Methods Development for the Analysis of VOCs on Carbopack X Sorbent Tubes Using TD/GC-TOF MS

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Why Carbopack X ?

In the beginning…

- 2004 – EPA RTP needed to develop a method to collect personal, indoor, and outdoor air samples for the Detroit Exposure and Aerosol Research Study (DEARS)

Method requirements…

- Passive/diffusive design – requiring no power to operate
- Small and easy for participants to wear
- Sensitive enough to perform 24-hour monitoring
- Rugged – able to withstand rigors of weather and being worn by individuals
- Accurate for general VOCs and 1,3-butadiene in particular

Why Carbopack X ? (cont.)

Solution…

- PerkinElmer style diffusive sampling tubes made of ceramic-coated stainless steel containing Carbopack X sorbent[1-3]

Why Carbopack X ? (cont.)

Outcome…

- Rugged method[4] that provided good results for DEARS and has been applied to numerous studies since 2004
- Carbopack X tubes now routinely used for fenceline monitoring of benzene around refineries[5]

Typical Selected VOCs for Carbopack X Diffusive Sampling[4]

1,2-Dichloro-1,1,2,2-tetrafluoroethane	Toluene
1,3-Butadiene	Tetrachloroethene
Trichlorofluoromethane	Chlorobenzene
1,1-Dichloroethene	Ethylbenzene
1,1,2-Trichloro-1,2,2-trifluoroethane	*m,p*-Xylene
1,1-Dichloroethane	Styrene
cis-1,2-Dichloroethene	*o*-Xylene
1,2-Dichloroethane	4-Ethyltoluene
1,1,1-Trichloroethane	1,3,5-Trimethylbenzene
Benzene	*m*-Dichlorobenzene
Carbon tetrachloride	*p*-Dichlorobenzene
1,2-Dichloropropane	*o*-Dichlorobenzene
Trichloroethene	

EPA Studies Using Carbopack X Sorbent Tubes

Study	Dates	Exposure Time	Use	Compounds of Interest
DEARS[6]	2004–2007	24 hours	Diffusive	1,3-Butadiene, selected VOCs
Detroit Children's Health Study[7]	2005	1 week	Diffusive	Selected VOCs
Dallas[8]	2006–2008	1 week	Diffusive	Selected VOCs
Beaumont/ Port Arthur	2007	1 week	Diffusive	Selected VOCs
Corpus Christi Fenceline Study[9]	2008–2009	2 weeks	Diffusive	Benzene

EPA Studies Using Carbopack X Sorbent Tubes (cont.)

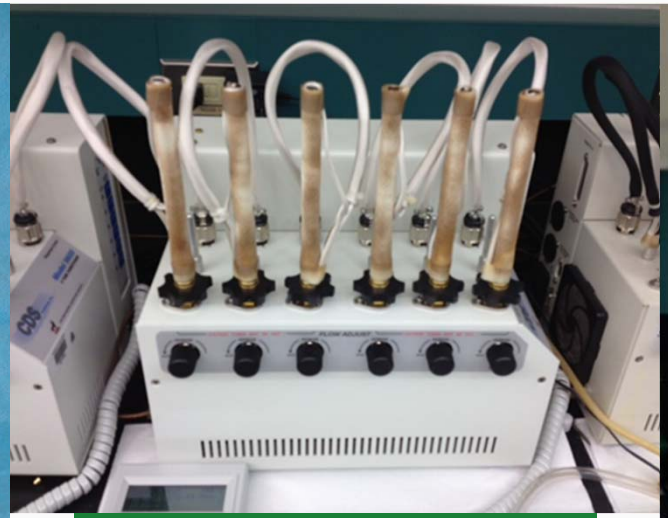
Study	Dates	Exposure Time	Use	Compounds of Interest
Low-Cost VOC Passive Sampling and Philadelphia Passive Sampler Study[10–13]	2013–2015	2 weeks	Diffusive	BTEX, 1,3-butadiene, selected VOCs
Tire Crumb Research Study	2016–2018	—	Active	General VOCs
Rubbertown Next Generation Emissions Measurements Study[14]	2017–present	2 weeks	Diffusive	1,3-Butadiene, general VOCs
Consumer Products Study[15]	Present	10 days	Diffusive	General VOCs

