0 u

0.1 kV

[ ] Use MS Program : Set...

Threshold : 100

Group#1 - Event#1

GC Program Time : 22.75 min

	Start Time (min)	End Time (min)	Acq. Mode	Event Time(sec)	Scan Speed	Start m/z	End m/z	Ch1 m/z	Ch2 m/z	C m
1	1.50	22.75	Scan	0.15	3333	35.00	500.00			
2	0.00	0.00	Scan	0.00	0	0.00	0.00			

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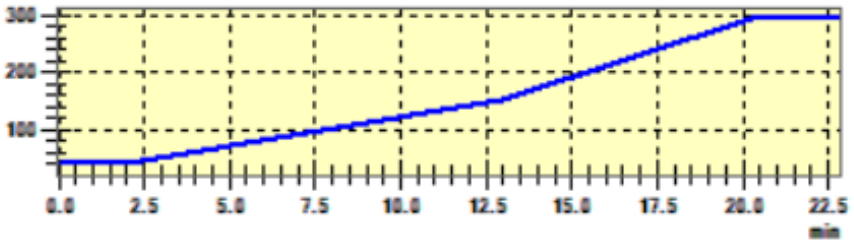
GC Conditions for 0.18 mm Columns with Helium Carrier

Inj. Port : SPL1 Inj. Heat Port : INJ1

Column Oven Temp. :	40.0	°C
Injection Temp. :	270.0	°C
Injection Mode :	Split	
Sampling Time :	1.00	min



Carrier Gas : He Prim. Press. : 500-900

Flow Control Mode :	Linear Velocity	
Pressure :	221.4	kPa
Total Flow :	20.8	mL/min
Column Flow :	1.84	mL/min
Linear Velocity :	60.0	cm/sec
Purge Flow :	0.5	mL/min
Split Ratio :	10.0	

Program : Column Oven Temperature

	Rate	Final Temperature	Hold Time
0	-	40.0	2.00
1	10.00	150.0	0.00
2	20.00	295.0	2.50
3	0.00	0.0	0.00

Total Program Time : 22.75 min

Column

Name Rxi5MS Thickness : 0.18 um

Length : 20.0 m Diameter : 0.18 mm

Set...

Detail of Injection Port...

Ready Check...

