VOCs in Field Air

Presenters: Randy Maddalena, Ph.D., LBNL

Overview of Non-Targeted Analysis for VOCs

- Sample collection methods
  - Laboratory based
    - emission chamber
    - direct thermal desorption
    - stir-bar sorptive extraction
  - Field based
    - on-site and off-site
    - spatially/temporally distributed
    - stratified elevation above surface
- Sample extraction and analysis
- Data analysis
  - Anatomy of a chromatogram
  - Targeted and non-targeted approach

Carbopak thermal desorption air sampling tube

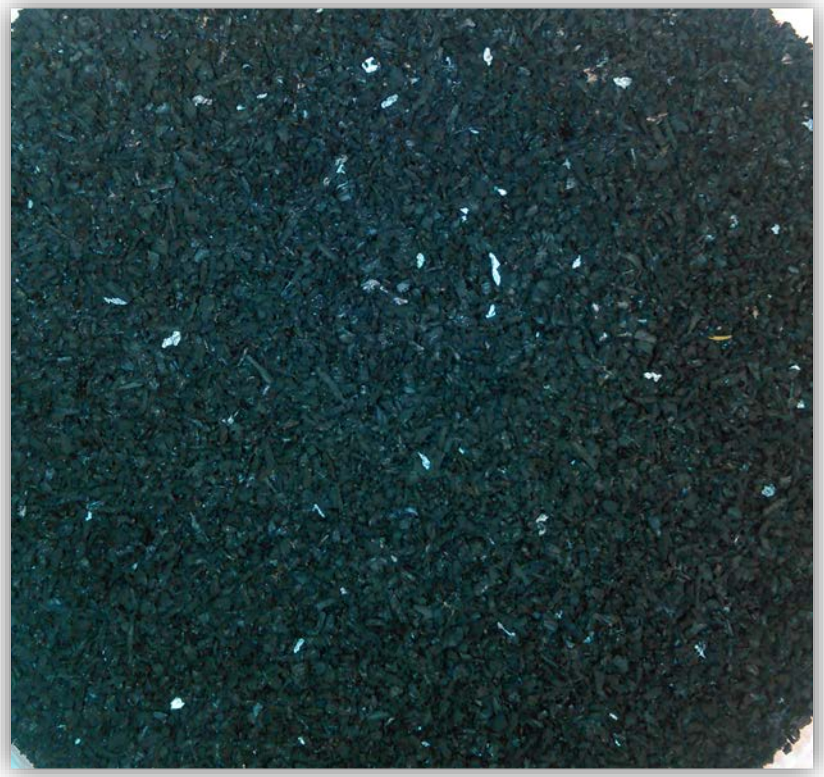
Sample Collection
Laboratory Based: Emission Chamber

Materials

Turf backing

Turf blades

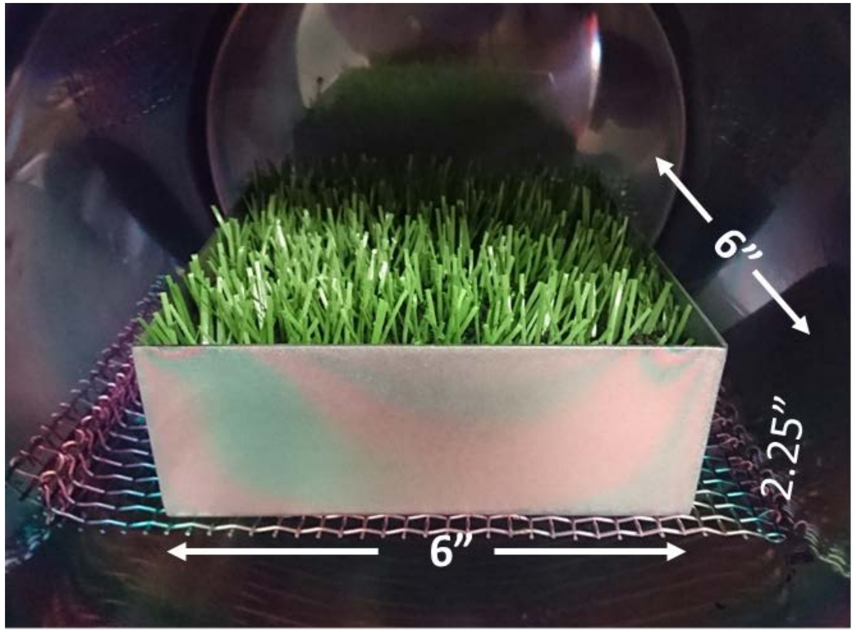
+



Crumb infill material

Emission Chamber: Experimental Unit

- 6 X 6 X 2 ¼ inch deactivated stainless steel tray with
- Synthetic turf backing and blade panels cut to fit and
- 100% crumb infill material added to ~ 2 inch depth