VOC Lab Instrumentation

GC-MS	Thermal Desorber	Trap
Varian Saturn 2000 GC-MS ion trap with cryo-oven programming	PE TurboMatrix ATD, 19:1 OS, ambient trap low temp	Carbopack X trap
Agilent GC-MS (6890/5975) with and without cryo-oven programming	PE TurboMatrix ATD, 19:1 and 10:1 OS, ambient trap low temp	SVI (soil vapor intrusion) trap
Markes TD/GC-TOF MS with and without cryo-oven programming	Unity Thermal Desorber 25:1 OS, subambient trap low temp	Air toxics trap

Tube Conditioning

Dynatherm

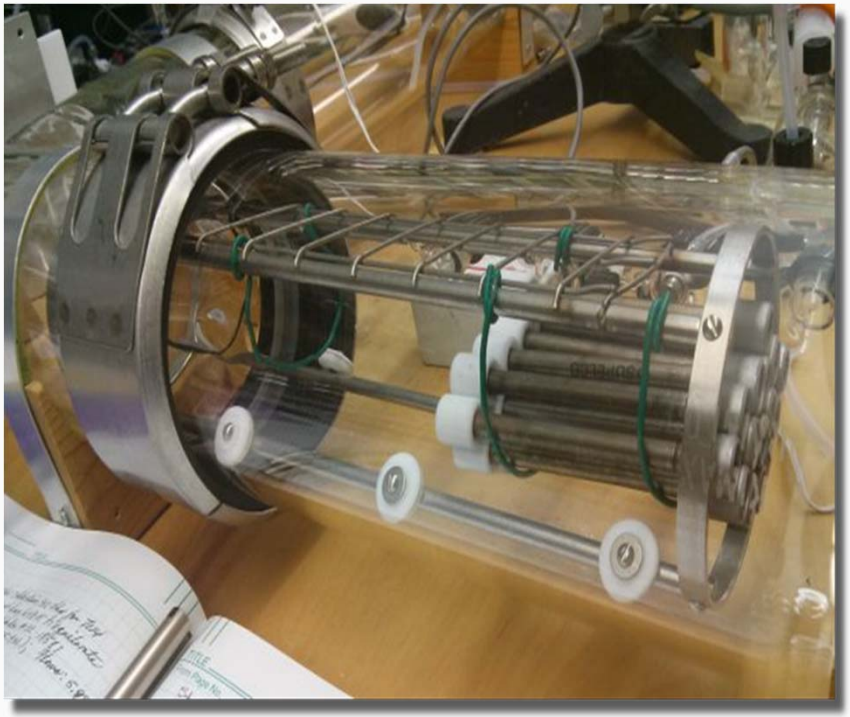


CDS Analytical 9600

Markes TC-20

Calibration Standard Preparation

- Passive 24-h exposures or active loading
- Linde or Apel-Reimer TO-14A 43-component gas cylinder standard
- 0–50 ppbv calibration range
- 8 levels, 3 at each level
- Quadratic curve



TD/GC-TOF MS System

Agilent 7890B GC/Markes BenchTOF-Select interfaced with Ultra TD 100, Unity 2, KORI, CIA Advantage, and can tower

Thermal Desorber Parameters

Parameter	Value
Trap	Air toxics focusing trap
Split flows	Inlet split – none; outlet split 25:1
Internal standards	1,4-difluorobenzene and chlorobenzene d-5