High Press. Injection Carrier Gas Saver

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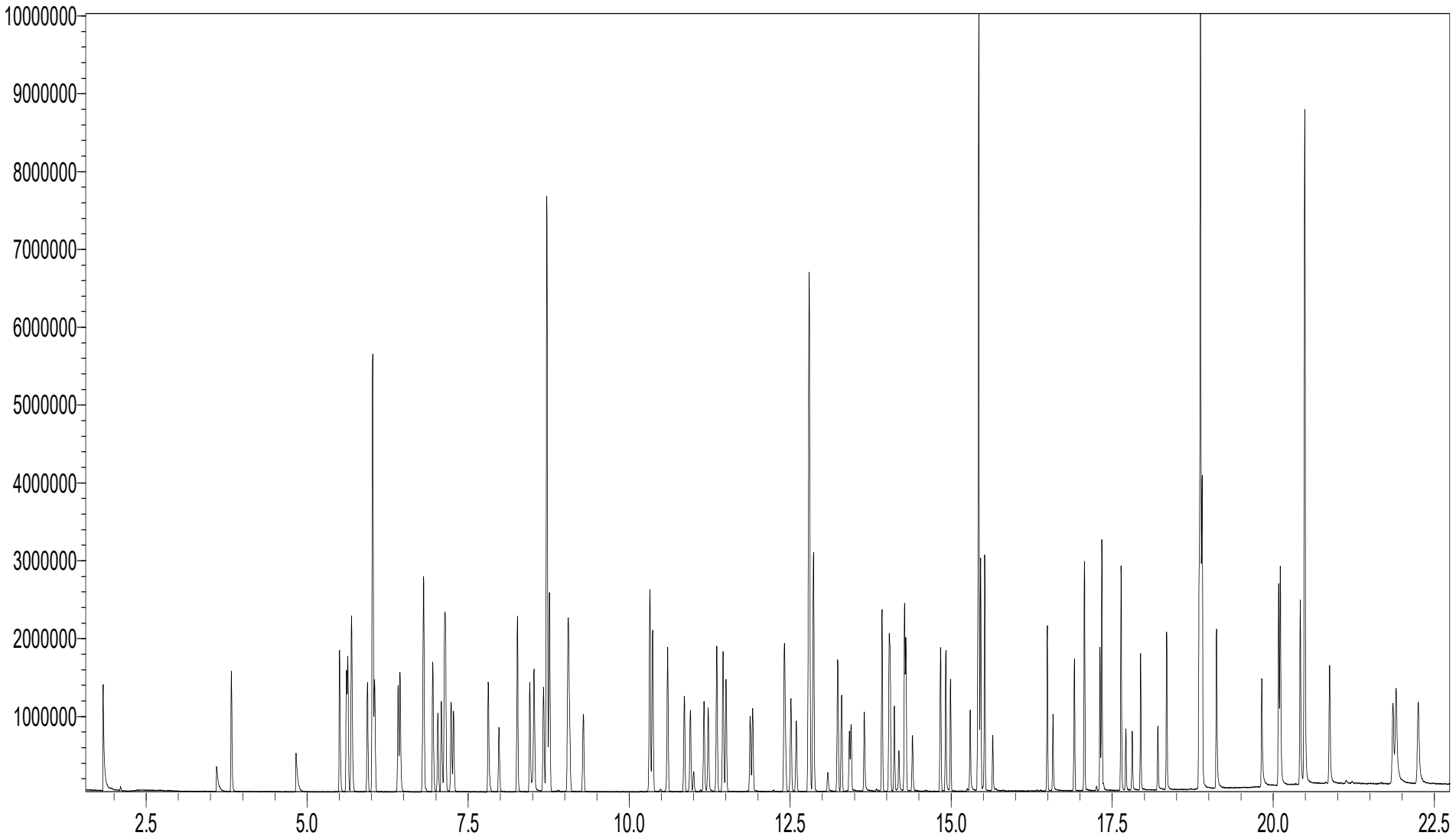
Chromatogram of a Standard with He Carrier



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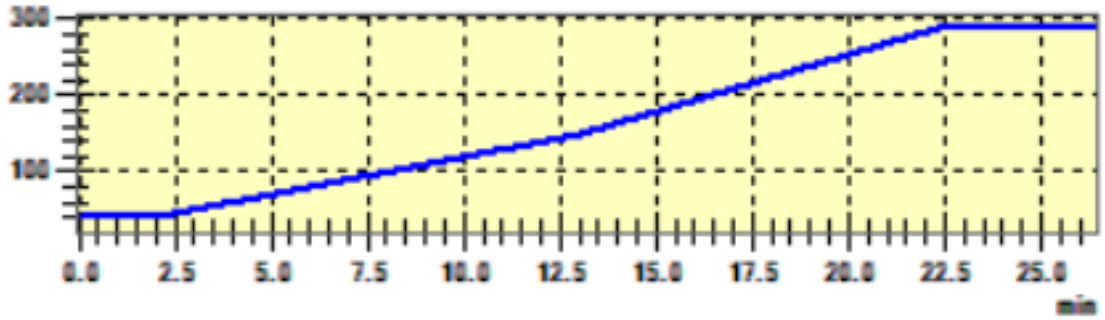
GC Conditions for 0.18 mm Columns with N2 Carrier

Column Oven Temp. :	40.0	℃
Injection Temp. :	270.0	℃
Injection Mode :	Split	
Sampling Time :	1.00	min

Carrier Gas : N2/Air Prim. Press. : 500-900

Flow Control Mode :	Linear Velocity	
Pressure :	117.4	kPa
Total Flow :	10.8	mL/min
Column Flow :	0.94	mL/min
Linear Velocity :	45.0	cm/sec
Purge Flow :	0.5	mL/min
Split Ratio :	10.0	



Program : Column Oven Temperature

	Rate	Final Temperature	Hold Time
0	-	40.0	2.00
1	10.00	150.0	0.00
2	15.00	290.0	4.00
3	0.00	0.0	0.00

Total Program Time : 26.33 min

Column

Name Rxi5MS Thickness : 0.18 um

Length : 20.0 m Diameter : 0.18 mm

Set...

