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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 2

In January, when we submitted the abstract, we were hoping this work would result in a presentation that could be considered “method ready”, or nearly “method ready”, but COVID-19 changed our plans, as it did for so many people.

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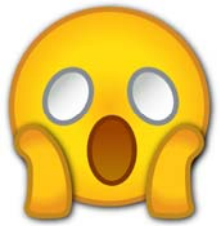
Why Nitrogen?

- **The helium shortage is real**
  - 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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Conclusions from Previous Work

- It seems that use of Nitrogen carrier may be a viable option for the solid waste methods.
- N2 seems to works better than hydrogen for the “difficult” compounds
- Detection limits and other results are encouraging
- BUT… N2 carrier unlikely to produce results equal to helium carrier

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Shimadzu GCMS-QP2020

All analyses were performed on a Shimadzu GCMS-QP2020

The Shimadzu GCMS-QP2020 is a research grade, state-of-the-art, differentially pumped, EI/CI/NCI single quadrupole GC/MS

Typical Manifold Vacuum

1 mL/Min helium: ~7E-7 torr

0.4 mL/min nitrogen: ~4E-6 torr

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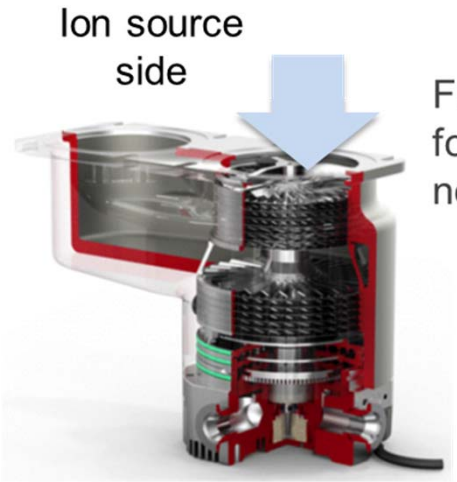
Can a GC/MS Pump Nitrogen?

- Most cannot – Especially older units
- Newest instruments can if equipped with the latest pump
- Shimadzu GCMS-QP2020 NX and GCMS-QP2020 are equipped to pump nitrogen
  - **Edwards nEXT-200/200D**
  - Differential pumping
  - Special Tune Needed



Further noise reduction for H2 and N2 with the new TMP

Dual inlet differential evacuation

+

High efficient TMP

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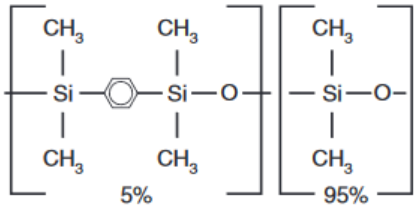
What have we tried to date?

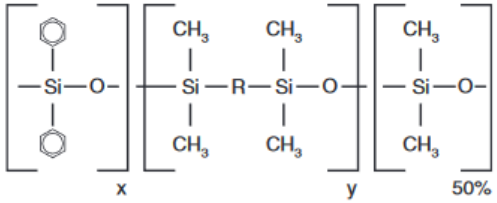
- Two column diameters
  - 20 m, 0.18 mm ID (Rxi-5Sil MS only)
  - 20 m, 0.15 mm ID

- Two stationary phases
  - Rxi-5Sil MS
  - Rxi-17Sil MS

Rxi®-5Sil MS Structure



Rxi®-17Sil MS Structure



Structures: https://www.restek.com/pdfs/GNSS2180-UNV.pdf

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What negative effects did we expect to see?

Using Nitrogen, we expected:

- 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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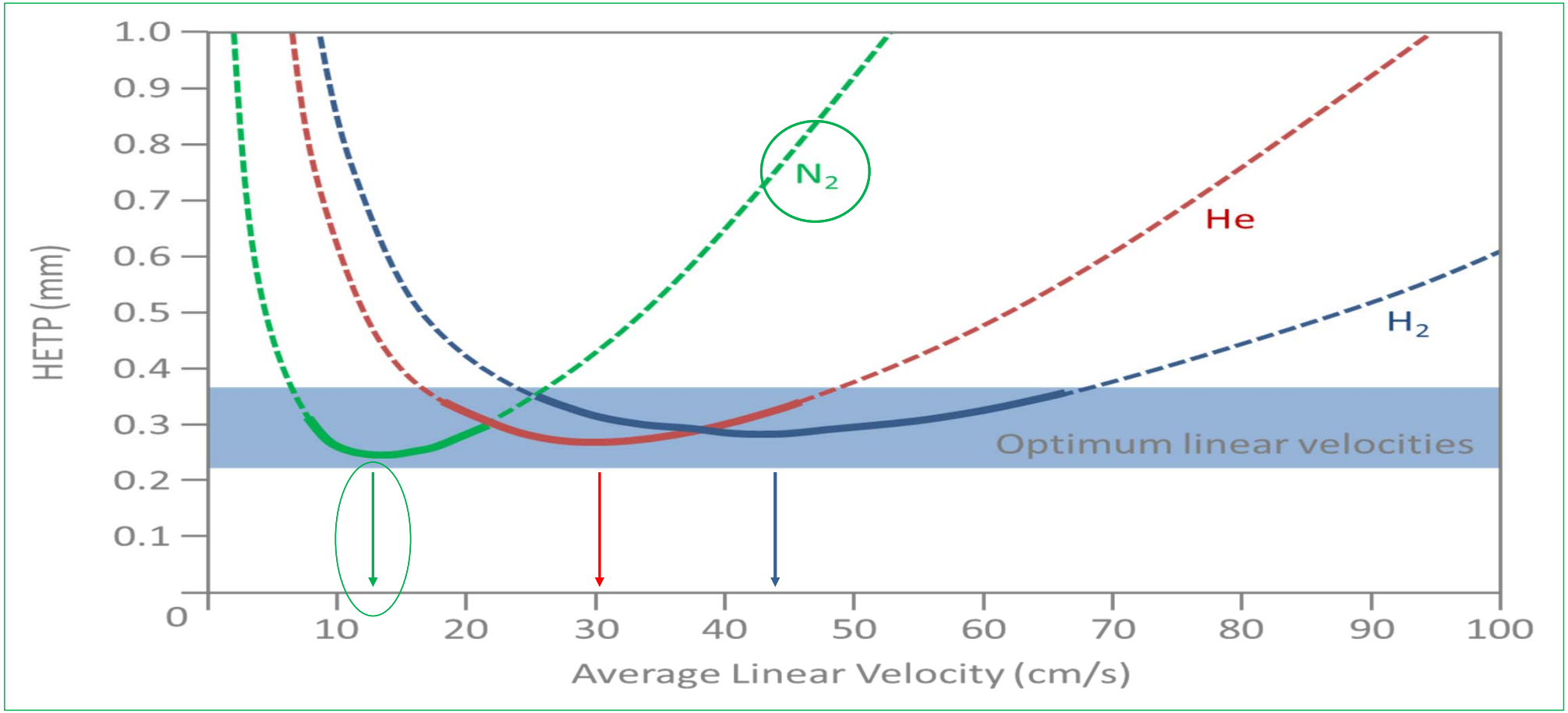
Van Deemter Plot