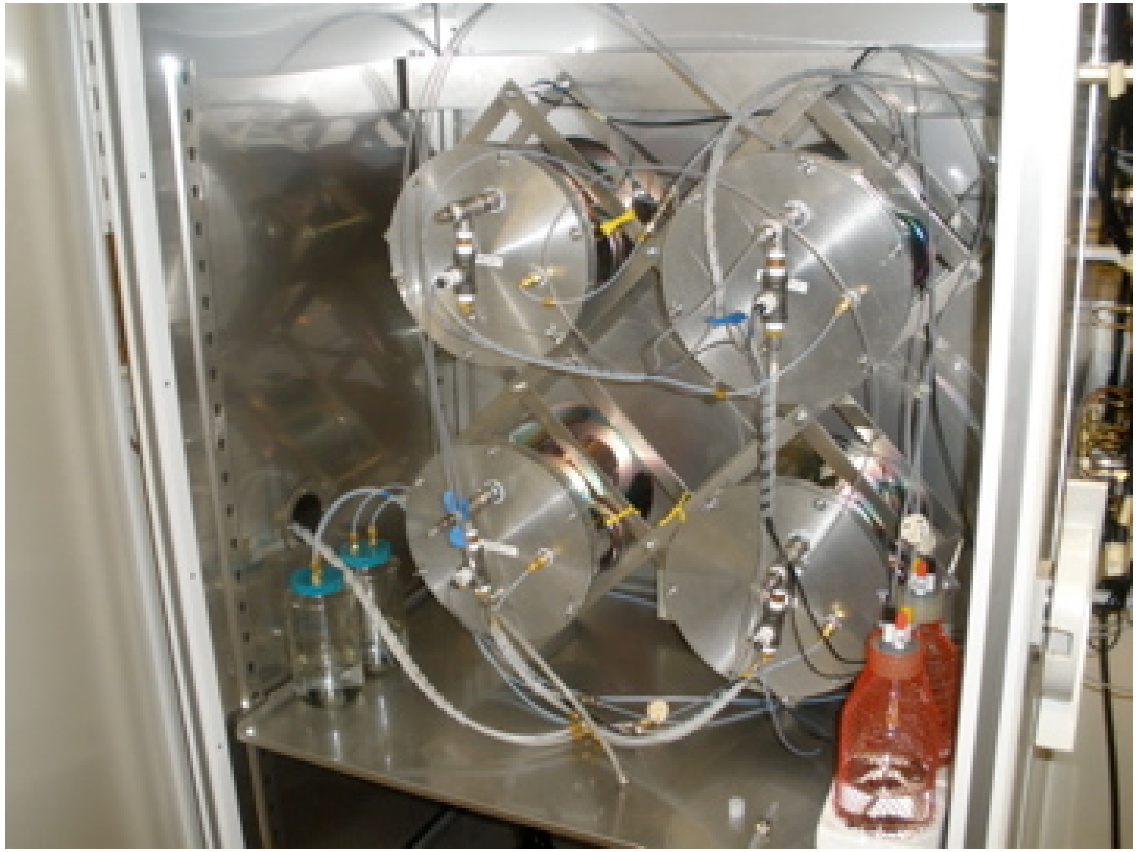


side view

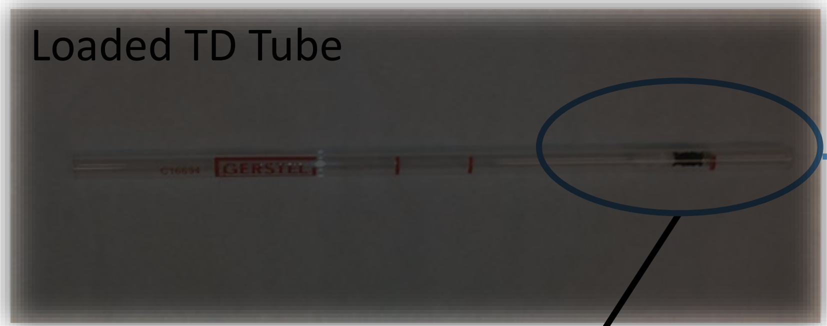
top view

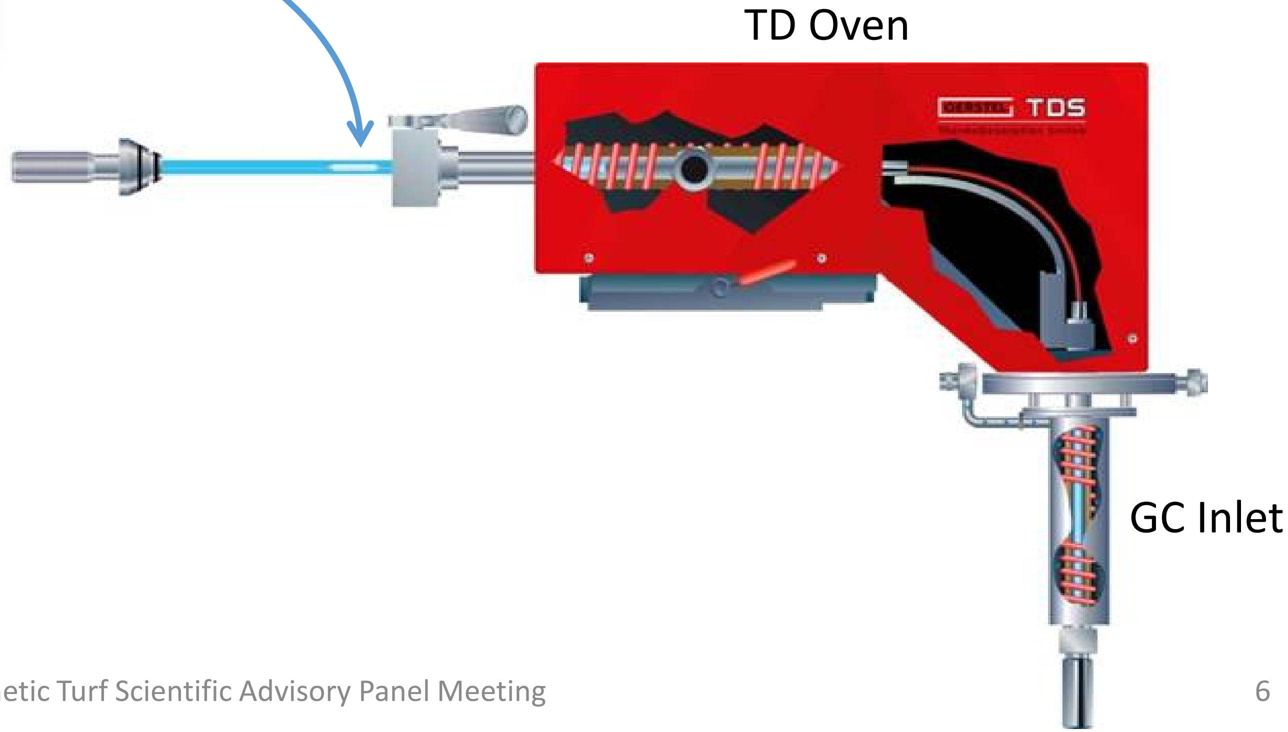
Emission Chamber: Test Protocol

- All wet surfaces deactivated (Sulfinert® and Teflon)
- Chamber volume 10.75 Liters
- Ventilation controlled @ ~ 1 LPM (ACH = 5.6 h^{-1})
- Temperature controlled @ 25 C
- Relative humidity controlled @ 50%
- Samples collected directly from chamber outflow onto TD tubes



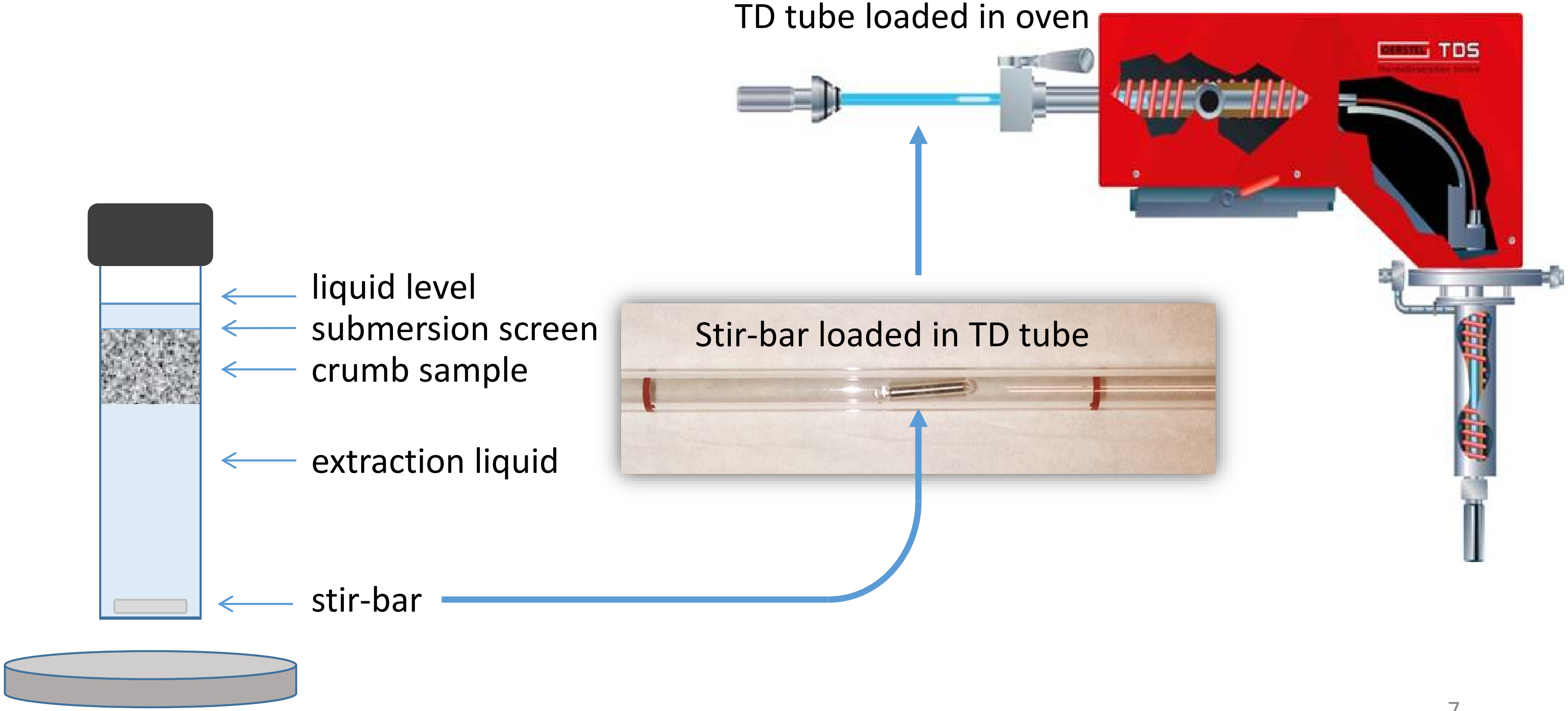
Sample Collection
Laboratory Based: Direct Thermal Desorption