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MS Conditions for 0.18 mm Columns with N2 Carrier

GCMS-QP Series

Ion Source Temp. : 230 ℃

Interface Temp. : 280 ℃

Solvent Cut Time : 2.15 min

Micro Scan Width : 0 u

Detector Voltage : (•) Relative to the Tuning Result ( ) Absolute

0.05 kV

☑ Use MS Program : Set...

Threshold : 700

Group#1 - Event#1

GC Program Time : 26.33 min

	Start Time (min)	End Time (min)	Acq. Mode	Event Time(sec)	Scan Speed	Start m/z	End m/z	Ch1 m/z	Ch2 m/z	
1	2.20	26.33	Scan	0.15	3333	35.00	500.00			
2	0.00	0.00	Scan	0.00	0	0.00	0.00			

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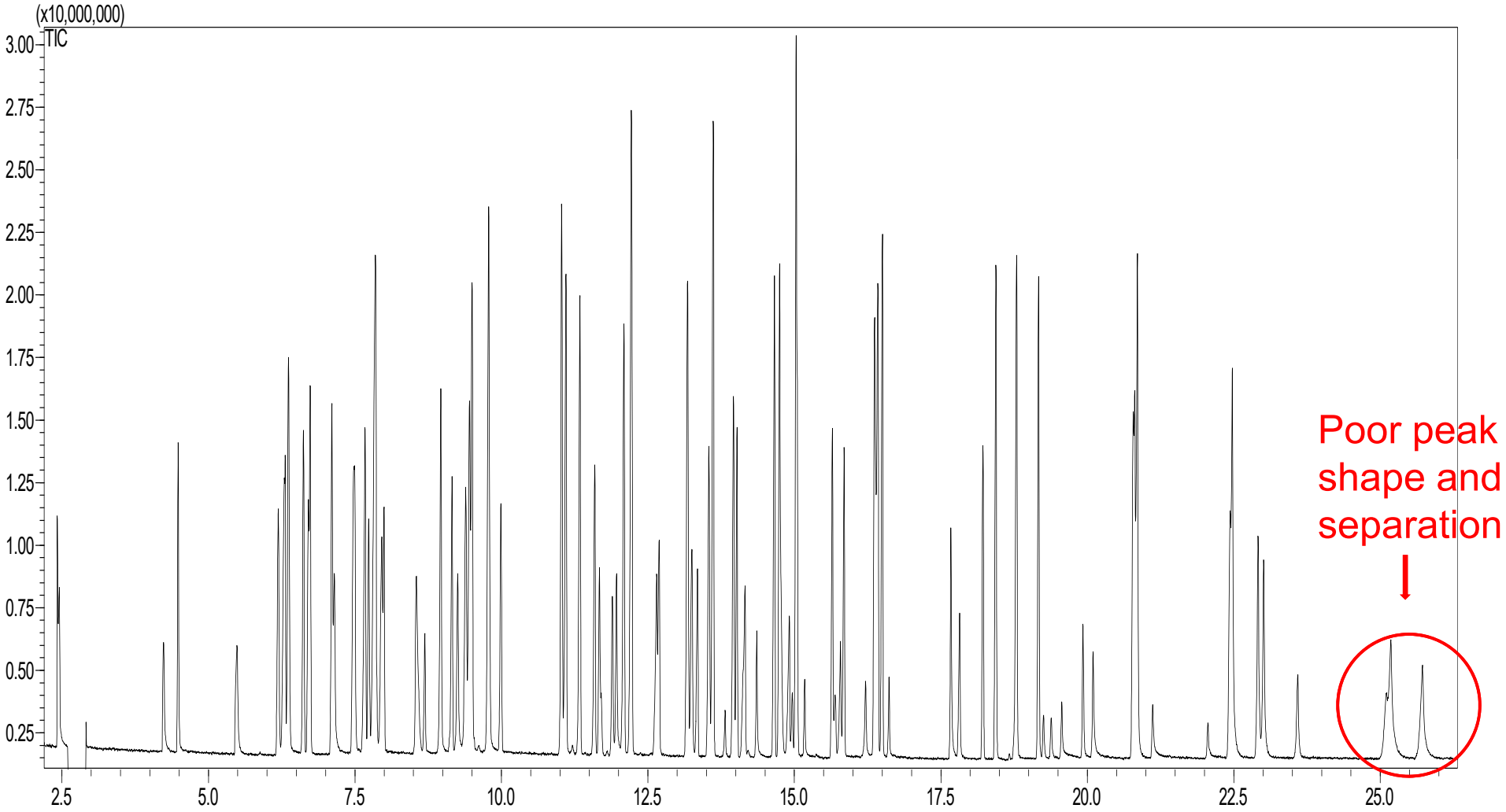
Chromatogram of a Standard with N_2 Carrier on a 0.18 mm ID column