Reference 4: LCGC's CHROMacademy

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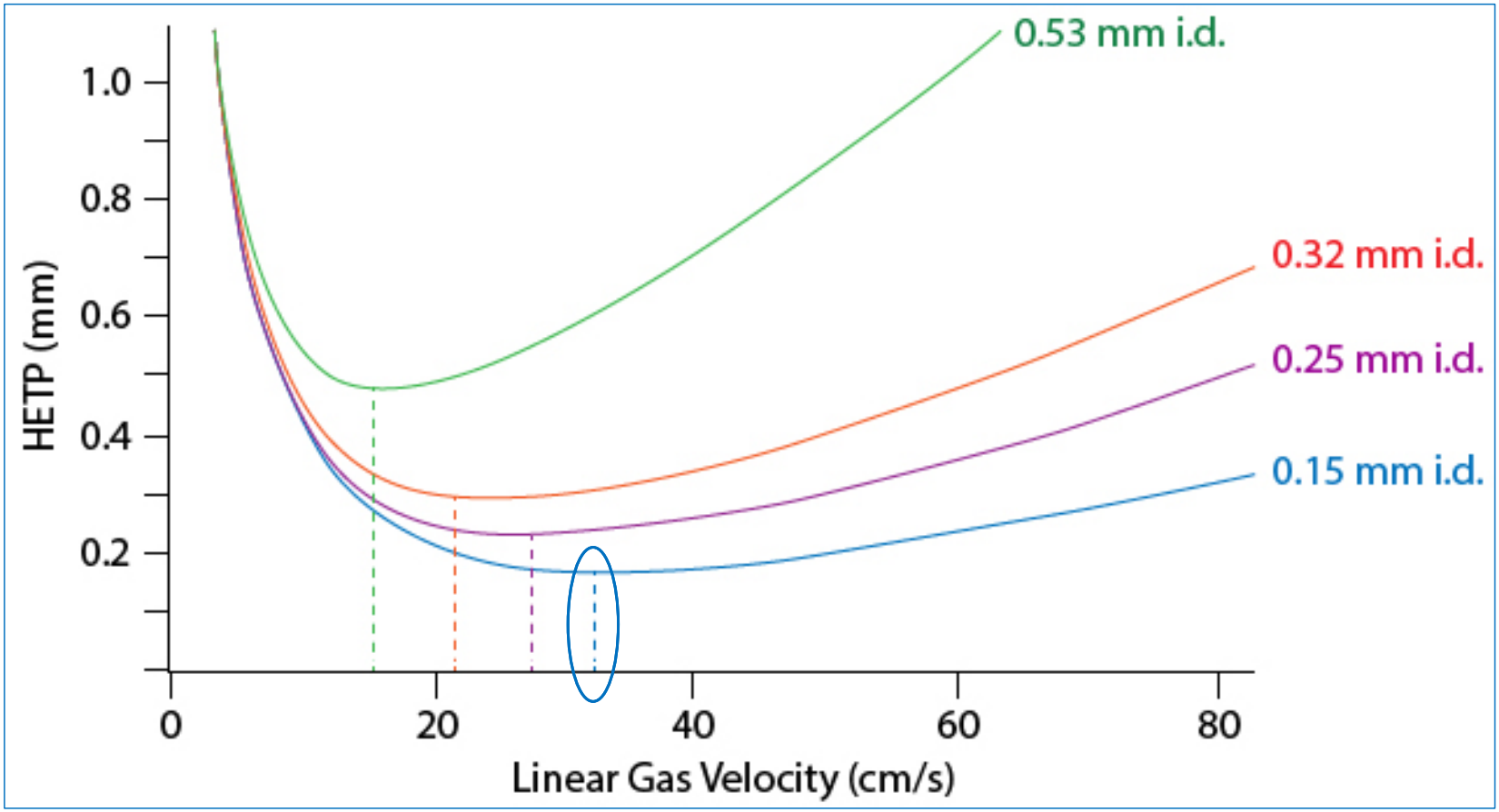
Efficiency Dependence on Column ID



Reference 4: LCGC's CHROMacademy

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Work with 0.18 mm ID column

- Bottom line: 0.18 mm columns 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

Work with 0.18 mm ID columns was abandoned

- Began working with 0.15 mm ID columns

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What positive effects did we see?

- We got better results with 0.15 mm ID columns
  - Optimum linear velocity *increases* as column ID decreases
  - We were able to operate closer to the optimum linear velocity for 0.15 mm ID columns
  - Lower flow minimizes effect of nitrogen on sensitivity
- We saw no chromatographic impact on active compounds
- There were no in-source reactions

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Unexpected Results

- Attenuation of the late eluting PNAs
  - Extreme on the Rxi-5Sil MS Column
  - Much less extreme on the Rxi-17Sil MS column
- High m/z 42 background
  - High enough to have an effect on library search results for low responders
  - Not present when using helium
  - Seems to be uniform throughout the chromatogram
  - Carrier was double filtered UHP N_2 Contamination is unlikely.
  - Appears to be a result of an in-source reaction involving the carrier
    - Cyanamide, Diazomethane
- Scanning from m/z 45 results in a much lower background

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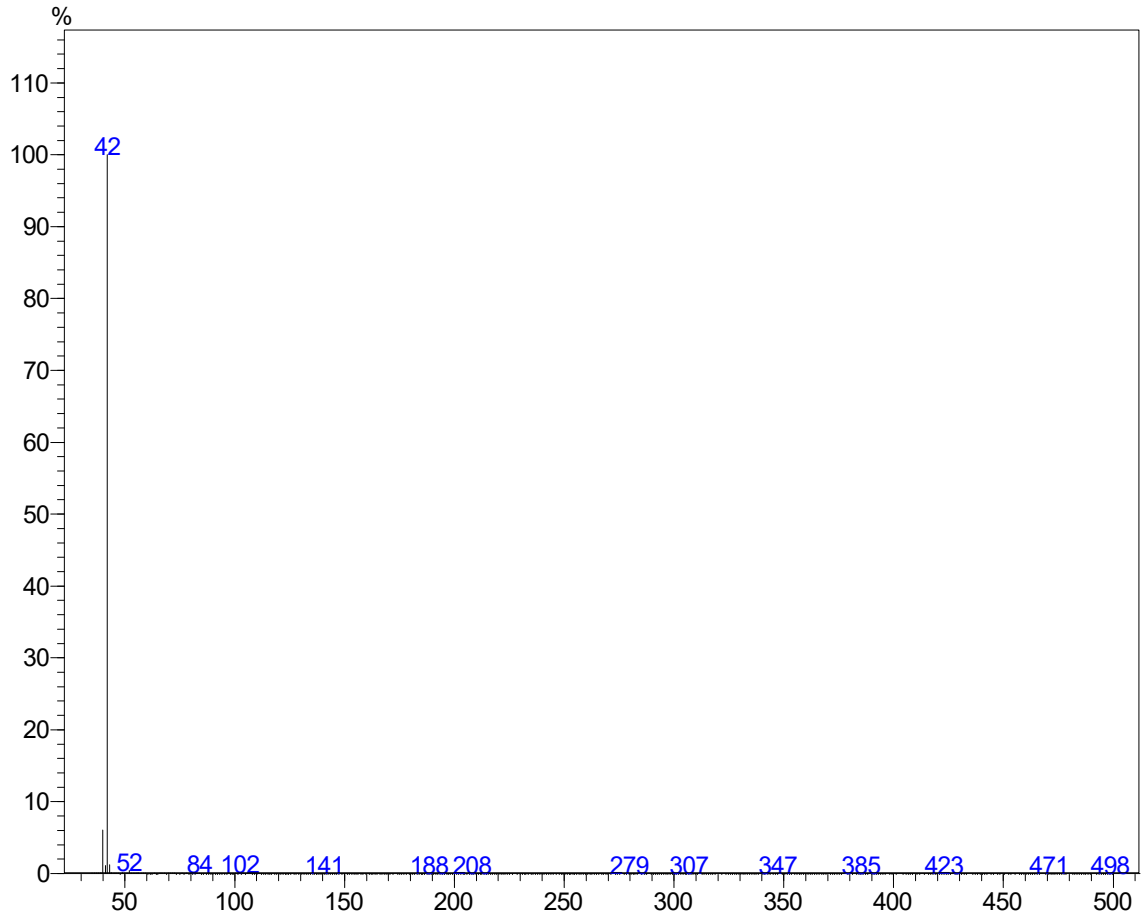
MS Background



