SAND2014-18516C

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Photos placed in horizontal position with even amount of white space between photos and header

A study of polymer-coated capillary column performance using air as a carrier gas at temperatures between 120 ºC and 220 ºC.

U.S. DEPARTMENT OF ENERGY

National Nuclear Security Administration

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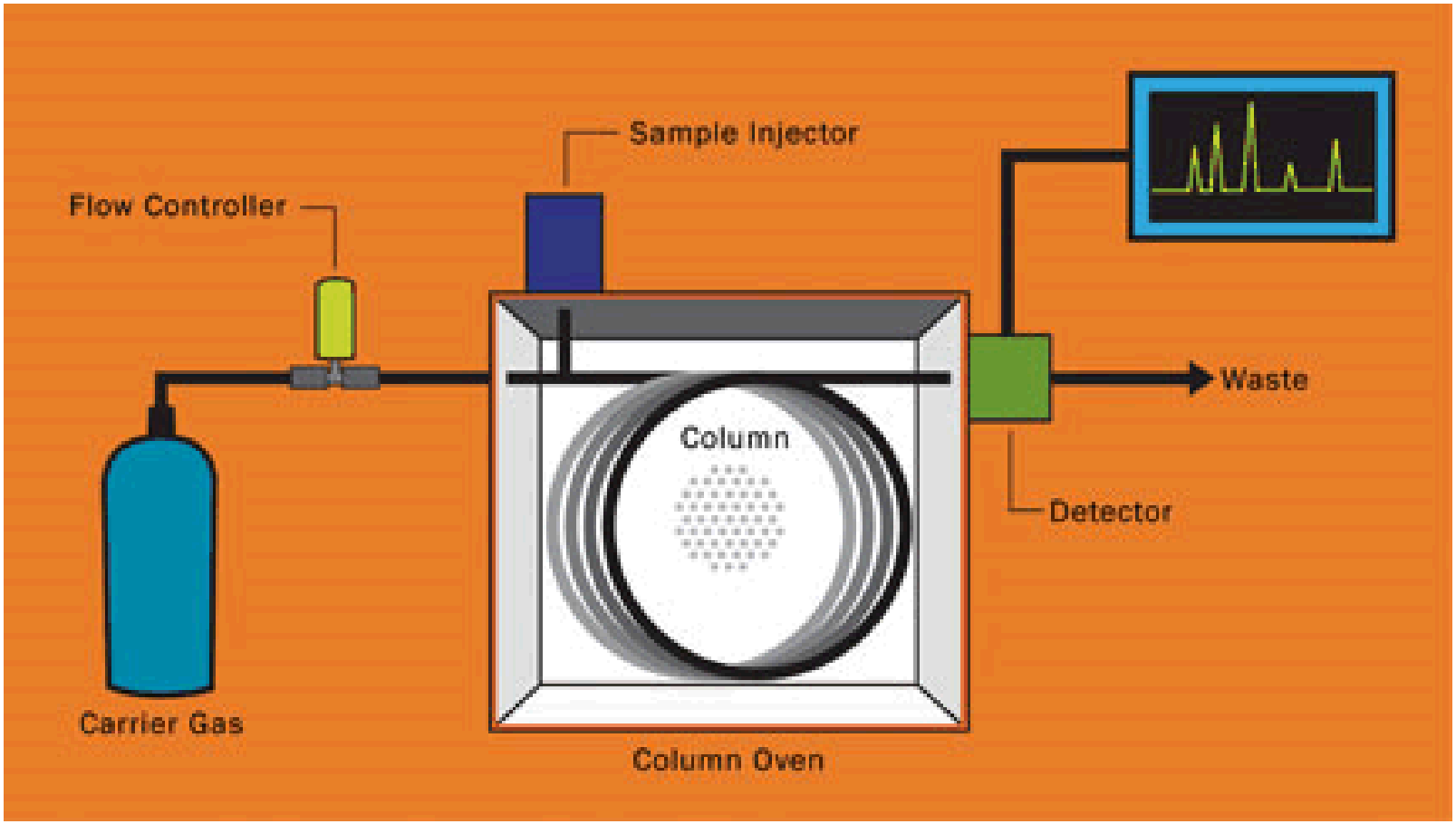
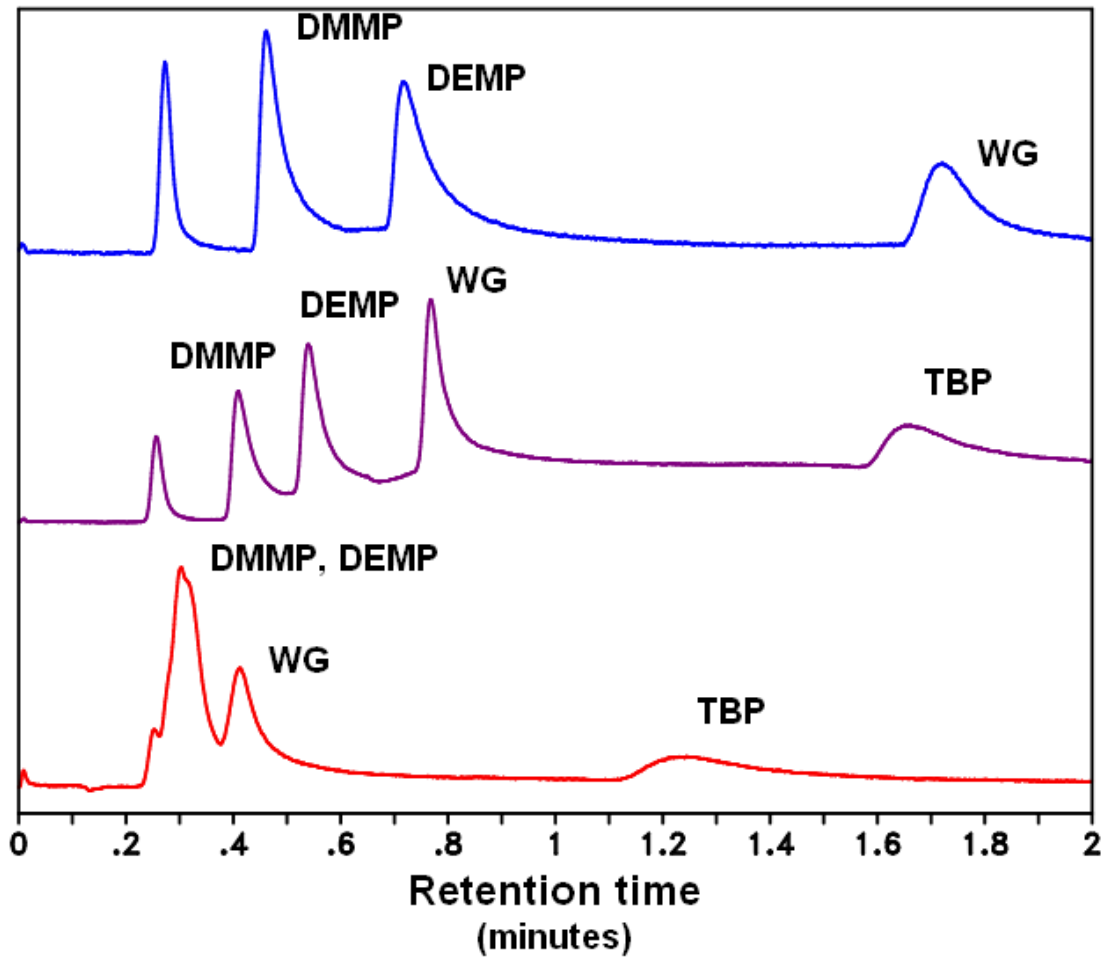
General Gas Chromatography system.