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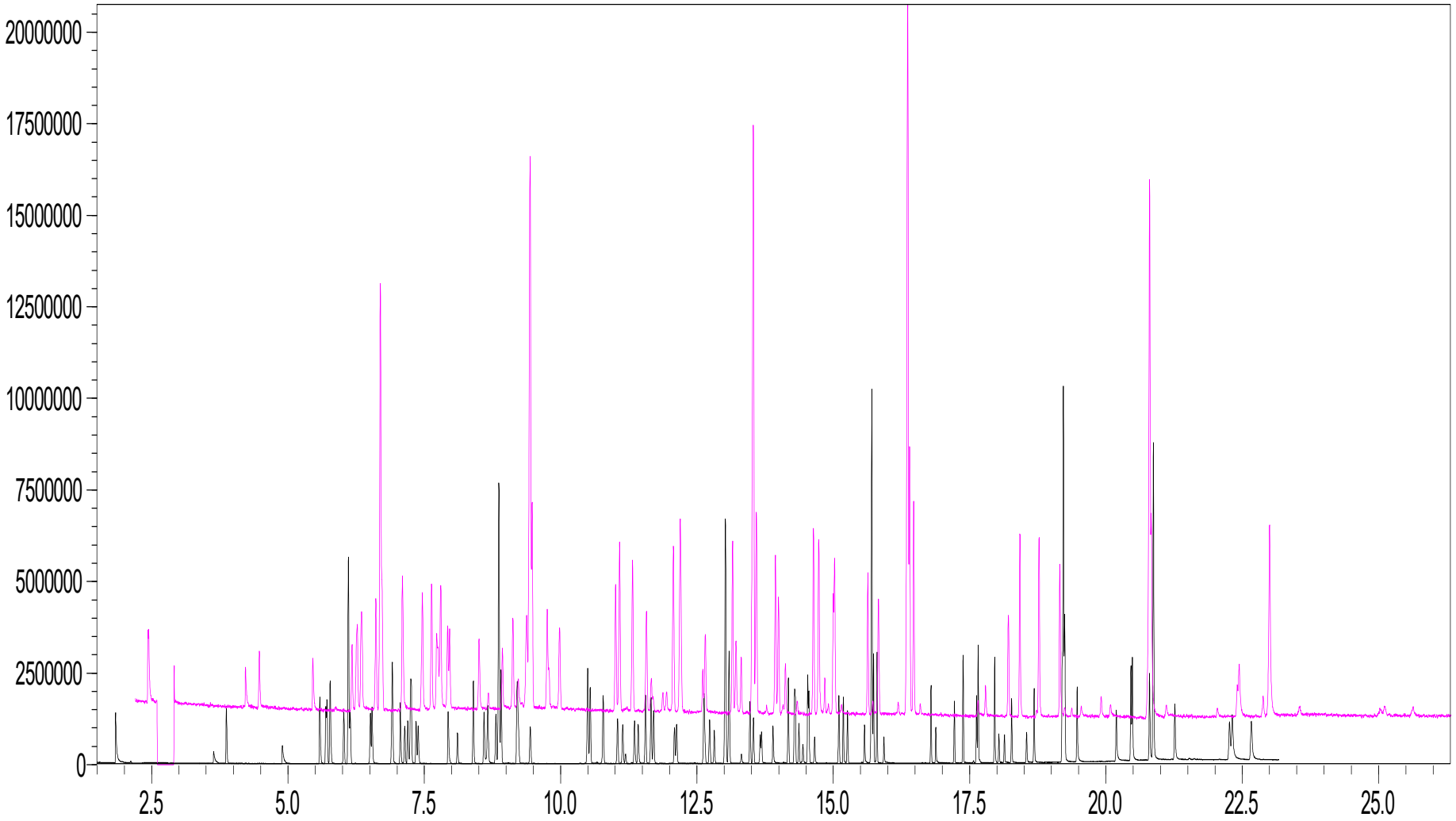
Overlay Chromatogram 0.18 mm ID
He Carrier (black) and N_2 Carrier (pink)