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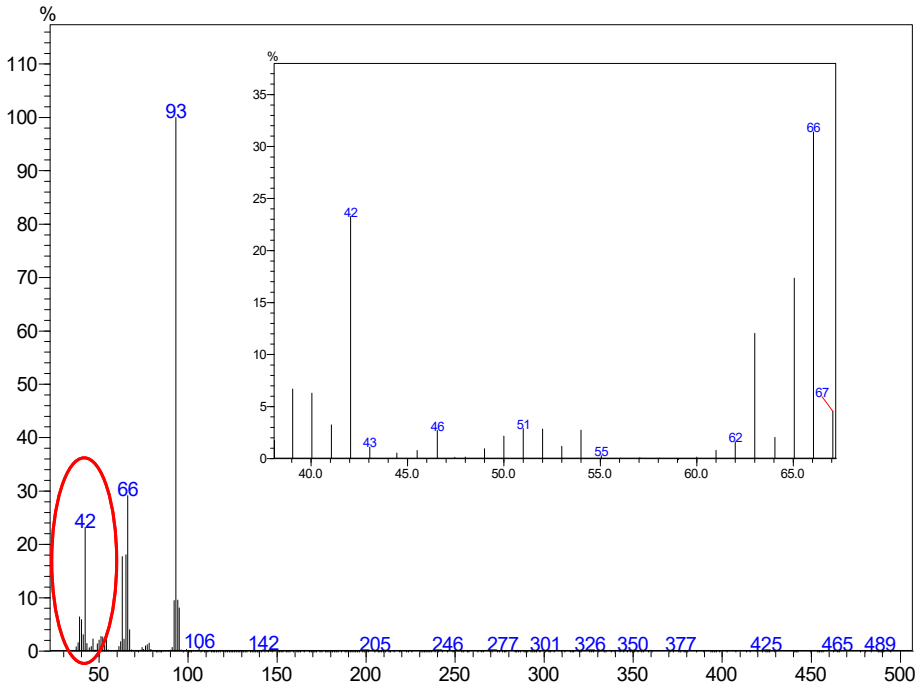
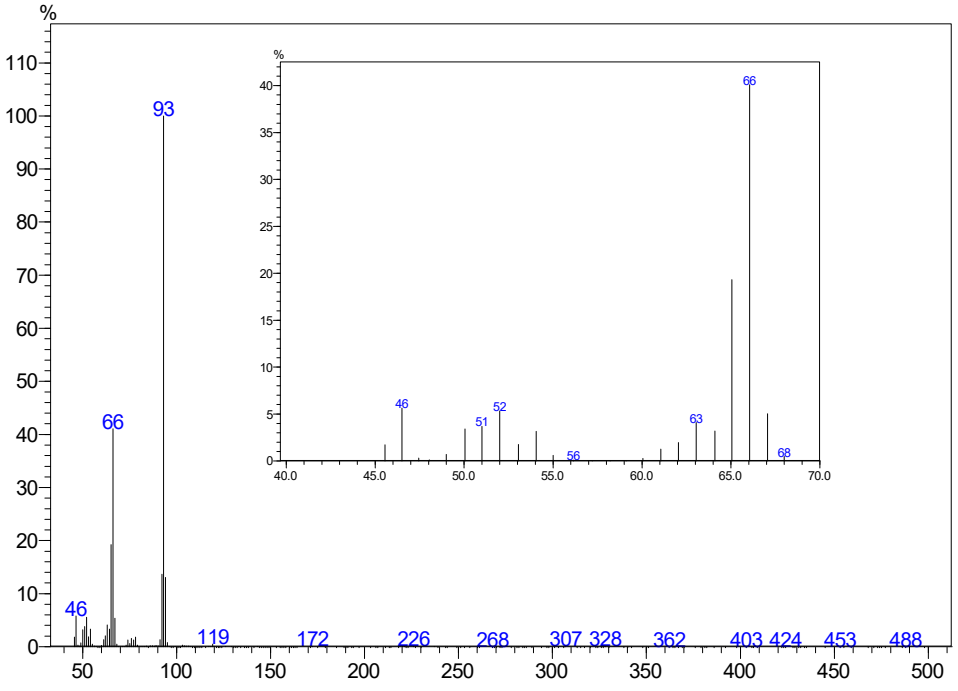
MS Background



Un-Subtracted Spectrum of Aniline Scanning 35-500 AMU



Un-Subtracted Spectrum of Aniline Scanning 45-500 AMU

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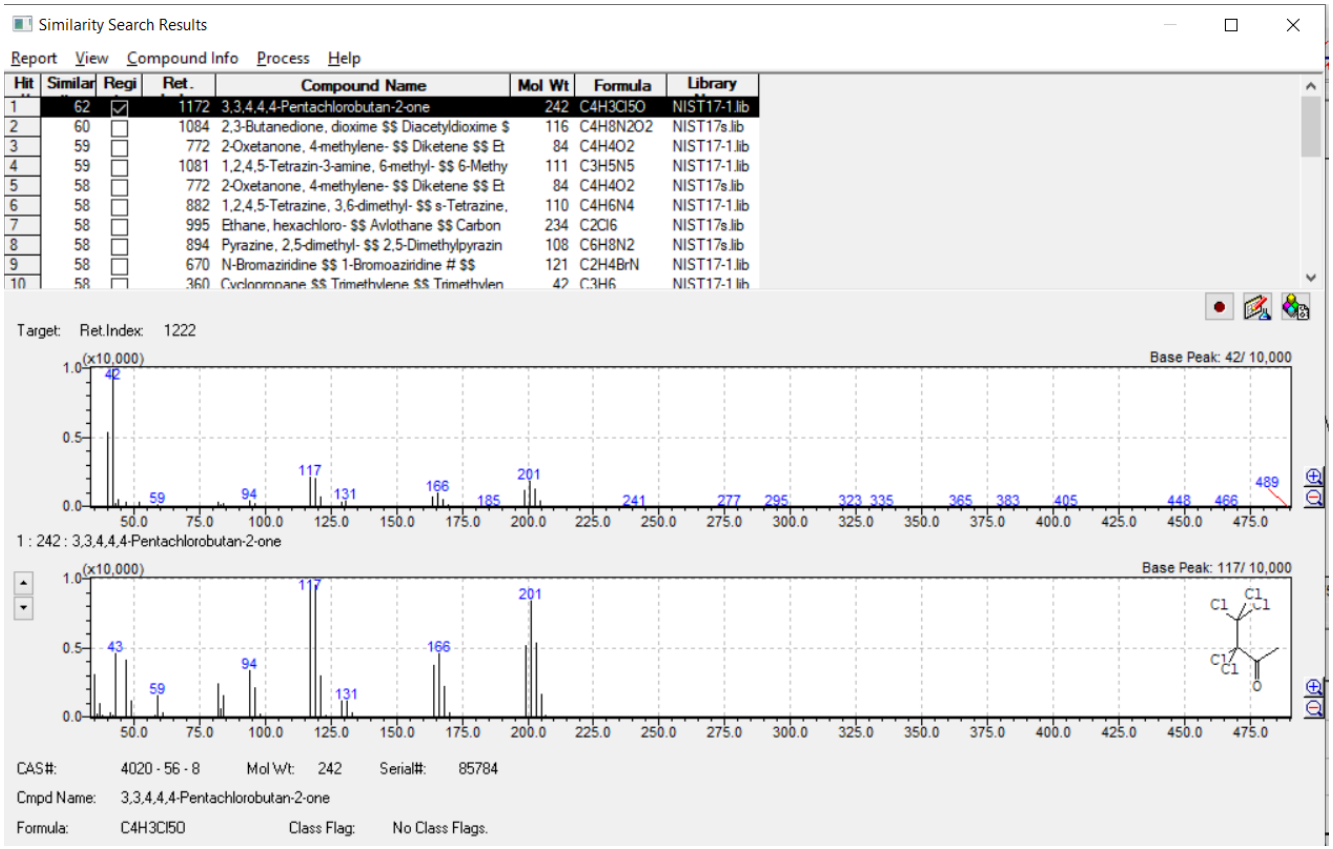
Un-Subtracted Library Search

Incorrect Library “hit” on 3,3,4,4,4-Pentachlorobutan-2-one



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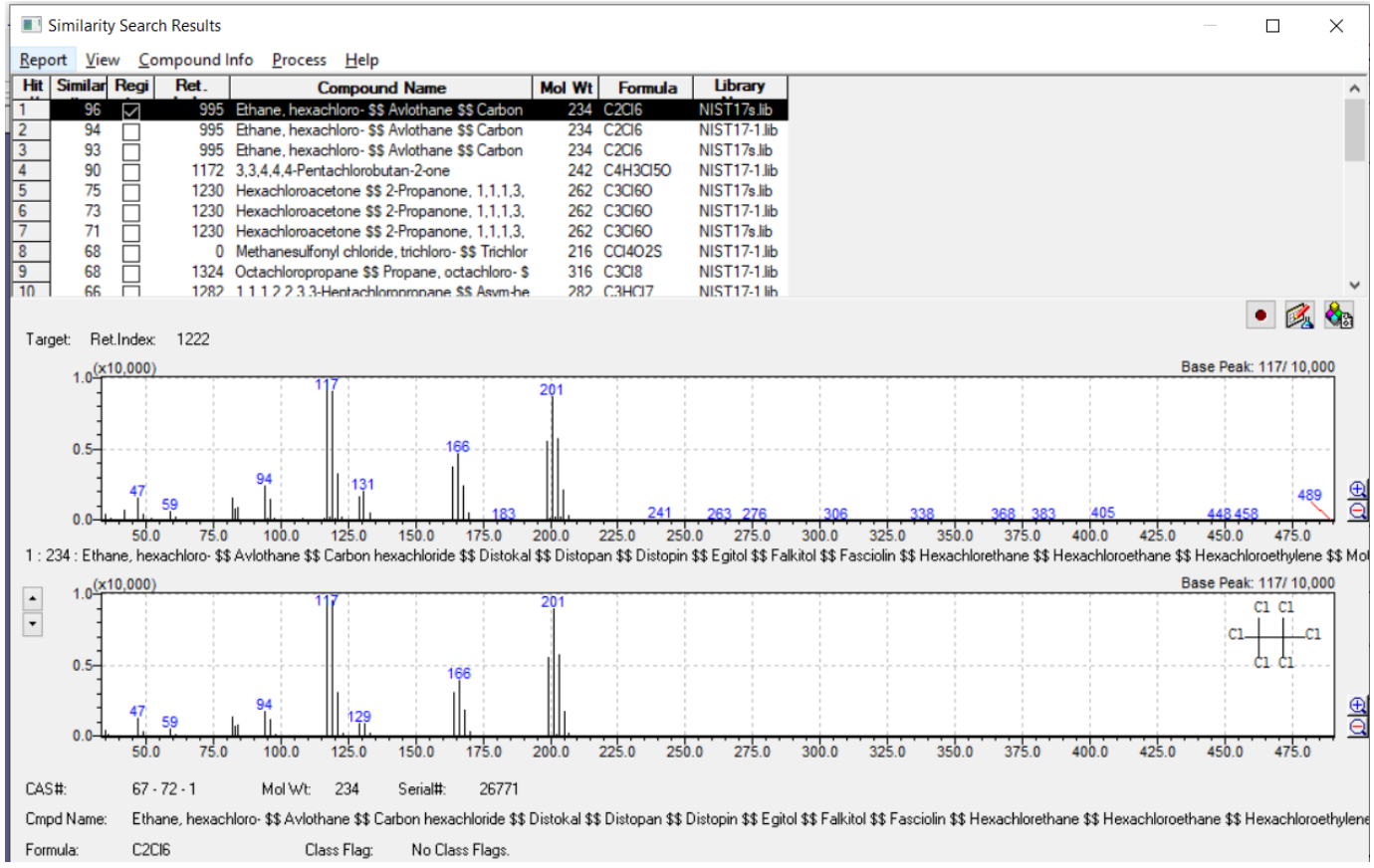
Subtracted Library Search