Sample collection
Laboratory Based: Stir-Bar Sorptive Extraction

Polymer coated glass covered magnetic stir bar immersed in liquid



TD tube loaded in oven

liquid level

submersion screen

crumb sample

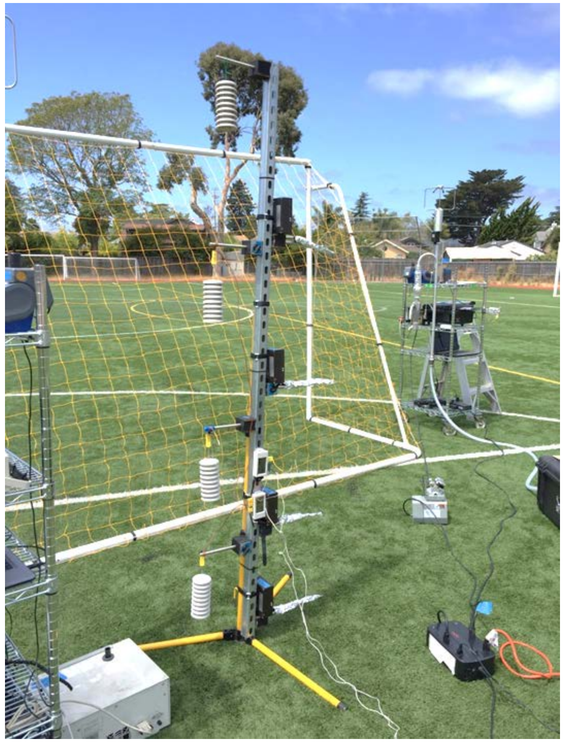
Stir-bar loaded in TD tube

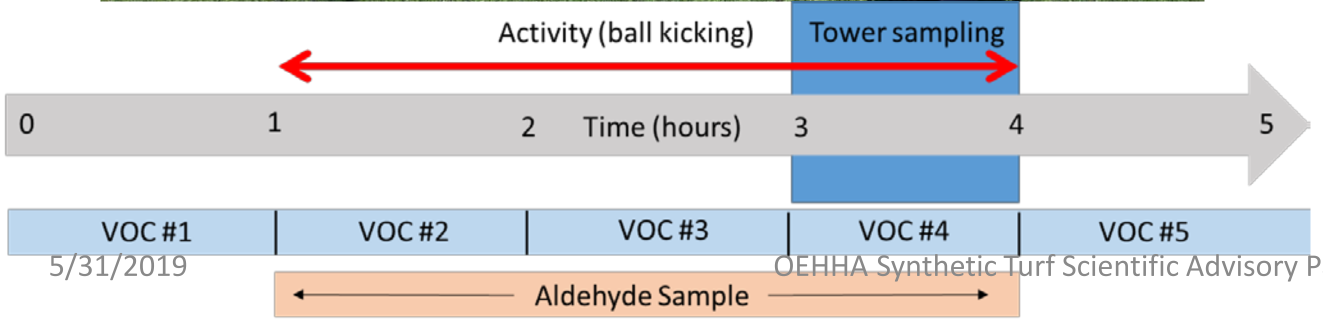
extraction liquid

stir-bar

Stirring & warming plate

Sample Collection
Field Based: Spatial and Temporal Coverage





Air samples collected from multiple locations **on** field and **off** field and at different **elevations** above surface at different **times** with and without **activity**

Sample Collection Summary

- Lab based samples provide highly controlled direct link between synthetic turf materials and chromatographic outcome, i.e., we have high confidence that detected chemicals are associated with crumb
- Field based samples capture wide range of spatial, temporal and environmental parameter variability adding complexity to chemical analysis but also adding representativeness

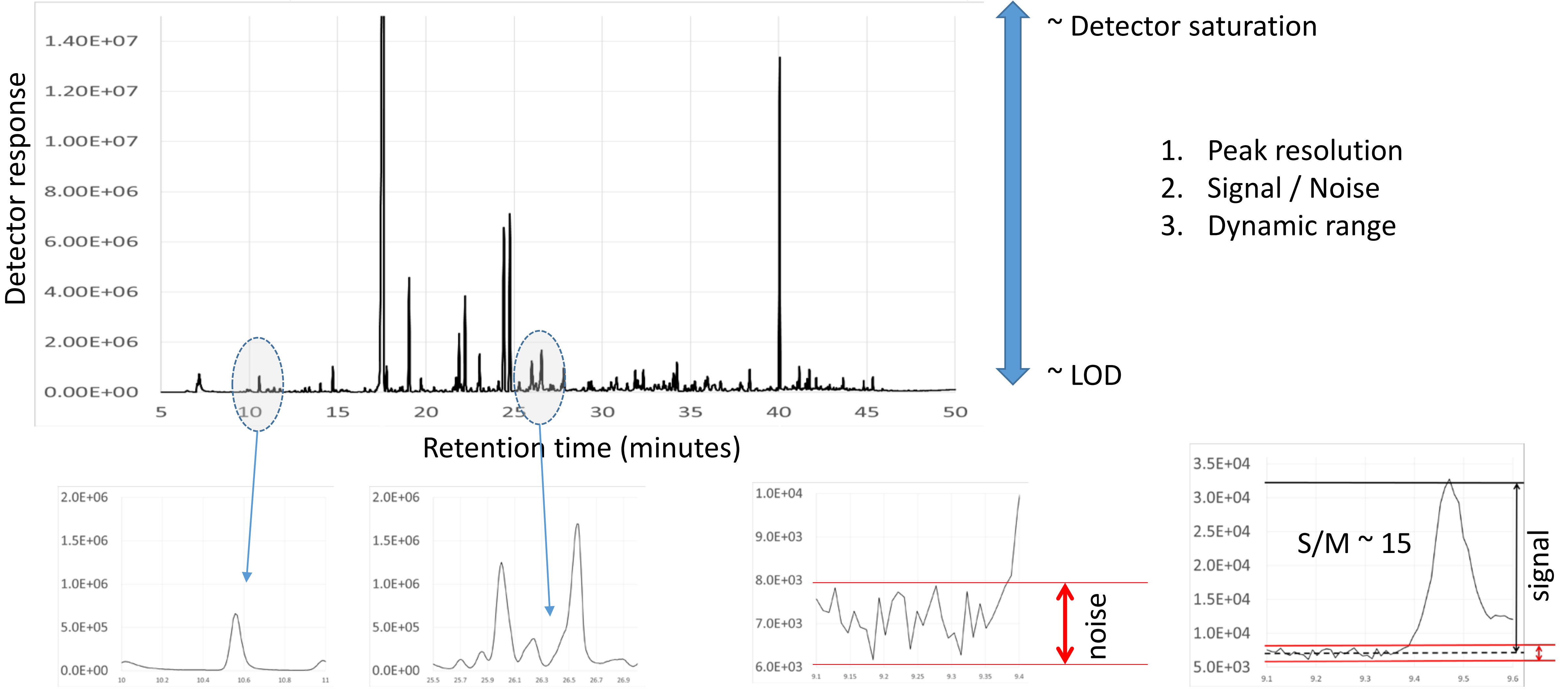
Sample Extraction and Analysis

- All VOC extractions performed by thermal desorption (Gerstel TDS3 oven with cryogenically cooled Tenax filled inlet liner and TDSA2 autosampler)
- All VOC analysis run on HP 6890 GC with Restek rxi624Sil (30 m X 250 μm w/ 1.4 μm film thickness) column and detected by HP 5973 quadrapole mass selective detector at 70 eV.
- Analysis conducted in full scan mode (typical quantification limits ~ 1 – 5 ng on column)