http://www.ece.vt.edu/news/ar08/gcmatrix.html

To Ramp or not to Ramp?



column conditions

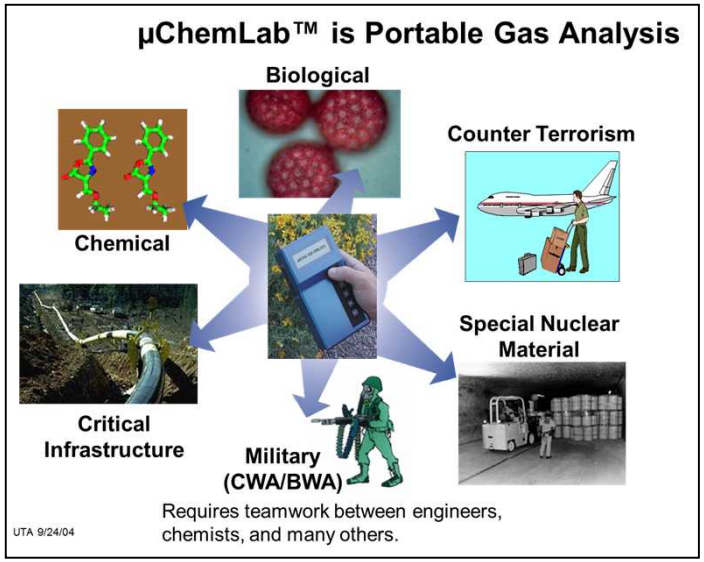
100°C isothermal

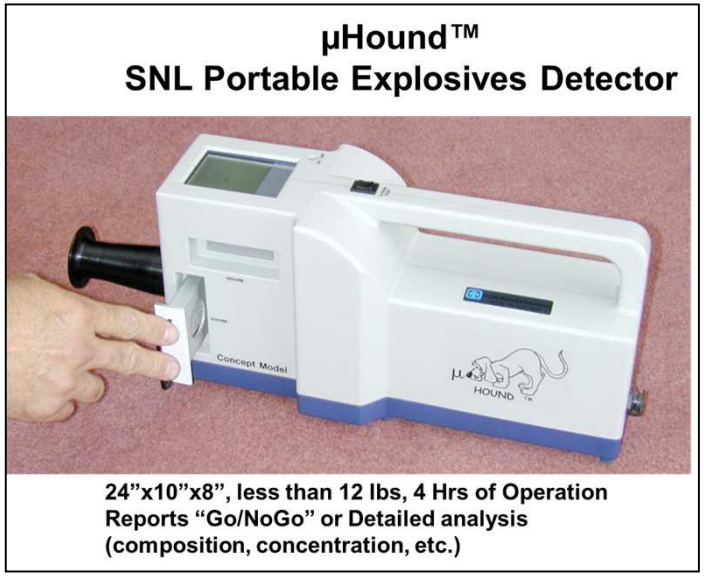
100°C, 10 sec. Ramp to 150°C In 30 sec.

150°C isothermal

DMMP = Dimethyl methyl phosphonate WG = methyl salicylate
DEMP = Diethyl methyl phosphonate TBP = Tributylphosphate

Why are we interested?





- Interest in obtaining separations of higher boiling, lower volatility compounds (DNT, TNT, chemical agent markers and by-products) which require higher (120 °C - 250 °C) temperature programs.
- Air as a carrier is attractive to reduce the footprint of field deployed sensor units.

construction

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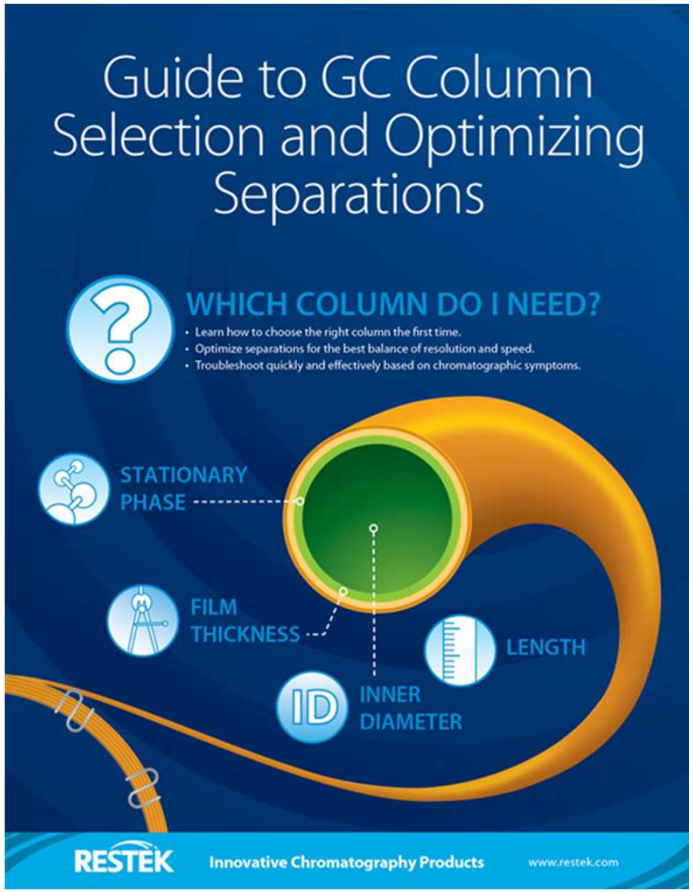
Column evolution

http://people.whitman.edu/~dunnivfm/C_MS_Ebook/CH2/Figures/Fig_2_11_Columns.jpg

Modern capillary columns routinely have temperature ranges of -60 ºC to 350 ºC.

SPME (Solid Phase Micro Extraction) is an inside-out column-on-a-stick. Acts like flypaper for compounds of interest.