Correct Library search hit on Ethane, hexachloro-



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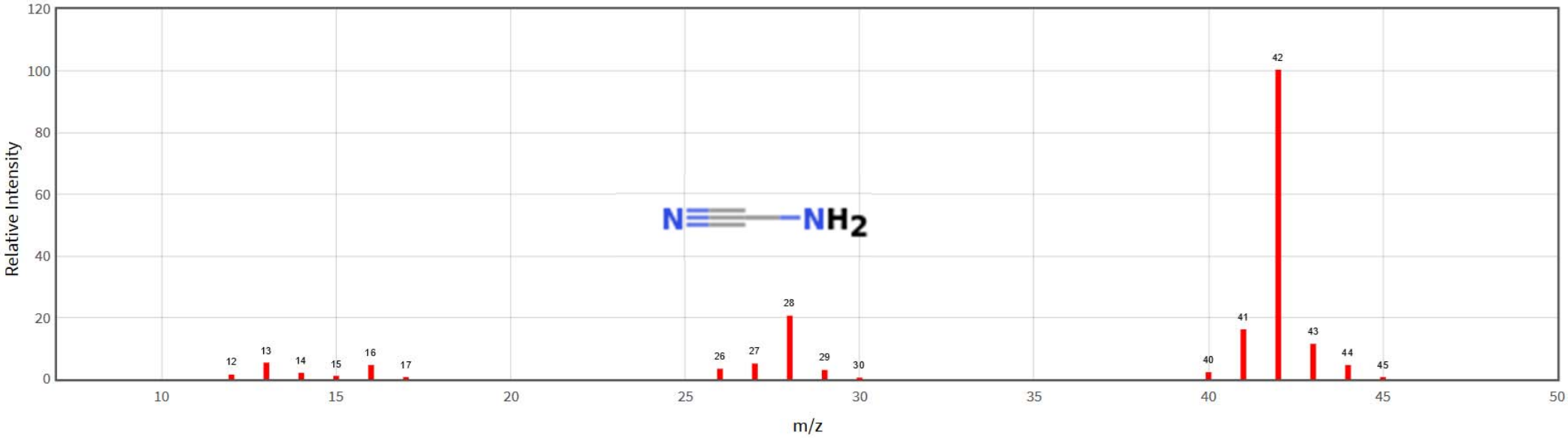
MS Background

Cyanamide



NIST Mass Spectrometry Data Center, William E. Wallace, director

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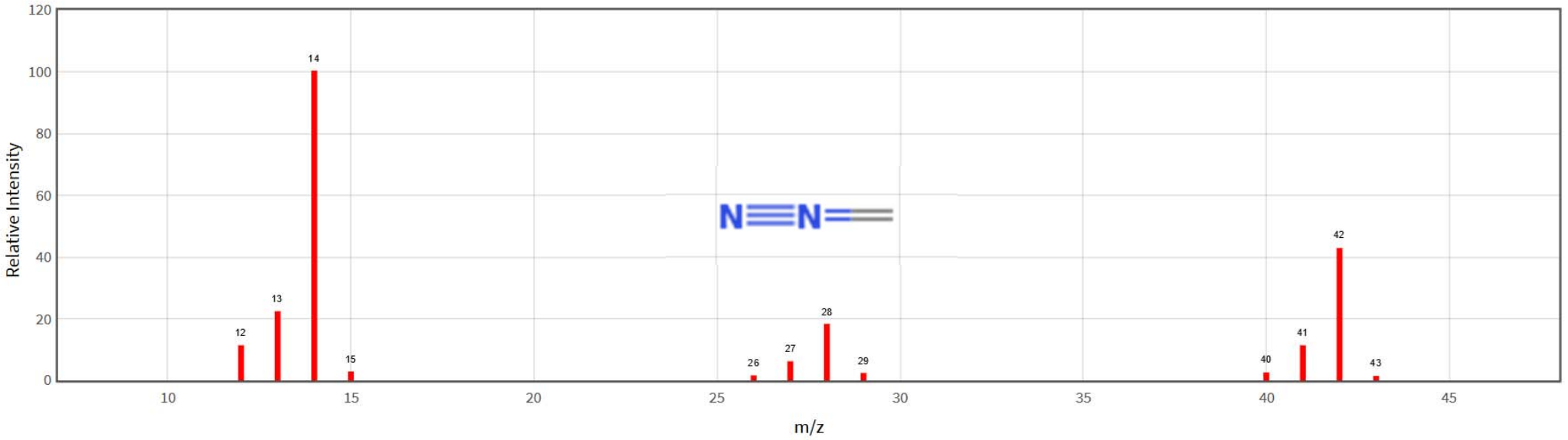
MS Background

Diazomethane



NIST Mass Spectrometry Data Center, William E. Wallace, director

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Results from the Rxi-5Sil MS Column

- Chromatically, results were OK except for:
  - Response attenuation of late eluting PNAs and some phthalates
    - Not a problem with helium carrier
  - Band Broadening on late eluting compounds
    - Unusual peak shapes
    - Also not a problem with helium carrier
  - Separation of early compounds was tricky
    - N-nitroso-dimethylamine and pyridine eluted prior to toluene 😱
    - Toluene is a solvent component of the standards 😑
    - Necessary to shut off the MS for a few seconds after pyridine elutes