GC Parameters

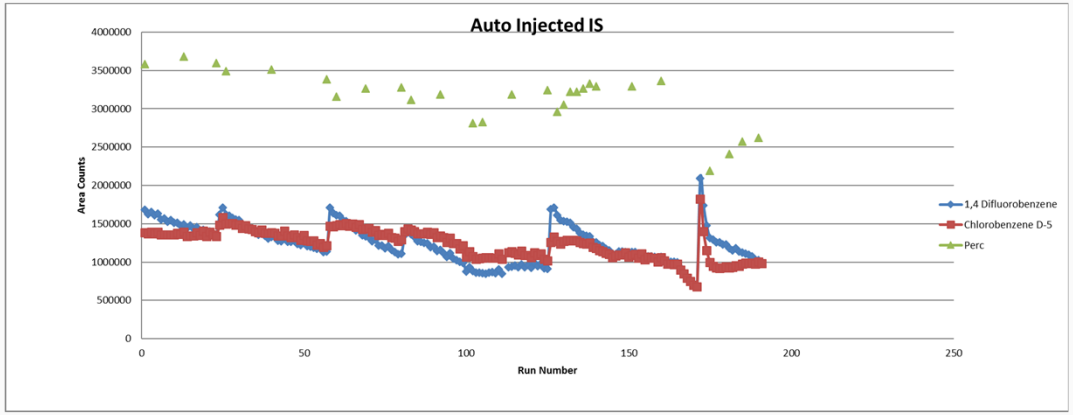
Parameter	Value
GC system	Agilent 7890B GC
Column	Rxi-1ms 60 m × 0.32 mm × 1 µm capillary GC column Column flow: 1.5 mL/min
Temperature program	Initial: -30 °C, hold 2.0 min Ramp 1: 3 °C/min to 69 °C, hold 0 min Ramp 2: 4 °C/min to 141 °C, hold 5.5 min Ramp 3: 40 °C/min to 240 °C, hold 3.52 min

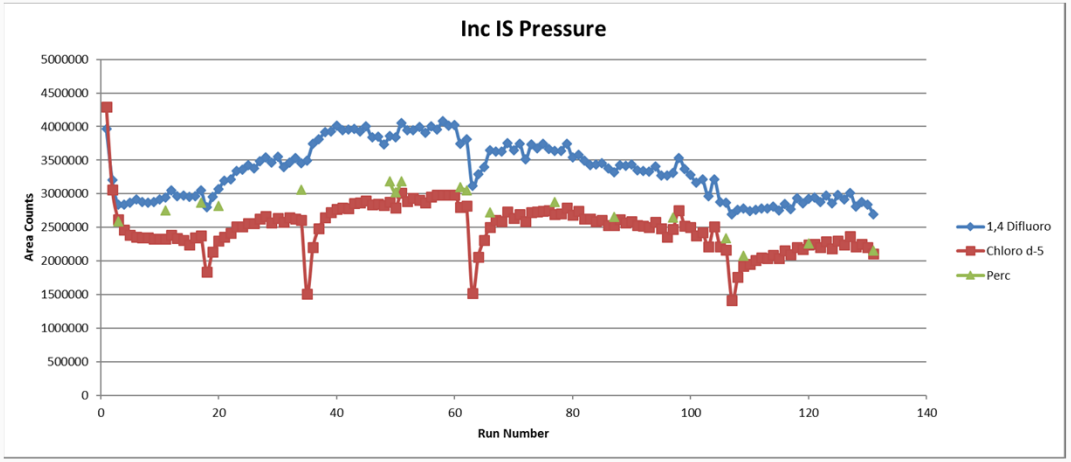
TOF MS Parameters

Parameter	Value
Mass range	35–350 m/z
Data rate	3 Hz
Transfer line temp	250 °C
Ion source temp	280 °C
Ionization voltage	70 eV
Filament voltage	1.6 V

Internal Standard Performance

- Previous work was based on external standards due to reproducibility issues with internal standards loading
- With TD/GC-MS TOF system – moved to internal standards
- Auto delivery not reproducible on our system





Internal Standard Performance (cont.)