Inside a column

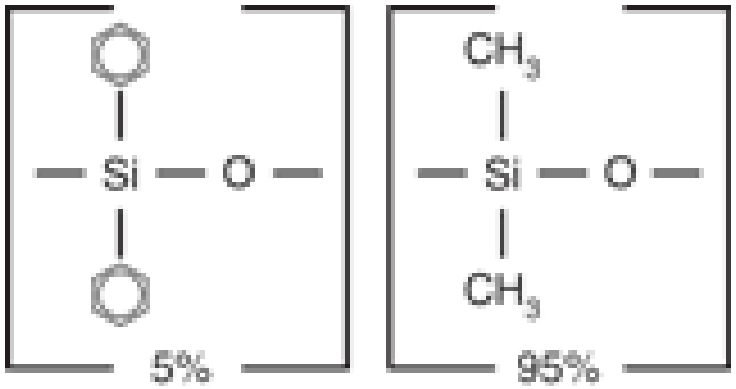


http://www.restek.com/news/view/?m=201304

Columns used in this study

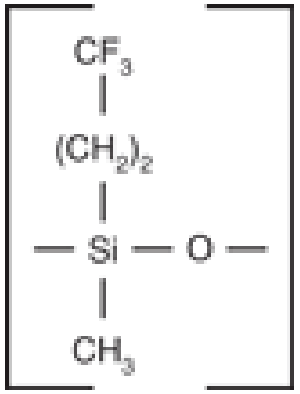
Rtx-5 and Rtx-5MS GC columns

- low polarity phase; Crossbond® 5% diphenyl 95% dimethyl polysiloxane
- Aromatic hydrocarbons, solvent impurities, pesticides, semivolatiles.



Rtx-200 GC columns

- midpolarity phase; Crossbond® trifluoropropylmethyl polysiloxane
- nitrosamines, organochlorine pesticides, chlorinated hydrocarbons



Oxygen the enemy!

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- Constant exposure to oxygen above ambient temperatures thought to cause severe damage to capillary columns
  - Loss of resolution
  - Peak tailing
  - Column bleed
- Polar stationary phases more susceptible to O_2 damage

Discuss what we did (method)