- Switched to Rxi-17Sil MS Column

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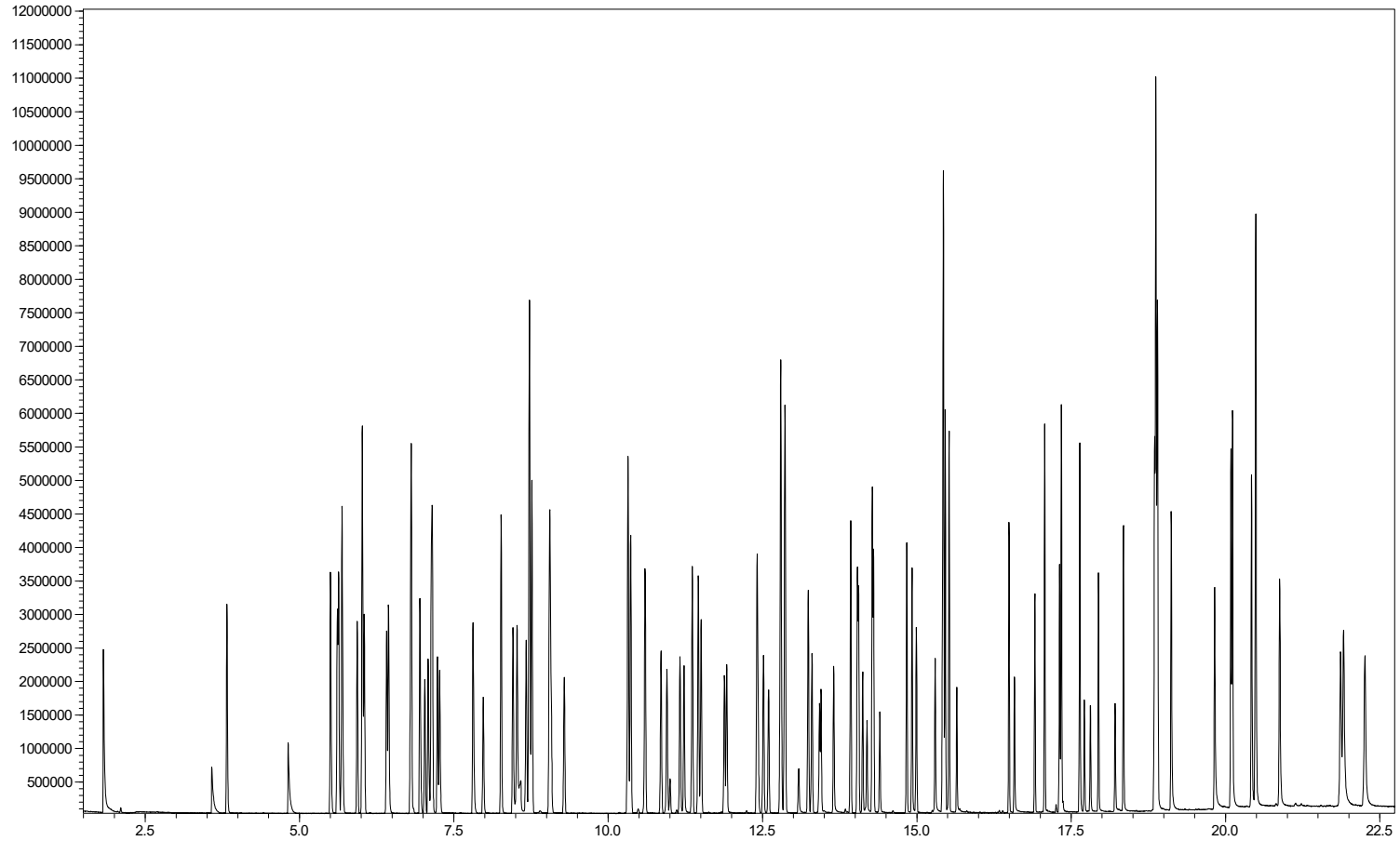
Chromatogram of a 20 ppm Standard on Rxi-5Sil MS with Helium Carrier



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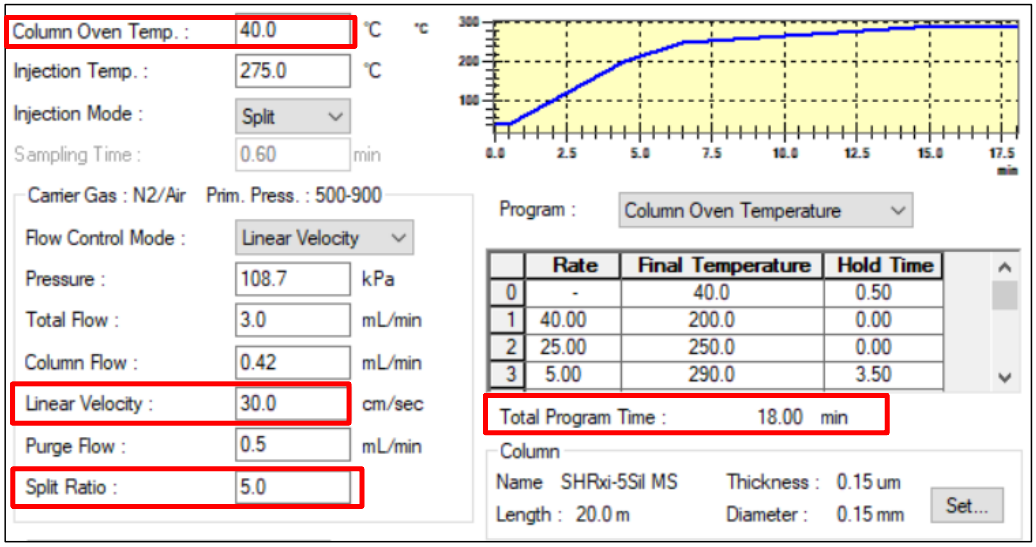
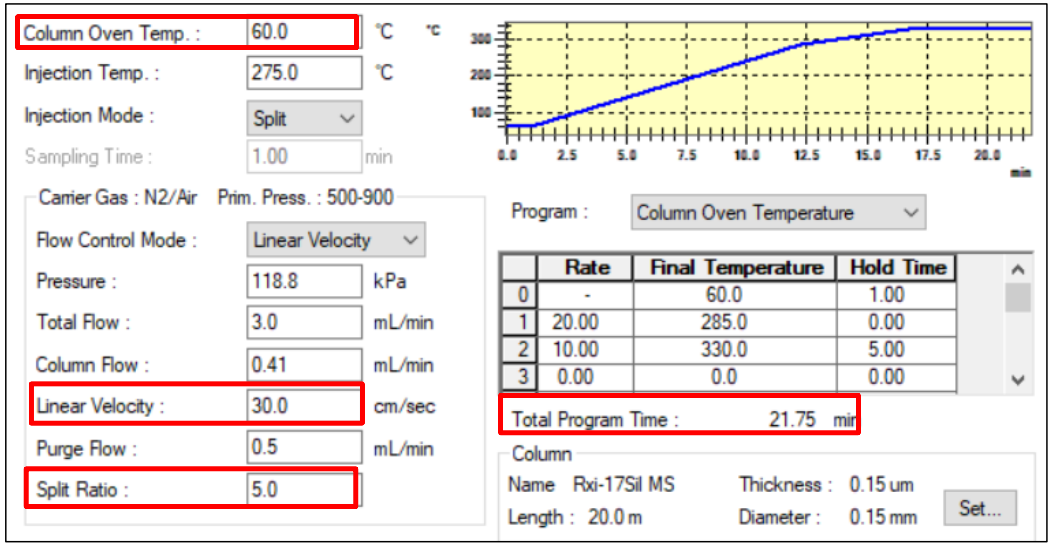
Chromatographic Conditions

Conditions for Rxi-5Sil MS Analyses



Conditions for Rxi-17Sil MS Analyses



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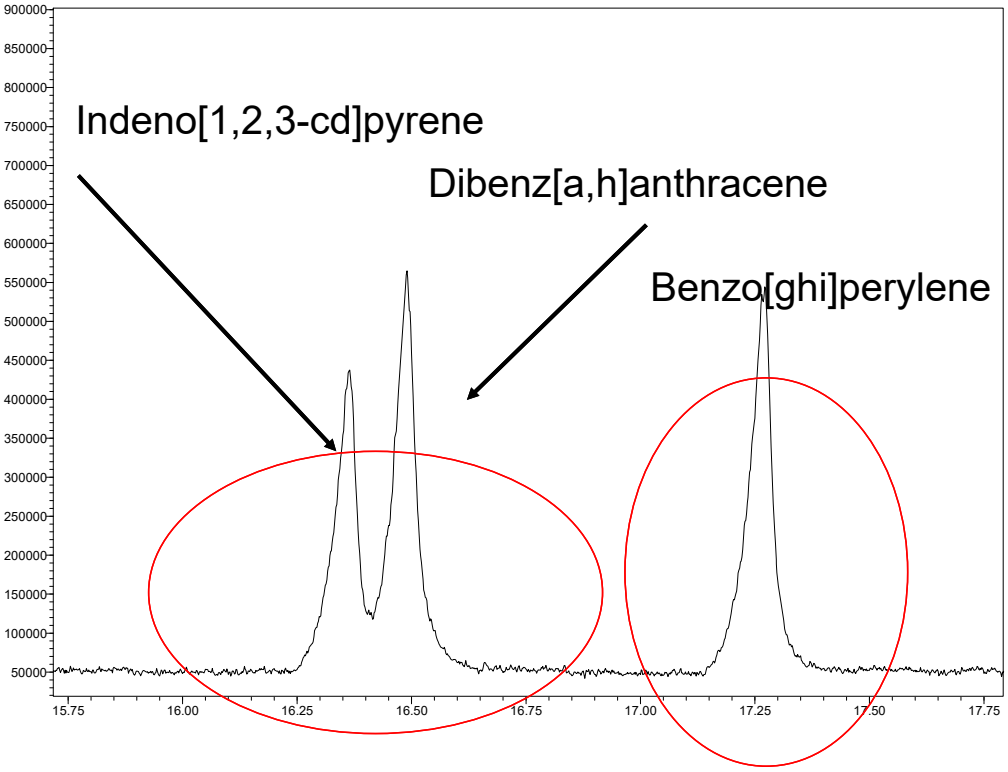
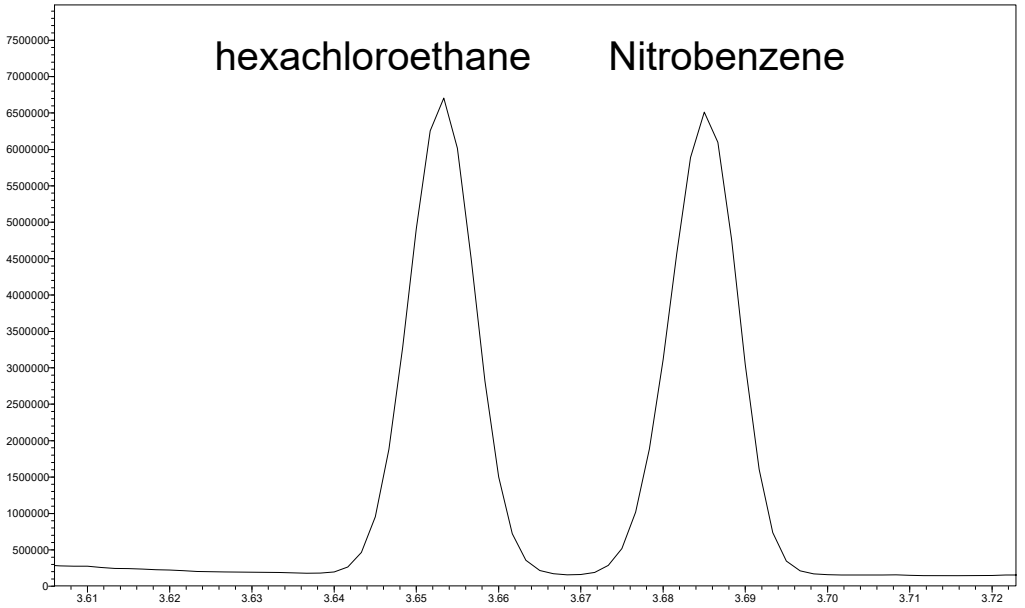
Chromatogram of Late Eluting PNAs on the Rxi-5Sil MS Column