- Moved to manual loading of internal standards onto each tube offline prior to sample analysis to improve reproducibility
- Very labor intensive and not our preference

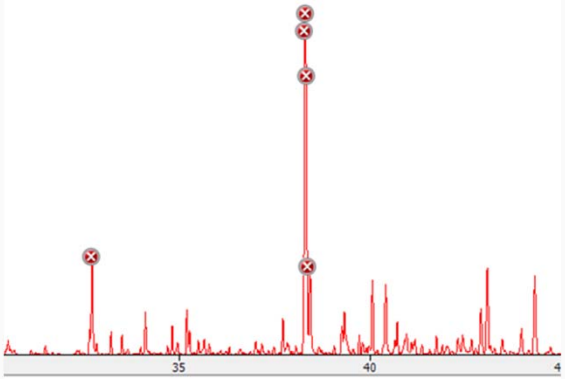
Filament Drops on TOF MS

Timed filament drops allow for a temporary decrease in sensitivity for compounds with high concentrations while preserving the life of the filament

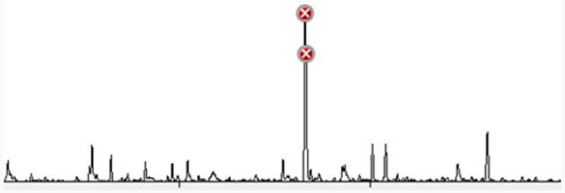
- Ionization voltage = 70 eV
- Filament voltage = 1.6 V
- 40.96 min: 1.49 V
- 41.27 min: 1.6 V

Filament Drops on TOF MS (cont.)