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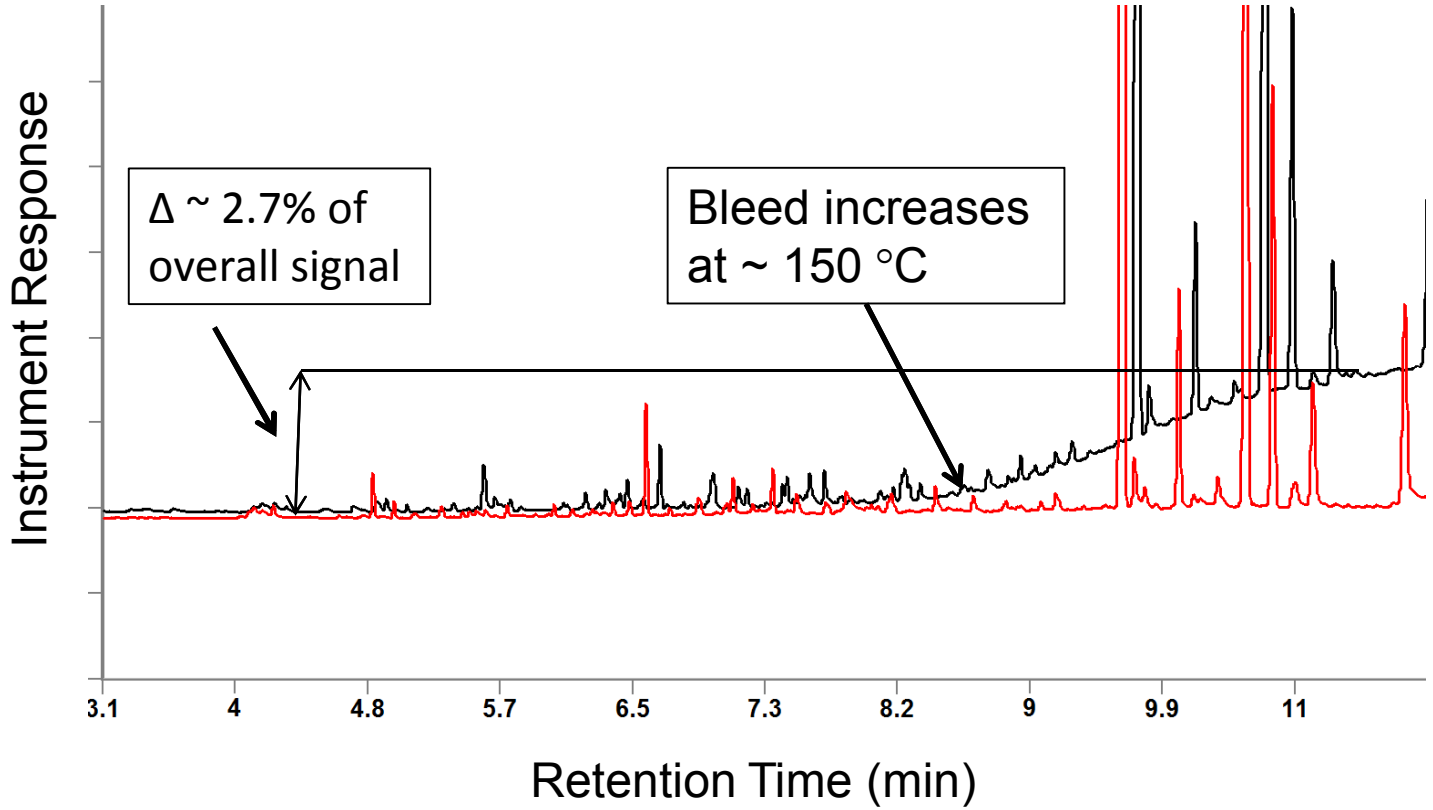
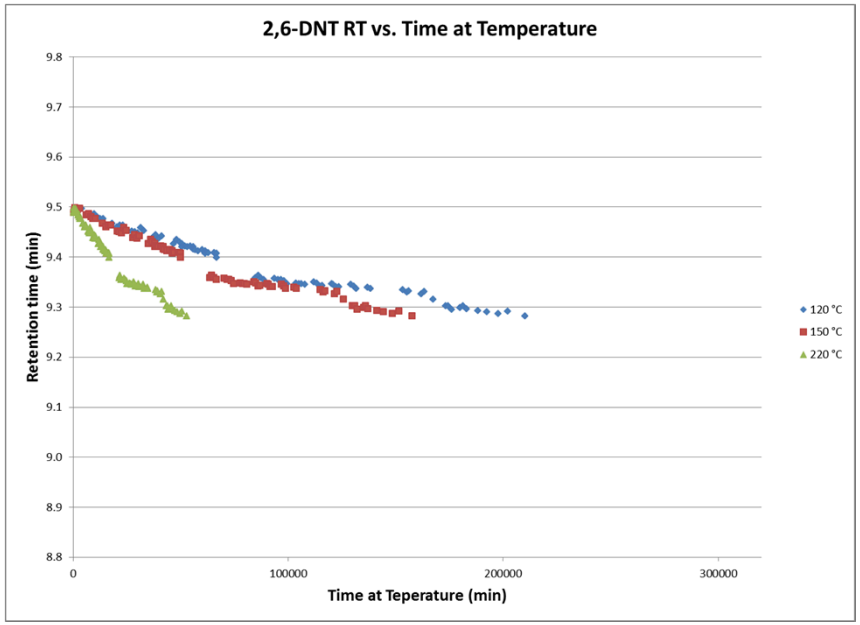
- Used dry house air as carrier
- Used DNT (2,4 and 2,6 present) as analyte
  - DNT is a precursor to TNT
  - Present as a contaminant in TNT
- Used SPME sample introduction
  - Exposed fiber to headspace of DNT
  - SPME mimics pre-concentration
- Ramped column oven temp for many cycles between SPME data points