Non-gaussian peak shape



Comparison: note gaussian peak shapes on earlier peaks



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Results from the Rxi-17Sil MS Column

- Generally, results were better on the Rxi-17Sil MS column
  - Much less response attenuation of late eluting PNAs
  - Less band broadening on late eluting compounds
    - Better (more gaussian) peak shapes
  - Separation of early compounds was much improved
    - N-nitroso-dimethylamine and pyridine eluted after toluene
      - No need to shut off the MS to cut out Toluene
    - Better separation on the front end compounds
    - Better beak shapes on the first 5 compounds than on the Rxi-5Sil MS

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Results from the Rxi-17Sil MS Column

- One critical separation ***cannot*** be accomplished on the Rxi-17Sil MS
  - Dibenz[a,h]anthracene / Indeno[1,2,3-cd]pyrene are not sufficiently separated for quantitation of Indeno[1,2,3-cd]pyrene in a reasonable timeframe
  - Separation can only be achieved with long run times (~50 min)

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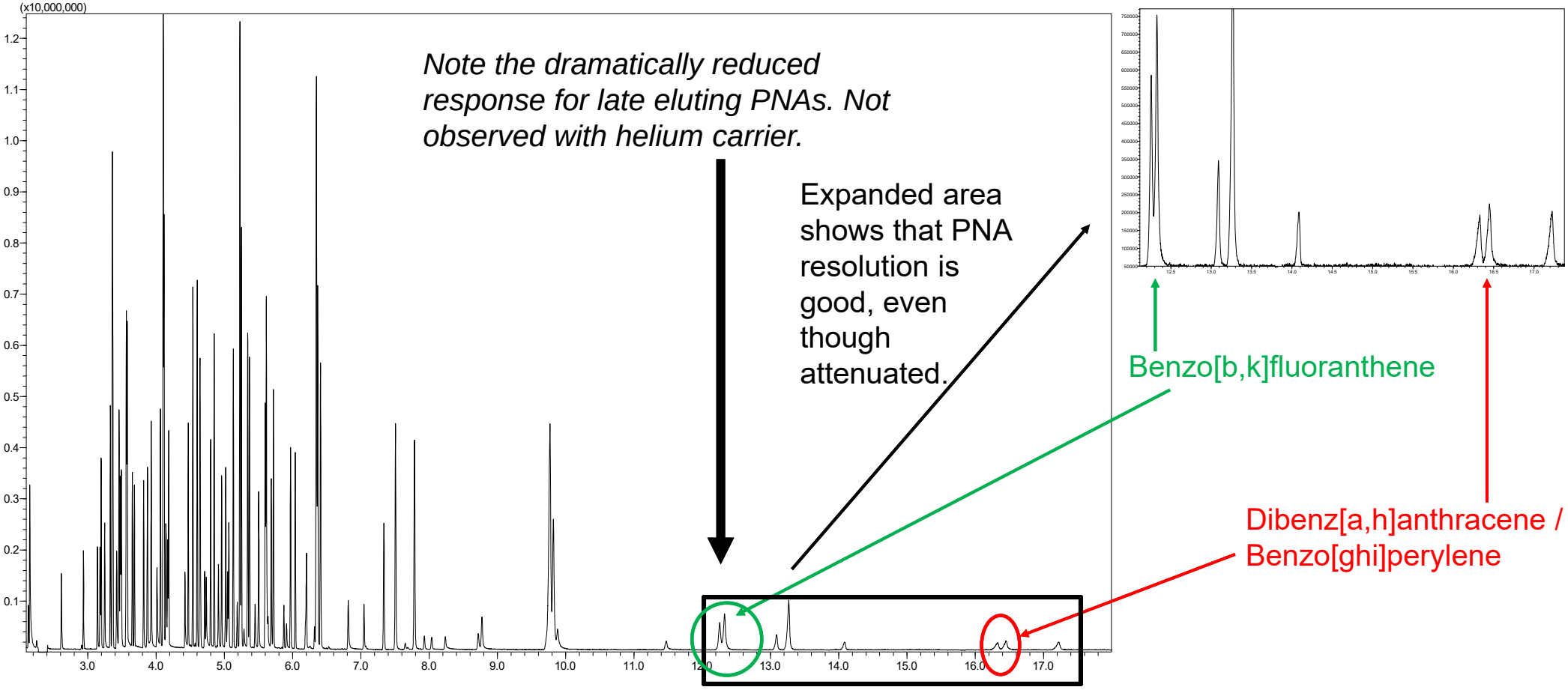
Chromatogram of a Standard on the Rxi-5Sil MS With N_2 Carrier



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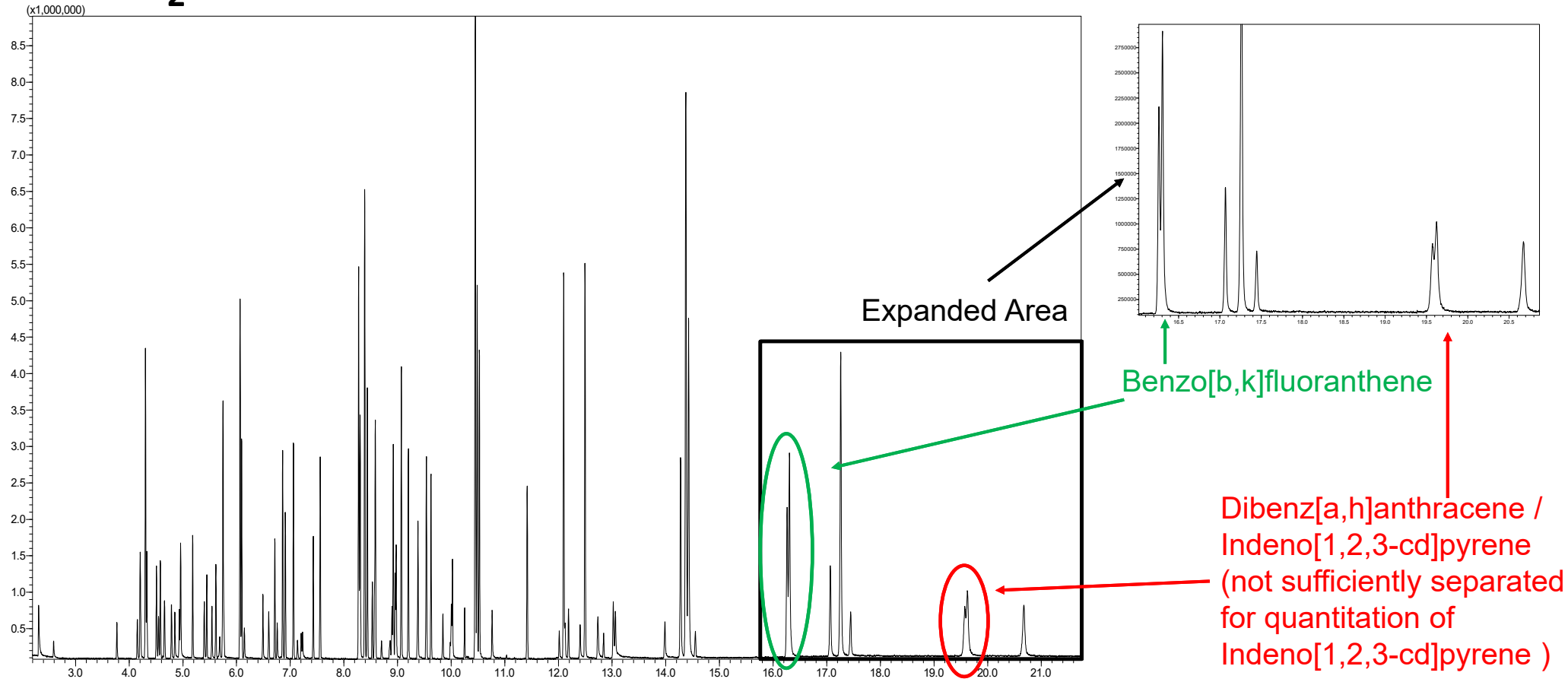
Chromatogram of a Standard on the Rxi-17Sil MS With N_2 Carrier