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Work with 0.15 mm ID column

- **Chromatography was easier to control**
  - Linear velocity of 27 cm/sec worked well
    - Manifold pressure ~1.5 x 10^{-6} Torr
  - PNA peak shapes looked better
  - Was able to compensate for flow with temperature
  - Tried various injection techniques and liner types
    - Large volume split injections with a **Restek** SkyBlue split liner worked well
    - Finally settled on a 4 µL injection with a 10:1 split

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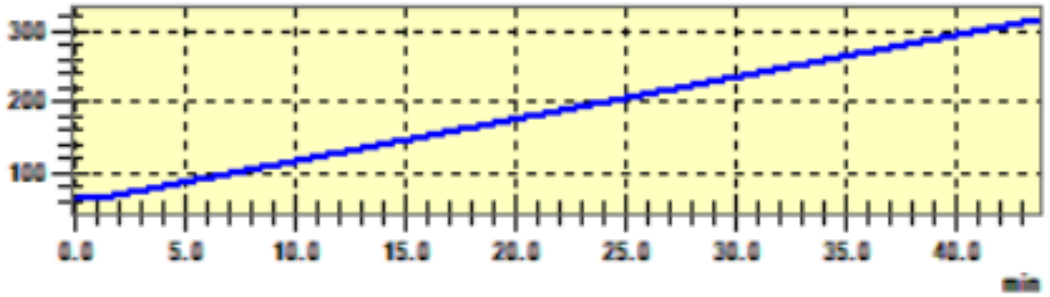
GC Conditions 0.15 mm ID Column

Column Oven Temp. :	62.0	℃
Injection Temp. :	270.0	℃
Injection Mode :	Split	
Sampling Time :	1.00	min

Carrier Gas : N2/Air Prim. Press. : 500-900

Flow Control Mode :	Linear Velocity	
Pressure :	97.7	kPa
Total Flow :	4.2	mL/min
Column Flow :	0.33	mL/min
Linear Velocity :	27.0	cm/sec
Purge Flow :	0.5	mL/min
Split Ratio :	10.0	



Program : Column Oven Temperature

	Rate	Final Temperature	Hold Time
0	-	62.0	1.00
1	6.00	318.0	0.00
2	0.00	0.0	0.00
3	0.00	0.0	0.00

Total Program Time : 43.67 min

Column

Name SHRxi-5Sil MS Thickness : 0.15 um

Length : 20.0 m Diameter : 0.15 mm

Set...

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MS Conditions 0.15 mm ID Column

Ion Source Temp. :	200	℃		
Interface Temp. :	280	℃		
Solvent Cut Time :	2.25	min	Detector Voltage :	Relative to the Tuning Resu
Micro Scan Width :	0	u	0.2	kV
Use MS Program :	Set...		Threshold :	700

Group#1 - Event#1

GC Program Time : 43.67 min

	Start Time (min)	End Time (min)	Acq. Mode	Event Time(sec)	Scan Speed	Start m/z	End m/z
1	2.30	43.66	Scan	0.15	3333	35.00	500.00
2	0.00	0.00	Scan	0.00	0	0.00	0.00