N_2 vs Air as carrier on Rtx-200

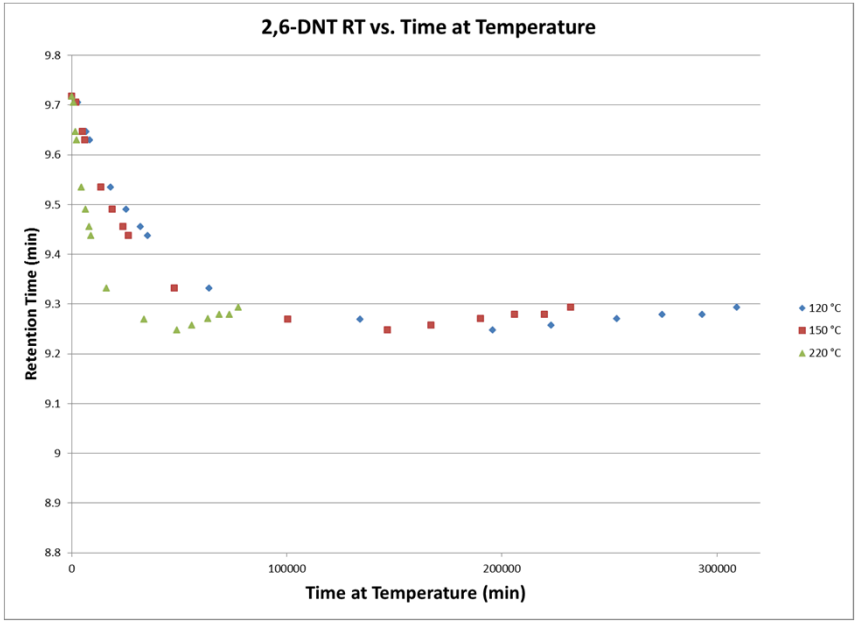


Retention Time

Rtx-5 RT plots



Rtx-200 RT plots



Rtx-5	At or above 120 °C	At or above 150 °C	At 220 °C
minutes	210194.5	157706.5	52682
hours	3503.2	2628.4	878.0
days	146.0	109.5	36.6

Rtx-200	At or above 120 °C	At or above 150 °C	At 220 °C
minutes	309273	231966	77343
hours	5154.6	3866.1	1289.1
days	214.8	161.1	53.7

Comparison of Full Width at Half Max

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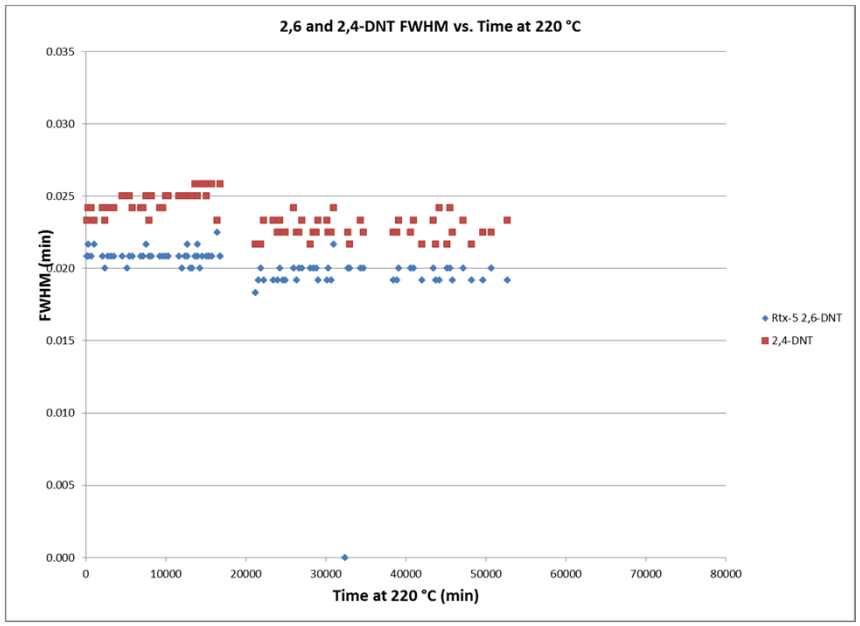
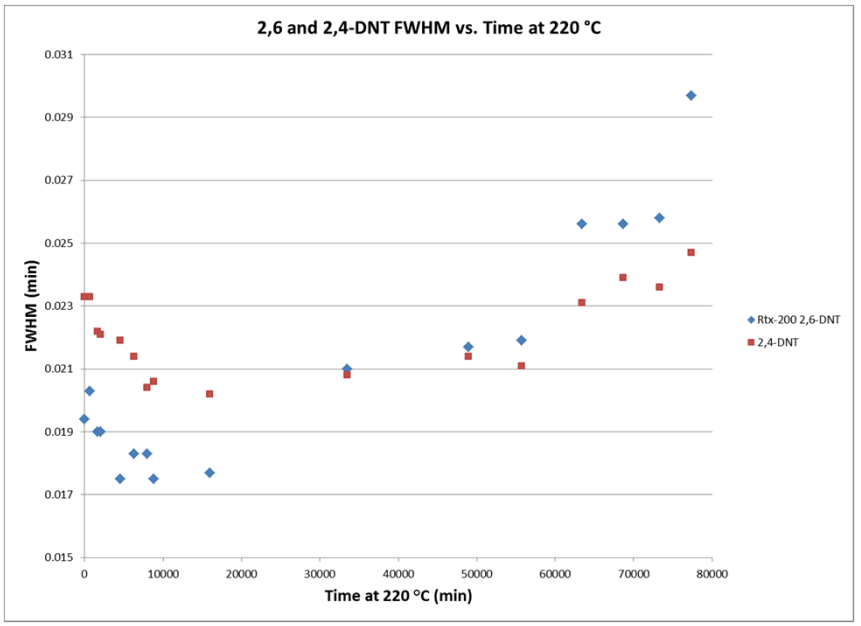
Rtx-5 FWHM