Data Analysis

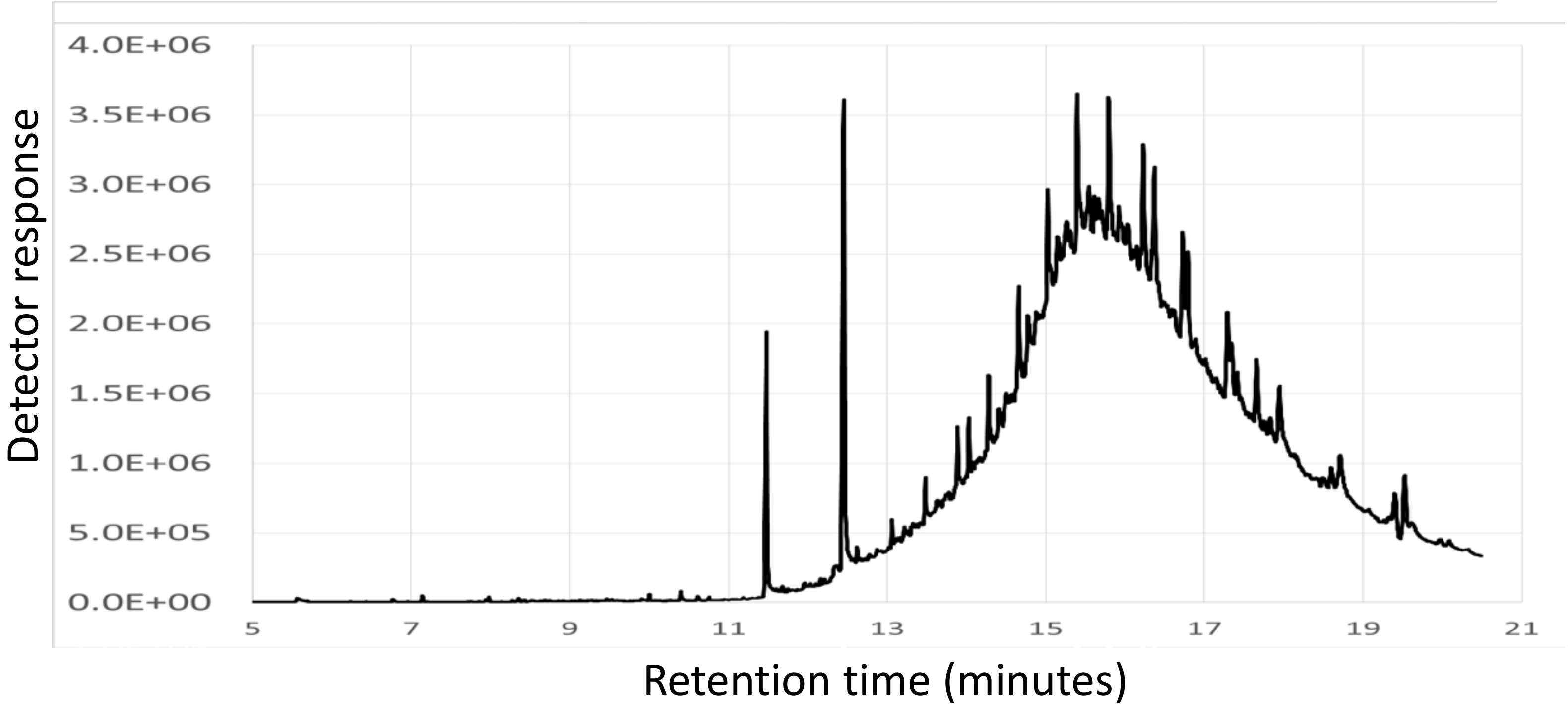
- Two basic approaches to identify chemicals in an analysis
  1. Targeted analysis – Is it in the sample? (we know what we are looking for, can we match it with a peak?)
  2. Non-targeted analysis – What is in the sample? (we have a peak, can we match it with a chemical?)
- Most efficient strategy uses a combination of these two approaches along with a healthy dose of professional judgement
- Either approach converges on matching mass spectra (or exact mass) AND matching a retention time to a known standard