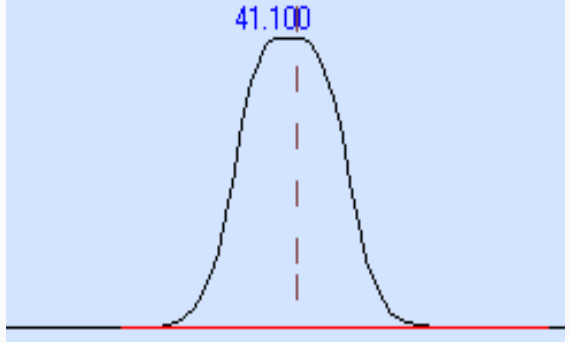
Filament drop 1.53V



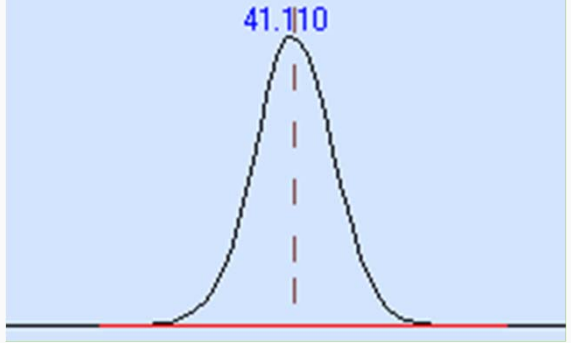
Filament drop 1.49V



Peak clipping at 1.53V



Better peak shape at 1.49V

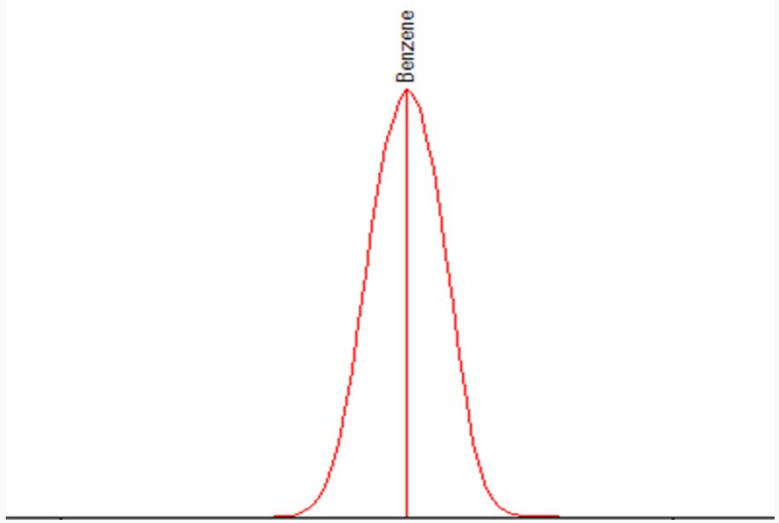


Data Processing

- Currently using ChemStation rather than Markes TOF DS software – expect to move to that platform in the future as Markes software is further refined for better integration of instrument control and data processing
- Database generated is taken offline and processed in Excel using area counts of VOCs and internal standards to generate background-corrected calibration curve
- Background subtraction techniques are used to correct for inherent sorbent background

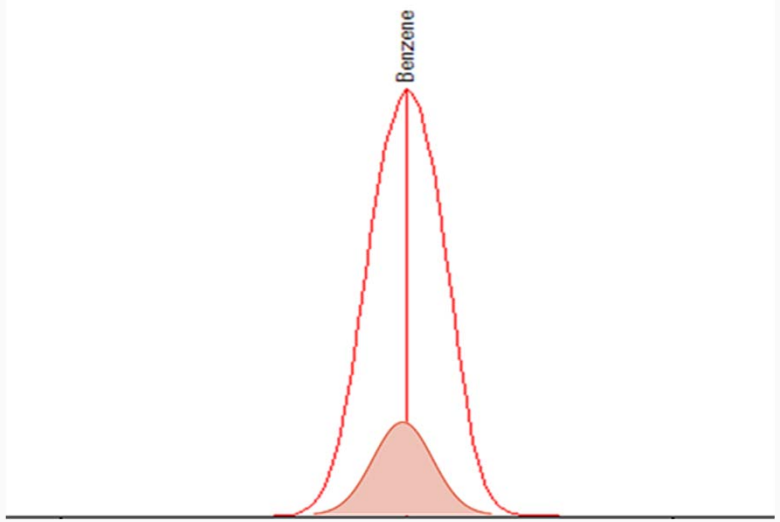
Need for Background-Corrected Calibration Curve