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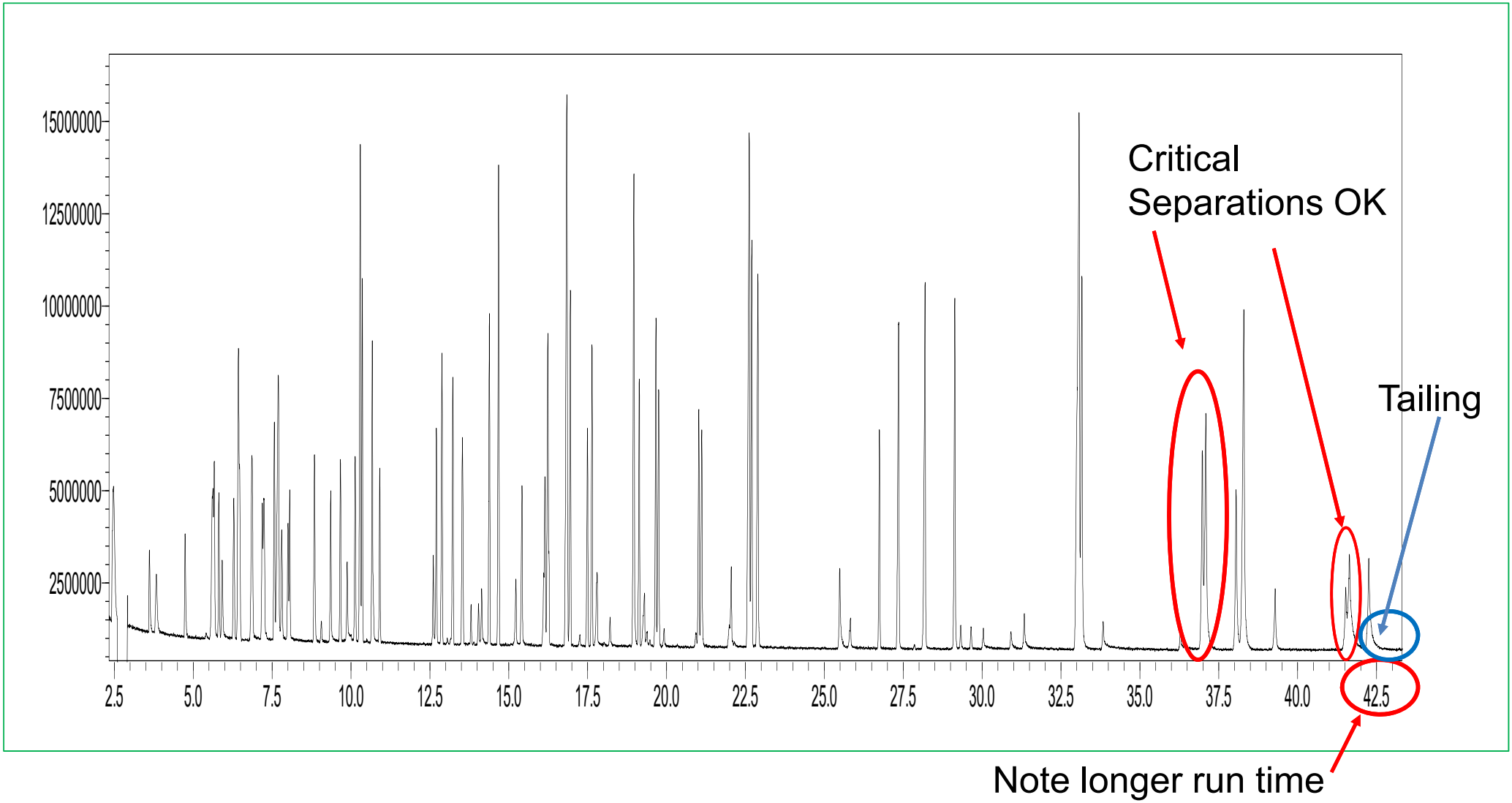
Chromatogram 0.15 mm ID with N_2 Carrier