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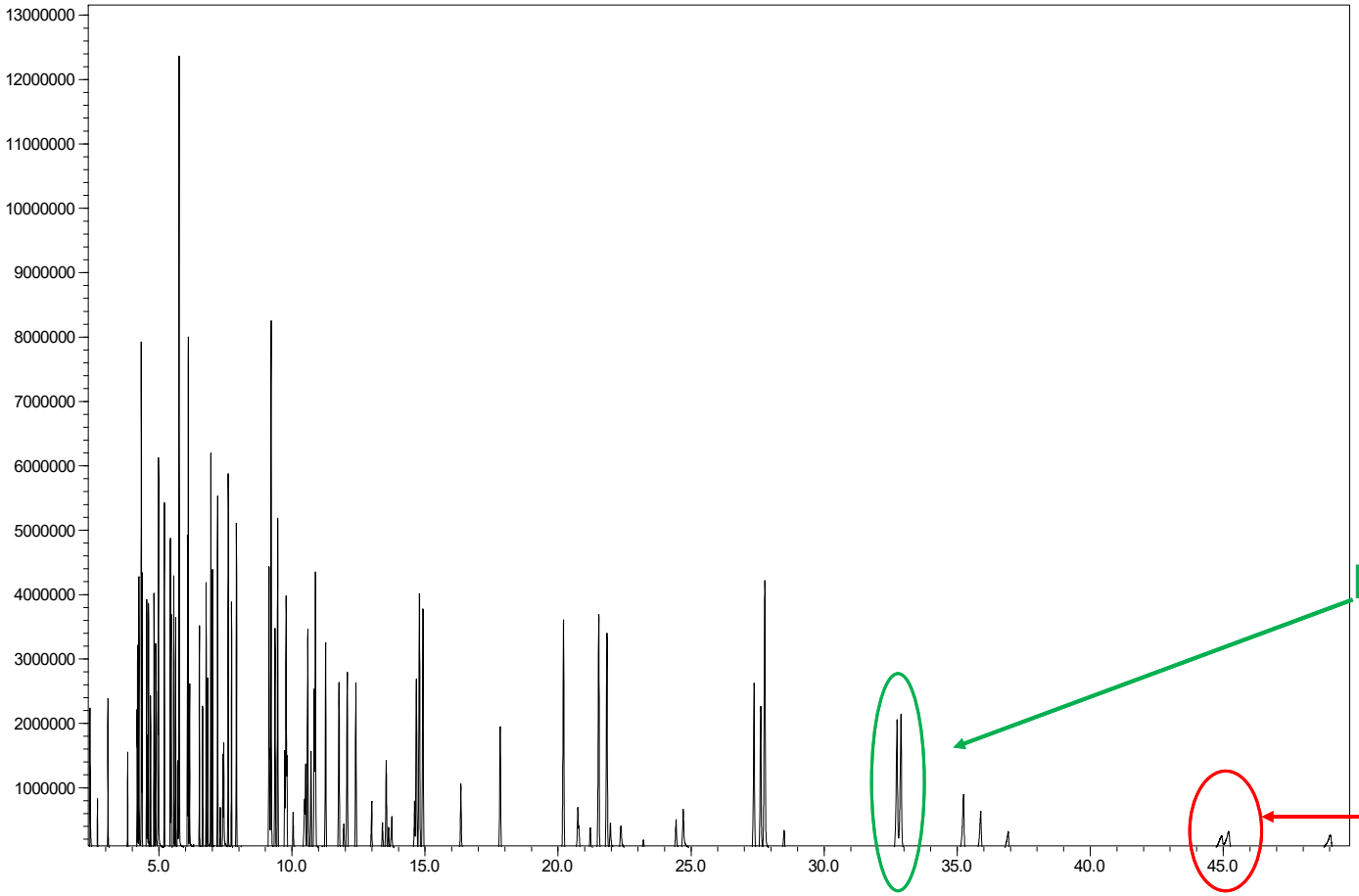
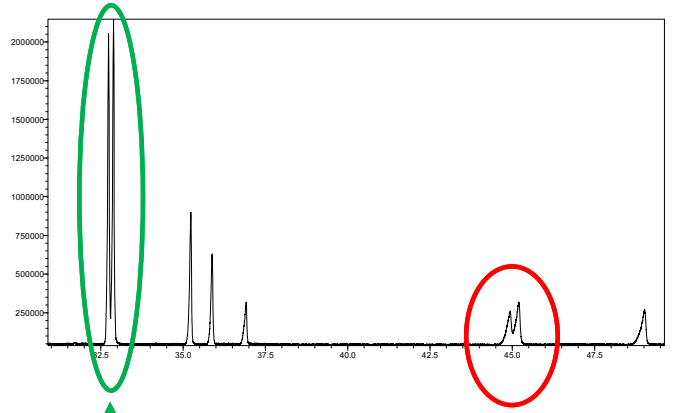
Chromatogram of a Standard on the Rxi-17Sil MS w/Separation





Benzo[b,k]fluoranthene

Dibenz[a,h]anthracene /
Benzo[ghi]perylene

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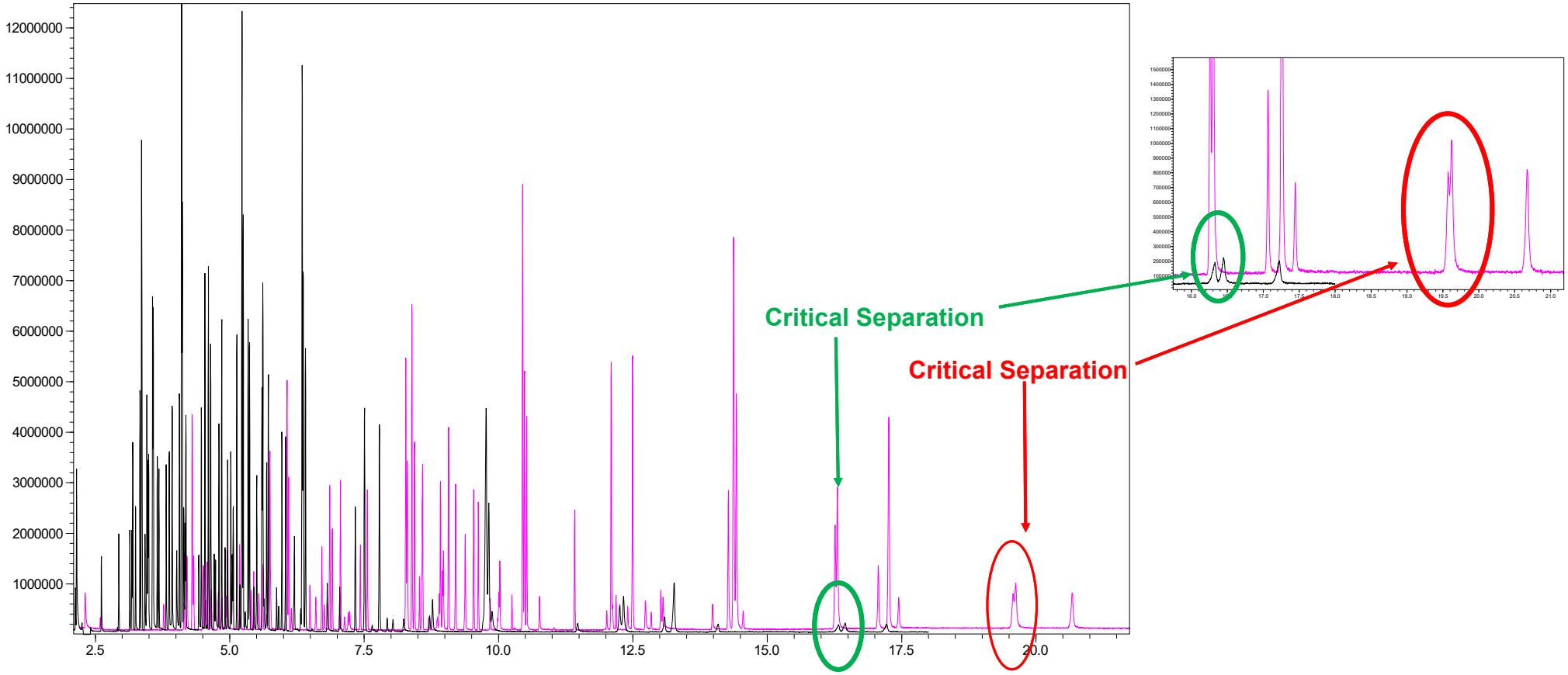
Overlay of 20 ppm Standard Rxi-5Sil MS and Rxi-17Sil MS with N_2 Carrier