Anatomy of Instrumental Analysis



1. Peak resolution
2. Signal / Noise
3. Dynamic range

Anatomy of Instrumental Analysis

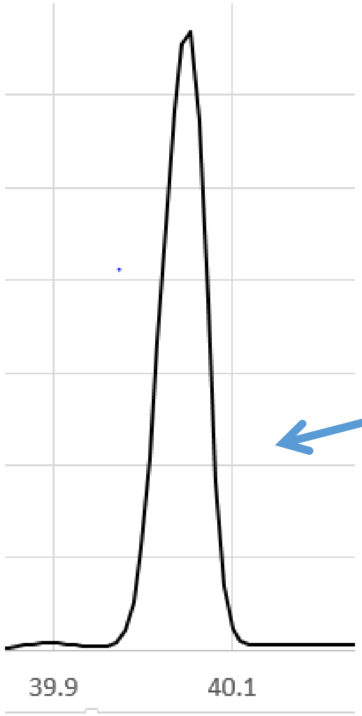


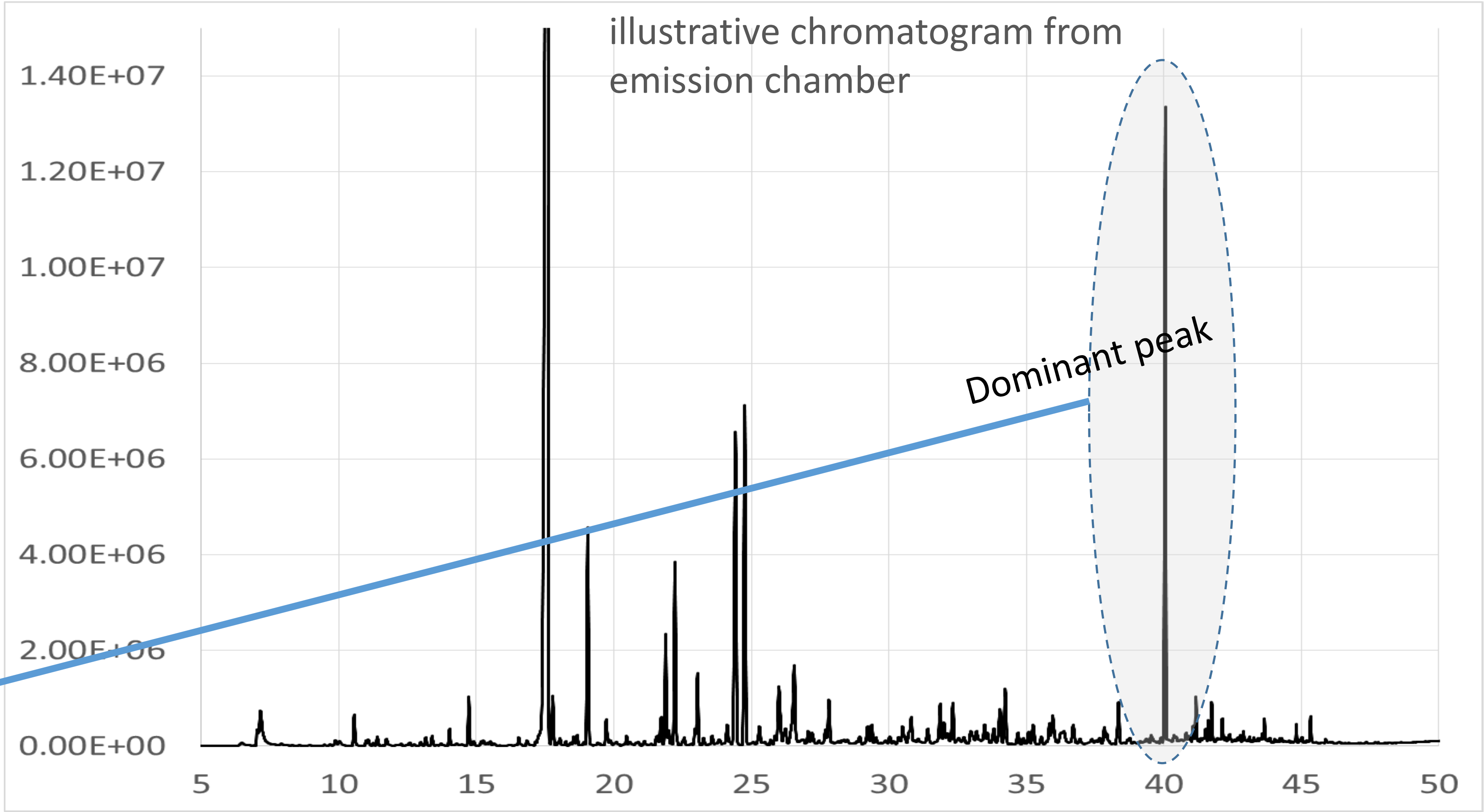
1. Peak resolution
2. Signal / Noise
3. Dynamic range
4. Complexity

What influences our ability to ID targets?

- Chromatographic resolution is the degree of separation in the signal
  - Different chemicals separate differently on a column
  - Tools are available to mathematically separate peaks given enough signal
- signal-to-noise is the difference between a small peak and “background”
  - A typical S/N ratio during peak identification is ~ 100 but can go much lower when we have specific targets
- dynamic range goes from detection limit to detector saturation
  - Can adjust by changing sample size/volume
  - Once set, this dictates the size of the smallest peaks
  - Can go after smaller peaks with pre-analysis chemistry
- sample complexity considers all of the above
  - Can reduce complexity using chemistry (i.e., cleanup, fractionation, enrichment, ...)

Finding Matches: Larger well resolved peaks

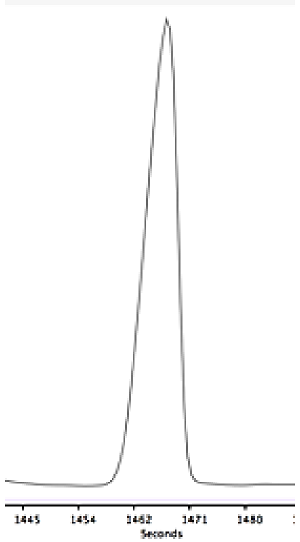




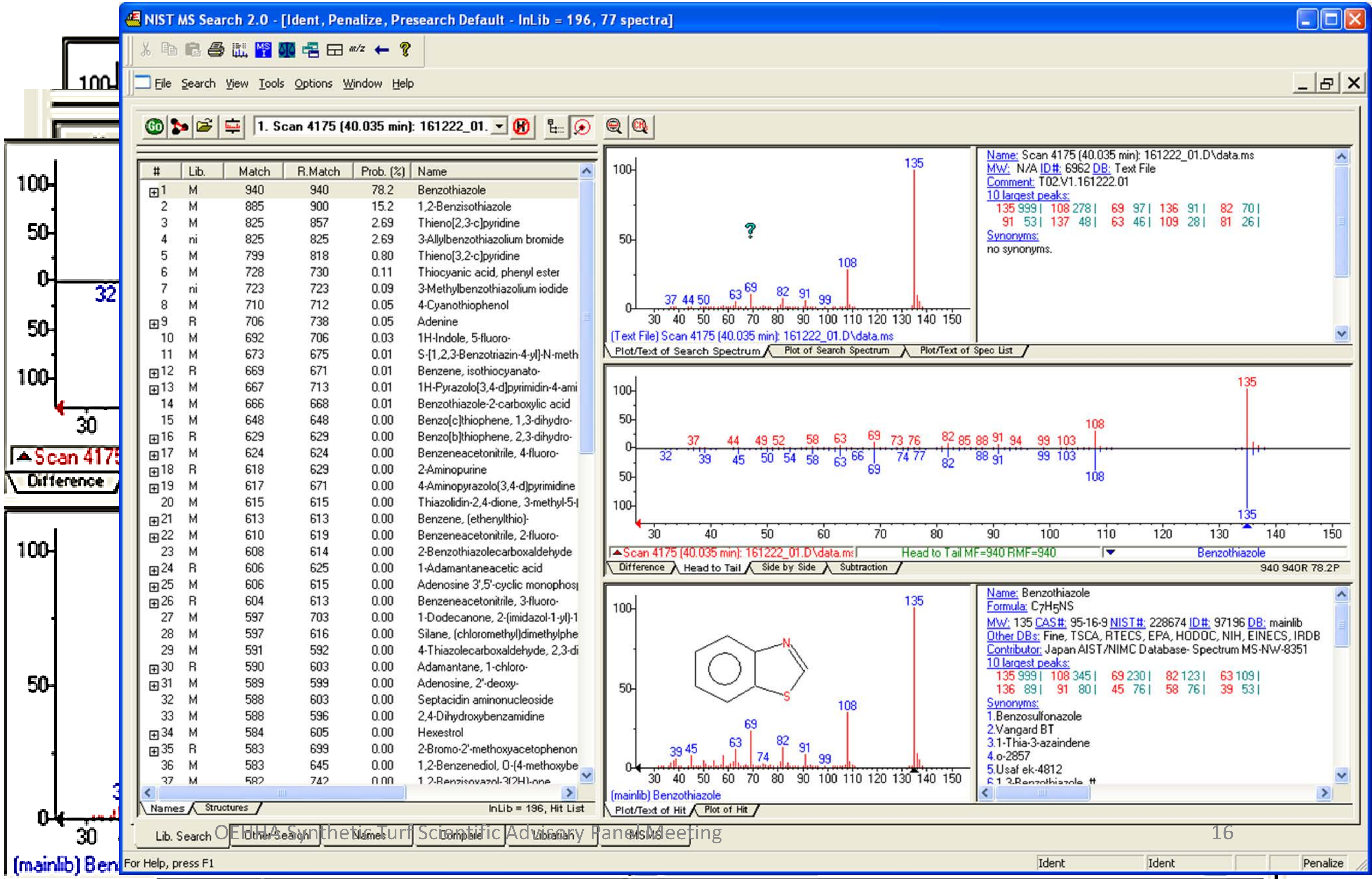
- Dominant peaks in samples are almost always readily available in mass spectral library