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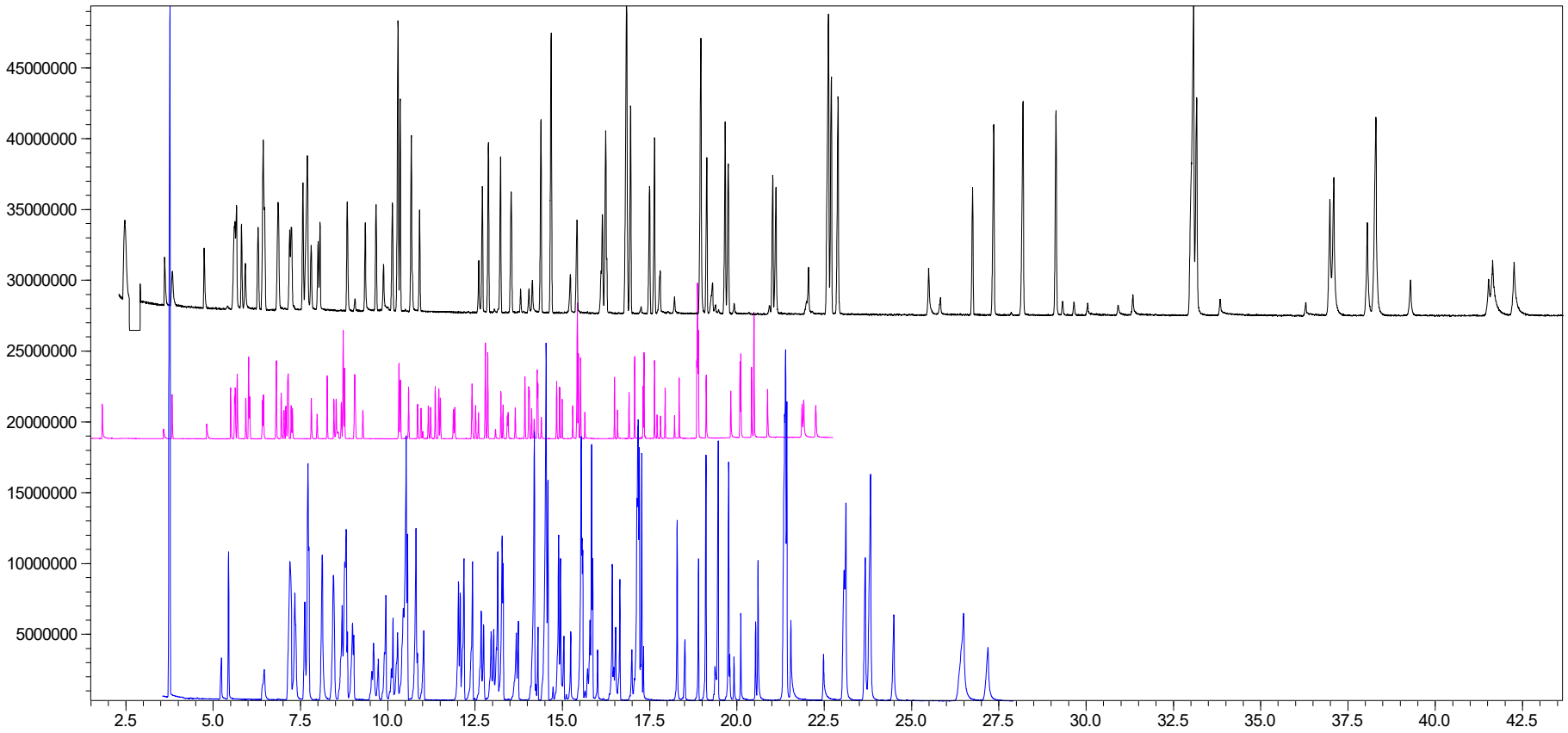
Chromatograms

Black: Nitrogen on a 0.15 mm column

Pink: Helium on a 0.18 mm column

Blue: Nitrogen on a 0.18 mm column



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Average IDLs on the 3 columns

Helium on the 0.18 mm ID column	0.096ng/µL
Nitrogen on the 0.18 mm ID column	0.555ng/µL
Nitrogen on the 0.15 mm ID column	0.331ng/µL