Uncorrected



$$Resp_{Total} = Resp_{Cmpd\ Loaded}$$

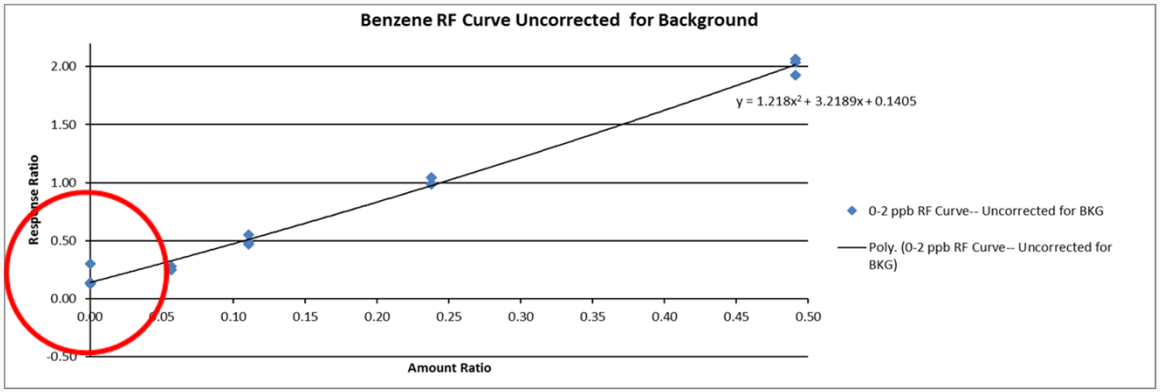
Corrected

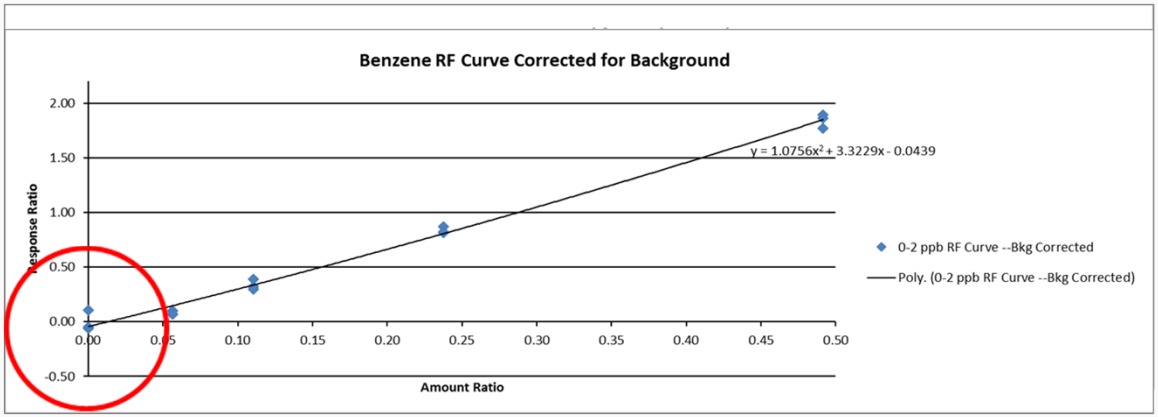


$$Resp_{Total} = Resp_{Cmpd\ loaded} + Resp_{Inherent\ Bkgd}$$

$$Resp_{cmpd\ loaded} = Resp_{Total} - Resp_{Inherent\ Bkgd}$$

Uncorrected vs Corrected Calibration Curves





MDLs

Compound	MDL, spikes* (ppbv)	MDL, blanks** (ppbv)
1,3-Butadiene	0.07	0.04
Trichlorofluoromethane (Freon 11)	0.01	0.19
Benzene	0.15	0.16
Carbon tetrachloride	0.05	0.00
Toluene	0.11	0.96
Tetrachloroethene	0.01	0.13
Ethylbenzene	0.04	0.12
m,p-Xylene	0.14	0.01
Styrene	0.05	0.19
m-Dichlorobenzene	0.07	0.00

*MDL calculated for 7 tubes diffusively loaded for 24 h with 0.25 ppbv TO-14 calibration standard
**MDL calculated using 7 randomly chosen laboratory blanks