Identifying dominant peaks

Peak in chromatogram



Send to data matching software



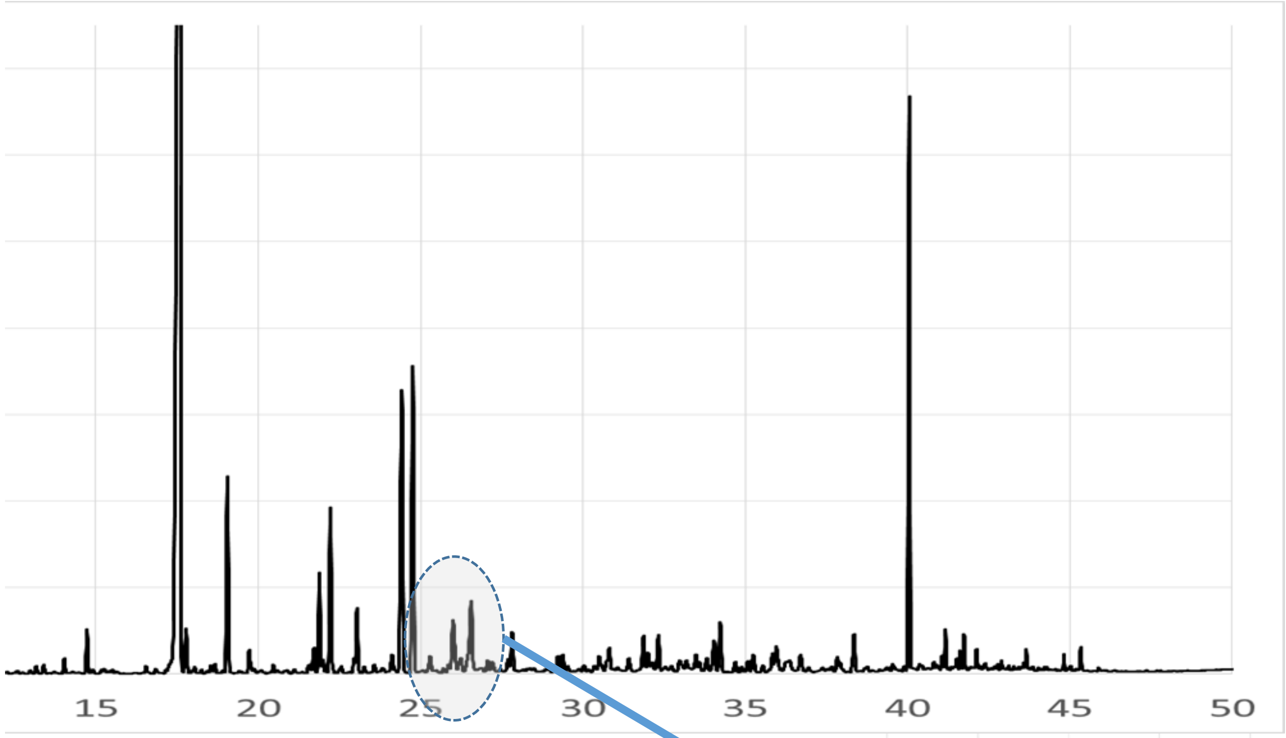
#	Lib.	Match	R.Match	Prob. (%)	Name
⊞1	M	940	940	78.2	Benzothiazole
2	M	885	900	15.2	1,2-Benzisothiazole
3	M	825	857	2.69	Thieno[2,3-c]pyridine
4	ni	825	825	2.69	3-Allylbenzothiazolium bromide
5	M	799	818	0.80	Thieno[3,2-c]pyridine
6	M	728	730	0.11	Thiocyanic acid, phenyl ester
7	ni	723	723	0.09	3-Methylbenzothiazolium iodide
8	M	710	712	0.05	4-Cyanothiophenol
⊞9	R	706	738	0.05	Adenine
10	M	692	706	0.03	1H-Indole, 5-fluoro-
11	M	673	675	0.01	S-[1,2,3-Benzotriazin-4-yl]-N-meth
⊞12	R	669	671	0.01	Benzene, isothiocyanato-
⊞13	M	667	713	0.01	1H-Pyrazolo[3,4-d]pyrimidin-4-ami
14	M	666	668	0.01	Benzothiazole-2-carboxylic acid
15	M	648	648	0.00	Benzo[c]thiophene, 1,3-dihydro-
⊞16	R	629	629	0.00	Benzo[b]thiophene, 2,3-dihydro-
⊞17	M	624	624	0.00	Benzeneacetonitrile, 4-fluoro-
⊞18	R	618	629	0.00	2-Aminopurine
⊞19	M	617	671	0.00	4-Aminopyrazolo(3,4-d)pyrimidine
20	M	615	615	0.00	Thiazolidin-2,4-dione, 3-methyl-5-[
⊞21	M	613	613	0.00	Benzene, (ethenylthio)-
⊞22	M	610	619	0.00	Benzeneacetonitrile, 2-fluoro-
23	M	608	614	0.00	2-Benzothiazolecarboxaldehyde
⊞24	R	606	625	0.00	1-Adamantaneacetic acid
⊞25	M	606	615	0.00	Adenosine 3',5'-cyclic monophos
⊞26	R	604	613	0.00	Benzeneacetonitrile, 3-fluoro-
27	M	597	703	0.00	1-Dodecanone, 2-(imidazol-1-yl)-1
28	M	597	616	0.00	Silane, (chloromethyl)dimethylphe
29	M	591	592	0.00	4-Thiazolecarboxaldehyde, 2,3-di
⊞30	R	590	603	0.00	Adamantane, 1-chloro-
⊞31	M	589	599	0.00	Adenosine, 2'-deoxy-
32	M	588	603	0.00	Septacidin aminonucleoside
33	M	588	596	0.00	2,4-Dihydroxybenzamidine
⊞34	M	584	605	0.00	Hexestrol
⊞35	R	583	699	0.00	2-Bromo-2'-methoxyacetophenon
36	M	583	645	0.00	1,2-Benzenediol, O-(4-methoxybe
37	M	582	742	0.00	1,2-Benzisoxazol-3(2H)-one

Name: Scan 4175 (40.035 min): 161222_01.D\data.ms
MW: N/A ID#: 6962 DB: Text File
Comment: T02.V1.161222.01
10 largest peaks:
135 999 | 108 278 | 69 97 | 136 91 | 82 70 |
91 53 | 137 48 | 63 46 | 109 28 | 81 26 |
Synonyms:
no synonyms.

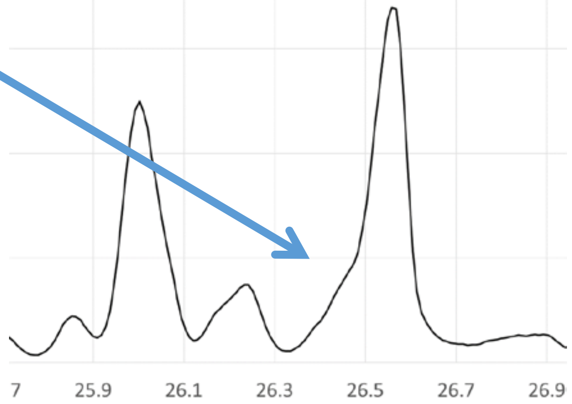
Name: Benzothiazole
Formula: C_7H_5NS
MW: 135 CAS#: 95-16-9 NIST#: 228674 ID#: 97196 DB: mainlib
Other DBs: Fine, TSCA, RTECS, EPA, HODOC, NIH, EINECS, IRDB
Contributor: Japan AIST/NIMC Database- Spectrum MS-NW-8351
10 largest peaks:
135 999 | 108 345 | 69 230 | 82 123 | 63 109 |
136 89 | 91 80 | 45 76 | 58 76 | 39 53 |
Synonyms:
1.Benzosulfonazole
2.Vangard BT
3.1-Thia-3-azaindene
4.o-2857
5.Usaf ek-4812
6.1,3-Benzothiazole, #