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Other Issues We Encountered

- **Linearity**
  - We were trying to run from 0.5 ng/µl to 100 ng/µl. Across that range many of the calibration curves were quadratic. That may not be the case over a smaller range (e.g. 20ng to160ng)
- **Minimum RF**
  - We failed to meet minimum RF criteria on half of the compounds that had defined limits. That may be a result of attempting to minimize detection limit.
- **Tuning**
  - Factory tuning algorithms for tuning with N_2 carrier are not as well developed as for helium. Manual intervention helped.
  - Were able to meet Method 8270D requirements with a little manual intervention, but not the older Method 625 criteria

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Tuning – Method 8270D criteria

DFTPP KEY IONS AND ION ABUNDANCE CRITERIA
Mass Ion Abundance Criteria

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68	<2% of *m/z* 69
69	Present
70	<2% of *m/z* 69
197	<2% of *m/z* 198
198	Base peak or present
199	5-9% of *m/z* 198
365	>1% of Base Peak
441	<150% of *m/z* 443
442	Base peak or present
443	15-24% of *m/z* 442

We were able to meet these criteria with little trouble. On some days, a little manual intervention was necessary.

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Conclusions

1. It seems that use of Nitrogen carrier is a viable option for the solid waste methods.
2. N_2 certainly works better than hydrogen for the “difficult” compounds
3. Detection limits and other results are encouraging
4. BUT… N_2 carrier unlikely to produce results equal to helium carrier
5. More work needs to be done
6. A work in progress

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Future Work

- **Linearity**
  - Even though the trend is toward lower detection limits, often detection limits are not an issue in the solid waste community.
  - Calibration curves will be analyzed over the narrow range typical of some solid waste labs.
- **Minimum RF**
  - A more concerning issue, but still one that may be alleviated by running higher level standards
  - Try columns with a higher phase ratio.
  - Also, try columns from different manufacturers
  - Try different liner geometries

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Future Work

- **Run time**
  - It would be advantageous to work on shortening the run time, but not at the cost of decreased sensitivity
- **Tuning**
  - This is probably a matter of practice in the short term
  - Waiting for the engineers to improve the tuning algorithms in the long term.
- **Robustness**
  - Trying the system with actual extracts
  - Will it work in a “real world” lab?

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Future Conversations

- **Has Method 8270 as we know it, reached an end point?**
- **Should it be broken up?**
  - "Easy" compounds to H_2 carrier.
  - Others to different techniques
- **Should we go to GC/MS/MS for some parts?**
  - MRM databases are ready now.
- **Should we go to LC/MS/MS for other parts?**
  - The "difficult" GC compounds are mostly acids and bases
  - Many (most?) should light-up with ESI or ACPI

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References

1) **"Evaluation of Hydrogen as a Carrier Gas for Gas Chromatography / Mass Spectrometry"**
   Shimadzu Application News No. SSI-GCMS-1303 February 2013

2) **EPA Method 8270D Analysis Using Narrow-bore GC Columns and Fast Data Acquisition with a Quadrupole GCMS System**
   Richard Whitney, Ph.D. GC/GCMS Senior Product Specialist; Zhuangzhi "Max" Wang, Ph.D. GC/GCMS Product Specialist; Clifford M. Taylor, GC/GCMS Product Manager; Shimadzu Scientific Instruments, Columbia, MD, USA

3) **Nitrogen Carrier Gas for GC – Is it Feasible? – Is it Practical?**
   Restek Chromablography, Jack Cochran, 2012

4) **Nitrogen as a Carrier Gas for Capillary GC**
   LC/GC's CHROMacademy

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References

5) **"Is Hydrogen the Best Carrier Gas for GC?"**
   5) LC/GC's CHROMacademy, Dawn Watson

6) **SW-846 Test Method 8270D: Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry**

7) **Changing from Helium to Nitrogen and Maintaining the Separation Efficiency in the Same Analysis Time**
   Jaap de Zeeuw[1] and Jack Cochran,[21]Restek Corporation, Middelburg, The Netherlands and [2]Restek Corporation, Bellefonte, US

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Questions?

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