Reproducibility

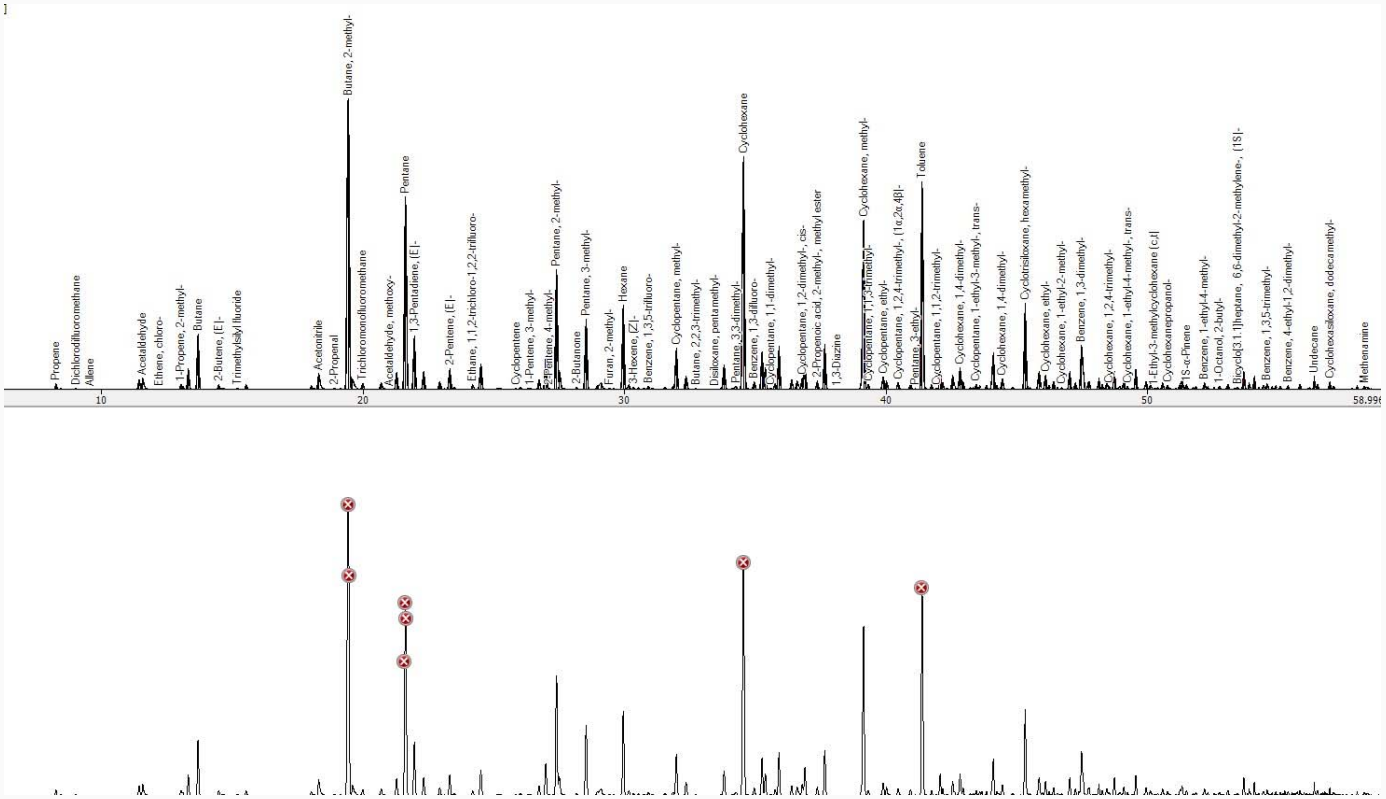
Compound	Reproducibility, % RSD*
1,3-Butadiene	5.59
Trichlorofluoromethane (Freon 11)	4.99
Benzene	5.40
Carbon tetrachloride	28.7
Toluene	22.7
Tetrachloroethene	2.93
Ethylbenzene	3.91
m,p-Xylene	4.99
Styrene	5.31
m-Dichlorobenzene	9.31

* 2 ppbv daily check standards diffusively loaded, n = 28

Re-collection

- Uses include…
  - Assessment of high-low splits on the TD in a single sequence for optimization of TD methods
  - Optimizing the TOF method
  - Comparing standard versus soft ionization using a single control sample
  - Preserving field samples for reanalysis (used for qualitative information only)
- Future work includes investigation of the re-collection feature for quantitation of data

Non-targeted Compounds



Conclusions

- Original TOF systems more traditionally used in research/academic laboratory settings for analysis of small numbers of samples
- TOF systems offered sensitivity and full spectral information that we previously had in years past with our Varian Saturn ion trap system that was used for the DEARS Carbopack X work
- Currently using TD/GC BenchTOF Select in our high throughput VOC laboratory for analysis of samples collected on Carbopack X sorbent tubes (Rubbertown ~750 to date; Tire Crumb Research Study ~550)
- Pleased with flexibility of instrument – quantitative and qualitative applications (deconvolution software techniques, re-collection option, filament drops, and capability for determining non-targeted compounds) have benefited our laboratory

Conclusions (cont.)

- MDLs, reproducibility similar to that achieved with our previous TD/GC-MS systems (PerkinElmer ATD/Varian Saturn GC-ion trap and PerkinElmer ATD/Agilent GC-quadrupole MS)
- Internal standard introduction has been problematic with our system
- System is either up and running and stable for months or instrument goes down and we may be down for awhile
- Acclimation to software and methods development takes a great deal of time and focus, we have a dedicated operator in our laboratory, there's no lack of data to process!!!

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