Finding Matches: Smaller less resolved peaks

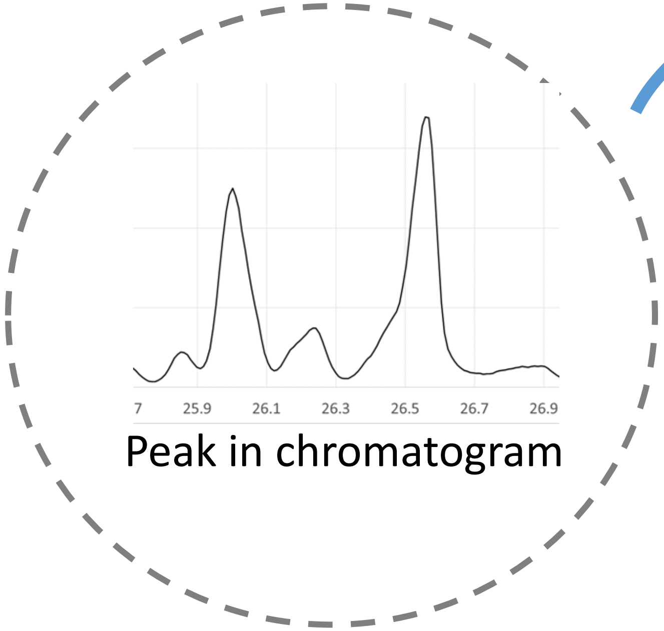
- Weak peaks or peaks that are not well resolved from other compounds sometimes do not match library because of interfering mass ions
- Options for improving chances of finding match



1. improve separation (modify method, new column, chemical techniques)
2. utilize a different detector (can narrow the possibilities)
3. increase sample volume (peak size) (also sometimes increases noise) and/or
4. mathematically “clean” the peak with deconvolution software

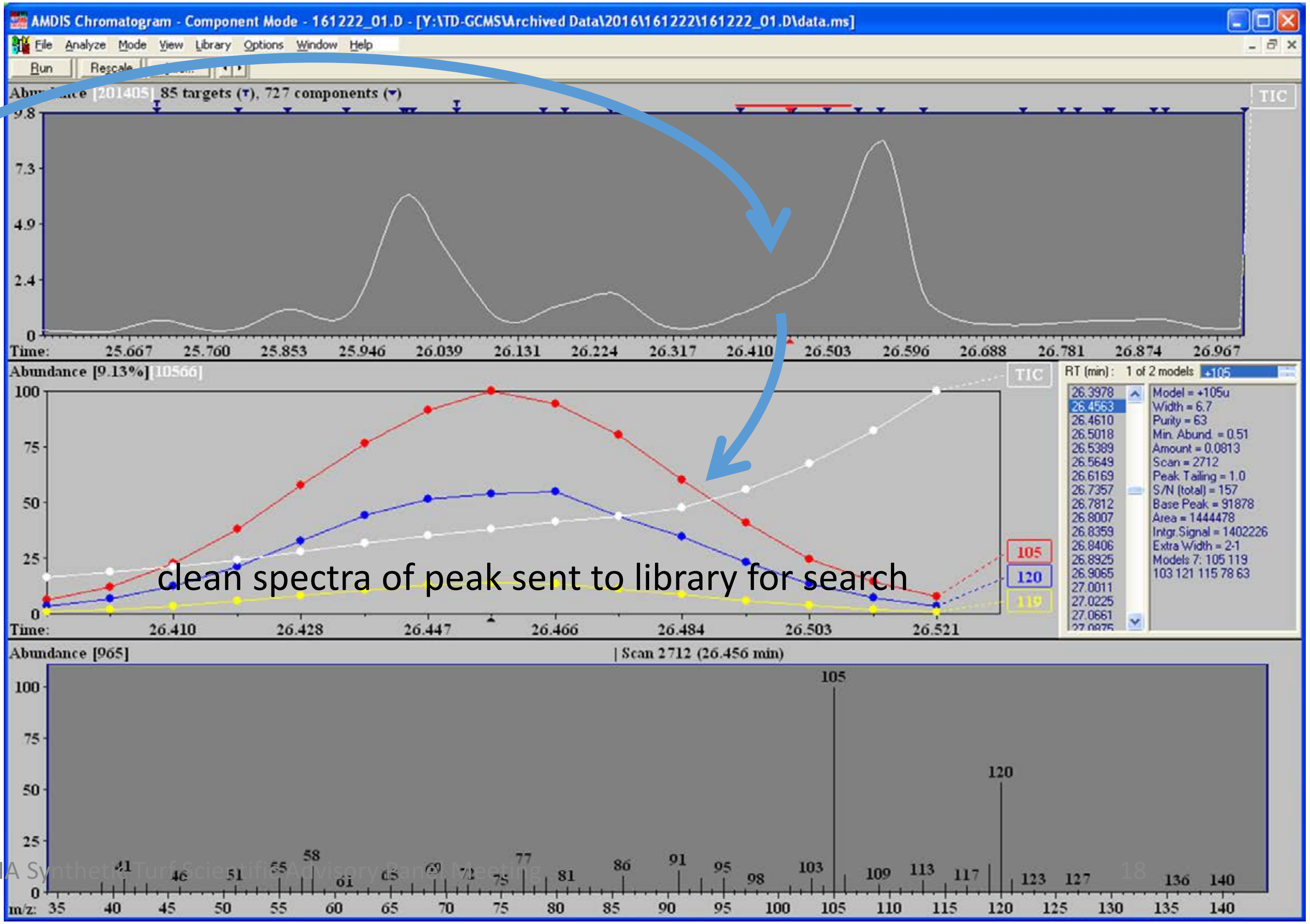


Cleaning up a convoluted peak



Peak in chromatogram

Automated Mass Spectral Deconvolution and Identification System (AMDIS)