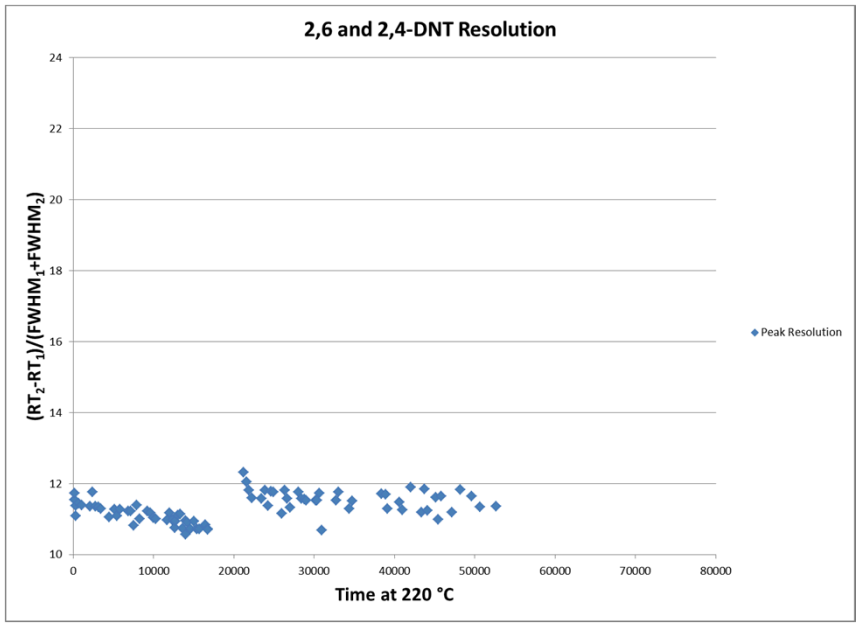


Rtx-200 FWHM

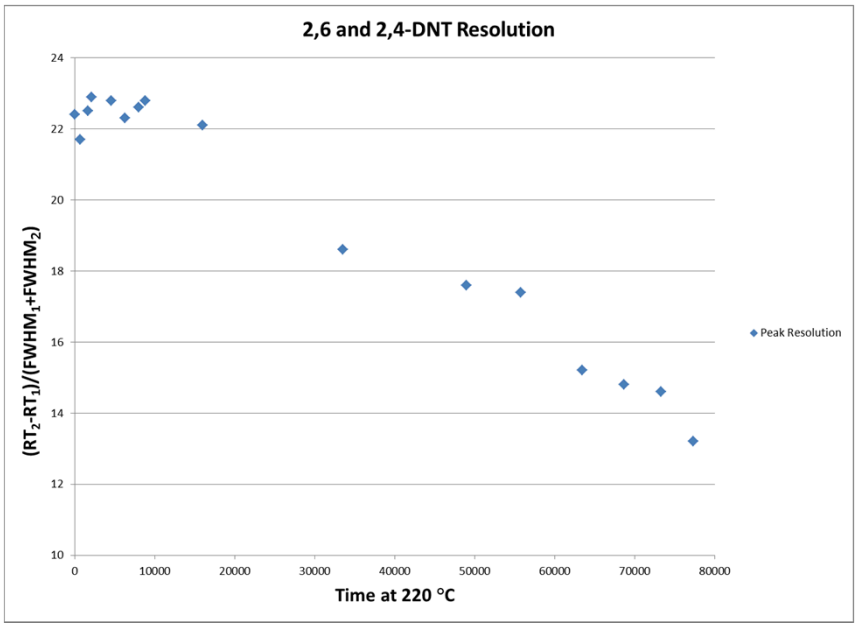


Resolution

Rtx-5 Resolution

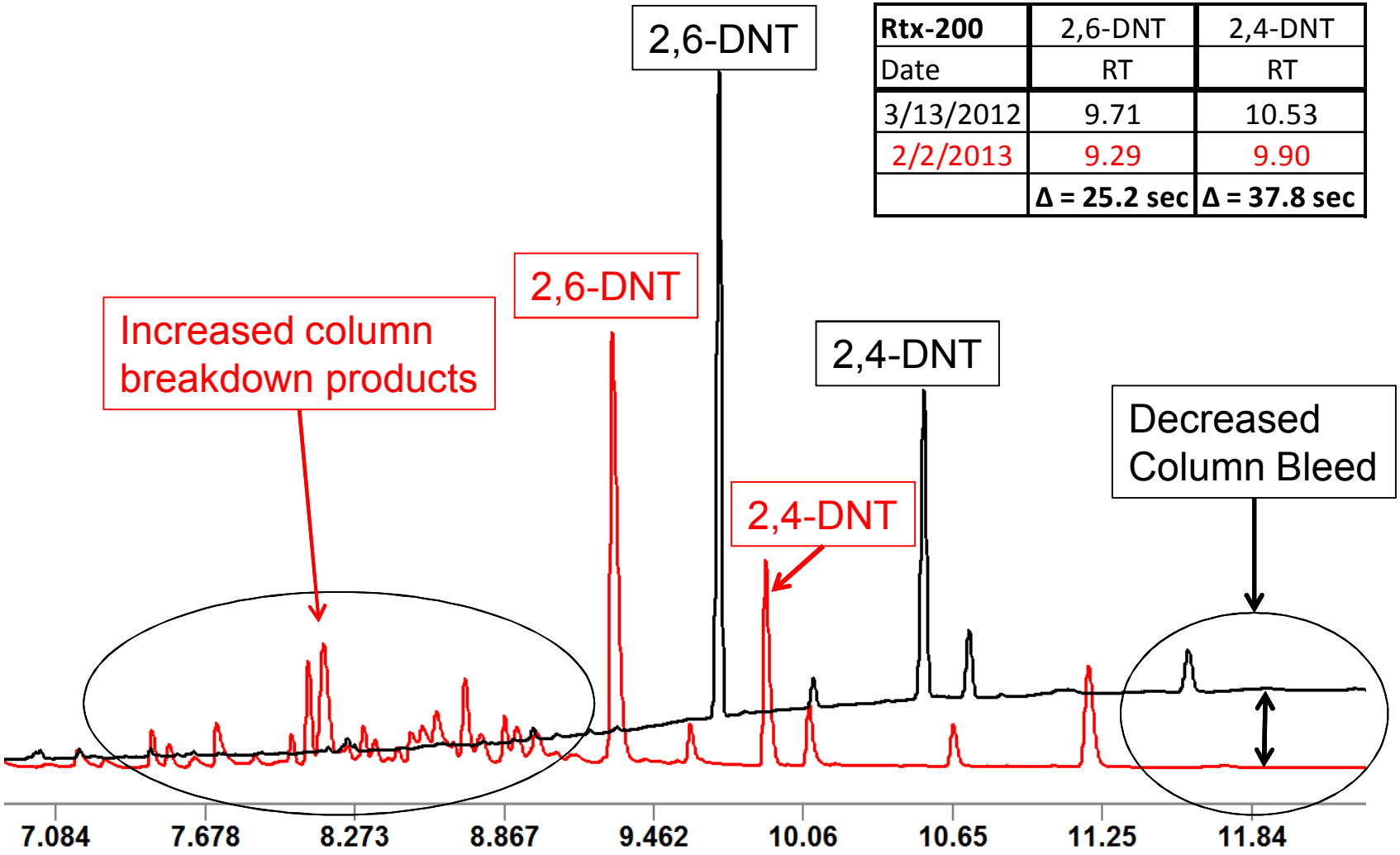


Rtx-200 Resolution



Rtx-200: Injection #3 and Injection #22083

Rtx-200	2,6-DNT	2,4-DNT
Date	RT	RT
3/13/2012	9.71	10.53
2/2/2013	9.29	9.90
	Δ = 25.2 sec	**Δ = 37.8 sec**



Discussion

- Why are these things changing?
- Column bleed?
- Column degradation
- Is moist air the real enemy?

Conclusions

- Column performance **far** better than expected!
- Rtx-5: >15K cycles (109 DAYS above 150 °C)
  - Δ RT = 12.4 sec. (2,6 DNT) and 14.6 sec (2,4-DNT)
  - Δ FWHM = 0.15 sec.
  - Δ Baseline width X seconds (from Y to Z sec)
  - Δ Resolution = 1.6
- Rtx-200: >22K cycles (161 DAYS above 150 °C)
  - Δ RT = 25.2 sec. (2,6 DNT) and 37.8 sec. (2,4-DNT)
  - Δ FWHM = 0.7 sec.
  - Δ Baseline width = 6 sec. (from 4.2 to 10.2 sec)
  - Δ Resolution = 9.7

References

- **Images for slide 4 : Presented at Univ. of Texas at Arlington Sept. 24, 2004. Unlimited unclassified release, SAND2004-4869.**
- http://webbook.nist.gov/chemistry/