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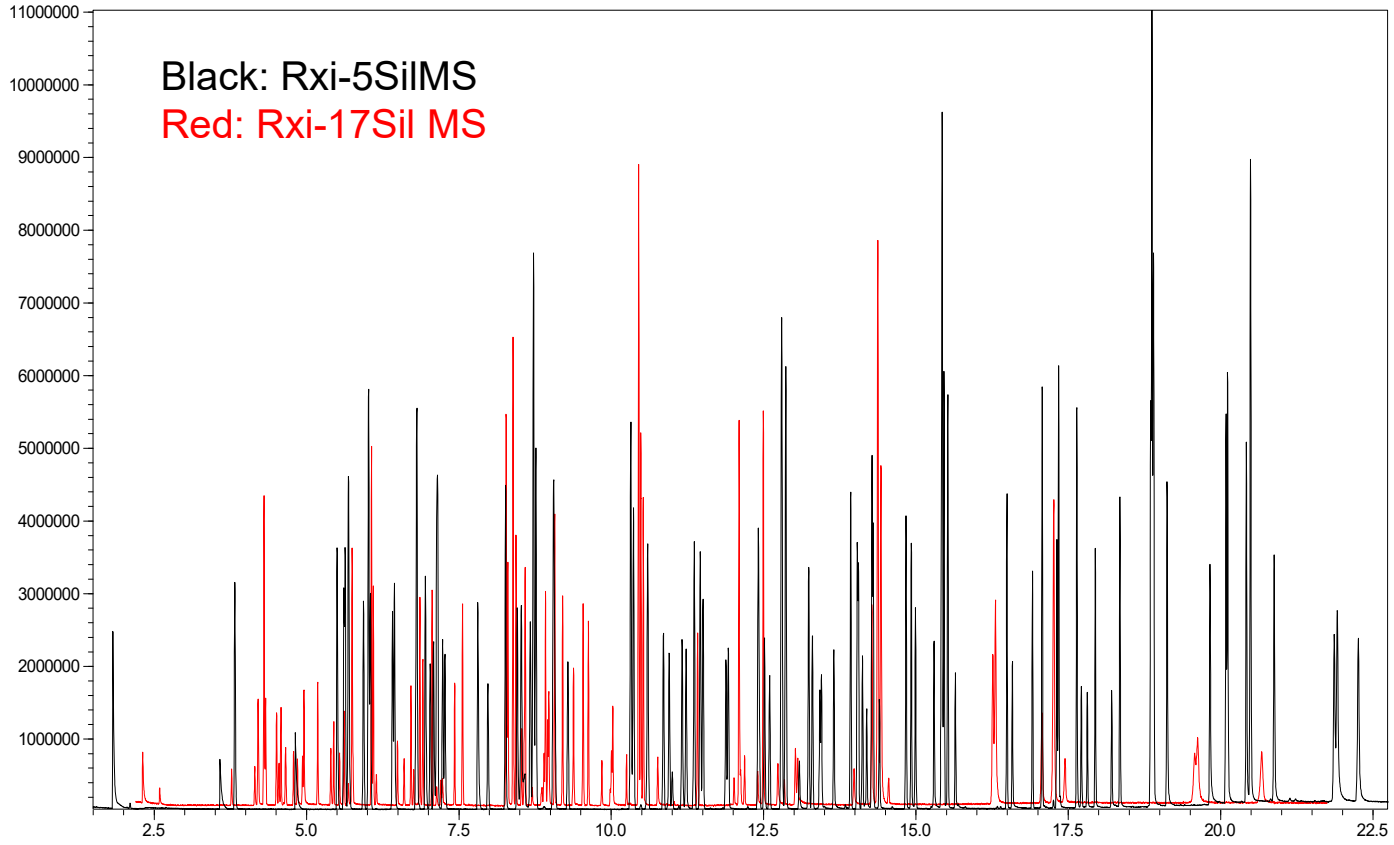
20 ppm Standard: Rxi-5Sil MS with Helium and Rxi-17Sil MS with N_2



Conditions: Rxi-5Sil MS:
Linear velocity: 60 cm/sec
Helium
10:1 split

Conditions: Rxi-17Sil MS:
Linear velocity: 30 cm/sec
Nitrogen
5:1 split

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Instrument Detection Limits (IDL)

- IDLs were determined via the “old” method from 40 CFR Part 136 Appendix B.
  - Most of the published MDLs were determined via that method.
- There was no sample preparation; standards only
  - We were evaluating chromatography and instrument performance
- We ran consecutive 11 reps for 10 degrees of freedom
  - “spike” level was 0.8 ng/µL
- Quantitation was performed by RRF calculated from a 0.8 ng/µL standard
- Average detection limits were similar on both columns
- Late eluting PNA detection limits were much better on the Rxi-17Sil MS

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Instrument Detection Limits (IDL)

- There are too many compounds to tabulate individually in this presentation
- For final concentration we calculated averages in ng/µL at the instrument and for calculational purposes assumed
  - 1 L for water and 30 g for solids

Mean DL for Rxi-5Sil MS

Water: 0.57 µg/L

Solid: 19 mg/Kg

Mean DL for Rxi-17Sil MS

Water: 0.55 µg/L

Solid: 18 mg/Kg

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Calibration

- 6-Point calibrations were performed on both columns
  - **4** ng/µL, **10** ng/µL, **20** ng/µL, **40** ng/µL, **80** ng/µL, **120** ng/µL
  - Linear velocity was 30 cm/sec on both columns
  - Both calibrations were run as split injections with a split ratio of 5.
  - Temp program was optimized to produce the best separation in the shortest time
    - Rxi-5Sil MS started at 40°C
    - Rxi-17Sil MS started at 60°C

- Linearity was a challenge on both columns
  - At least partly because of overloading on the 120 ng/µL standard
  - The “usual suspects” phenols, benzidine, etc. were not detected well at 4 ng/µL

- Because of COVID-19 delays, we were unable to address calibration issues

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8270 Tuning

- The purpose of this study was to determine feasibility of nitrogen carrier
- Special DFTPP tune algorithms for nitrogen have not yet been developed
- The MS was tuned by Shimadzu's High Sensitivity Autotune algorithm
  - No attempt was made to adjust the mass pattern to meet DFTPP criteria or to compensate for nitrogen in the manifold

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8270 Tuning

- DFTPP was analyzed *pro forma* to monitor daily instrument drift
- Usually, the DFTPP met or came close to meeting 8270D criteria

.

- The DFTPP rarely met the older 1970's tuning requirements
- The analyst made liberal use to the NIST library search in setting up the RT table for the "17" column. Matches for uncontaminated spectra typically were greater than 90%. There was no evidence of spectral distortion

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Conclusions

- Except for one separation, the data from the “17” column were promising
- The N_2 results were *not* as good as for helium, but that was expected
- As long as helium is available and affordable, it is by far the best option
- The data were much better than those produced by hydrogen carrier
  - That was the purpose of the study; to set up a method that was superior to what has been obtained with hydrogen carrier
- Nitrogen carrier needs more development before helium is unavailable

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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.; Zhuangzhi "Max" Wang, Ph.D.; Clifford M. Taylor; Shimadzu Scientific Instruments

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?”** 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 and Jack Cochran, Restek Corporation

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Questions

???Questions???

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