RT (min): 1 of 2 models +105

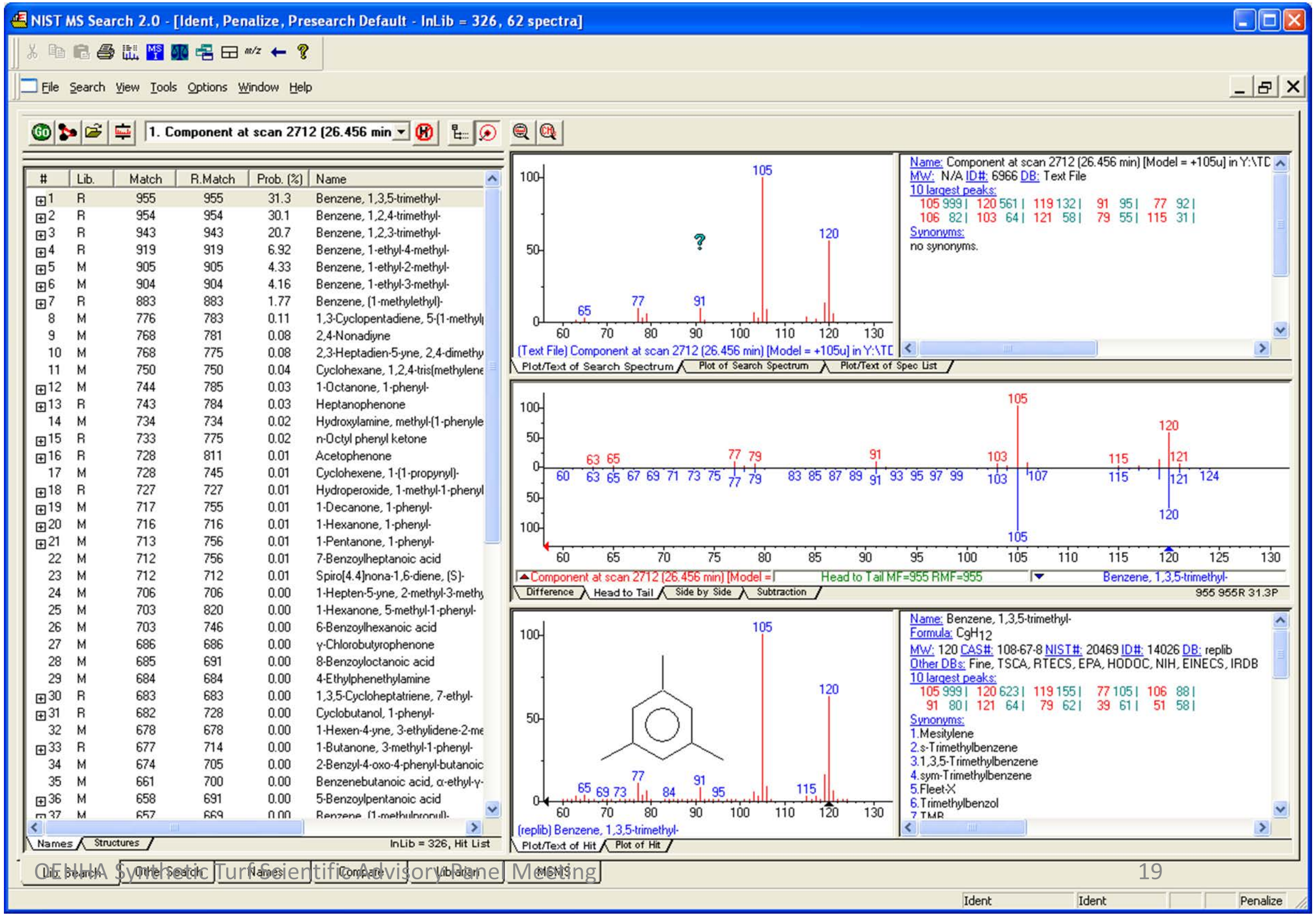
26.3978
26.4563
26.4610
26.5018
26.5389
26.5649
26.6169
26.7357
26.7812
26.8007
26.8359
26.8406
26.8925
26.9065
27.0011
27.0225
27.0661

Model = +105u
Width = 6.7
Purity = 63
Min. Abund. = 0.51
Amount = 0.0813
Scan = 2712
Peak Tailing = 1.0
S/N (total) = 157
Base Peak = 91878
Area = 1444478
Intgr.Signal = 1402226
Extra Width = 2-1
Models 7: 105 119 103 121 115 78 63

clean spectra of peak sent to library for search

Identifying deconvoluted spectra

- The deconvoluted mass spectra provide higher likelihood of finding match
- Specific congeners may not be identified
- Confirmation requires compare mass spectra AND retention time on specific instrument with pure standard



#	Lib.	Match	R.Match	Prob. (%)	Name
⊞1	R	955	955	31.3	Benzene, 1,3,5-trimethyl-
⊞2	R	954	954	30.1	Benzene, 1,2,4-trimethyl-
⊞3	R	943	943	20.7	Benzene, 1,2,3-trimethyl-
⊞4	R	919	919	6.92	Benzene, 1-ethyl-4-methyl-
⊞5	M	905	905	4.33	Benzene, 1-ethyl-2-methyl-
⊞6	M	904	904	4.16	Benzene, 1-ethyl-3-methyl-
⊞7	R	883	883	1.77	Benzene, (1-methylethyl)-
8	M	776	783	0.11	1,3-Cyclopentadiene, 5-(1-methyl
9	M	768	781	0.08	2,4-Nonadiyne
10	M	768	775	0.08	2,3-Heptadien-5-yne, 2,4-dimethy
11	M	750	750	0.04	Cyclohexane, 1,2,4-tris(methylene
⊞12	M	744	785	0.03	1-Octanone, 1-phenyl-
⊞13	R	743	784	0.03	Heptanophenone
14	M	734	734	0.02	Hydroxylamine, methyl-(1-phenyle
⊞15	R	733	775	0.02	n-Octyl phenyl ketone
⊞16	R	728	811	0.01	Acetophenone
17	M	728	745	0.01	Cyclohexene, 1-(1-propynyl)-
⊞18	R	727	727	0.01	Hydroperoxide, 1-methyl-1-phenyl
⊞19	M	717	755	0.01	1-Decanone, 1-phenyl-
⊞20	M	716	716	0.01	1-Hexanone, 1-phenyl-
⊞21	M	713	756	0.01	1-Pentanone, 1-phenyl-
22	M	712	756	0.01	7-Benzoylheptanoic acid
23	M	712	712	0.01	Spiro[4.4]nona-1,6-diene, (S)-
24	M	706	706	0.00	1-Hepten-5-yne, 2-methyl-3-methy
25	M	703	820	0.00	1-Hexanone, 5-methyl-1-phenyl-
26	M	703	746	0.00	6-Benzoylhexanoic acid
27	M	686	686	0.00	γ-Chlorobutyrophenone
28	M	685	691	0.00	8-Benzoyloctanoic acid
29	M	684	684	0.00	4-Ethylphenethylamine
⊞30	R	683	683	0.00	1,3,5-Cycloheptatriene, 7-ethyl-
⊞31	R	682	728	0.00	Cyclobutanol, 1-phenyl-
32	M	678	678	0.00	1-Hexen-4-yne, 3-ethylidene-2-me
⊞33	R	677	714	0.00	1-Butanone, 3-methyl-1-phenyl-
34	M	674	705	0.00	2-Benzyl-4-oxo-4-phenyl-butanoic
35	M	661	700	0.00	Benzenebutanoic acid, α-ethyl-γ-
⊞36	M	658	691	0.00	5-Benzoylpentanoic acid
⊞37	M	657	669	0.00	Benzene, (1-methylpropyl)-

InLib = 326, Hit List

Name: Component at scan 2712 (26.456 min) [Model = +105u] in Y:\TD
MW: N/A ID#: 6966 DB: Text File
10 largest peaks:
105 999 | 120 561 | 119 132 | 91 95 | 77 92 |
106 82 | 103 64 | 121 58 | 79 55 | 115 31 |
Synonyms:
no synonyms.

(Text File) Component at scan 2712 (26.456 min) [Model = +105u] in Y:\TD

Component at scan 2712 (26.456 min) [Model =
Head to Tail MF=955 RMF=955
Benzene, 1,3,5-trimethyl-
955 955R 31.3P

Name: Benzene, 1,3,5-trimethyl-
Formula: C_9H_{12}
MW: 120 CAS#: 108-67-8 NIST#: 20469 ID#: 14026 DB: replib
Other DBs: Fine, TSCA, RTECS, EPA, HODOC, NIH, EINECS, IRDB
10 largest peaks:
105 999 | 120 623 | 119 155 | 77 105 | 106 88 |
91 80 | 121 64 | 79 62 | 39 61 | 51 58 |
Synonyms:
1.Mesitylene
2.s-Trimethylbenzene
3.1,3,5-Trimethylbenzene
4.sym-Trimethylbenzene
5.Fleet-X
6.Trimethylbenzol
7.TMB

(replib) Benzene, 1,3,5-trimethyl-

Identified Chemicals in Field Air

Chemical Class/Matrix	Instrumental Analysis	No. of Confirmed Chemicals	No. of Tentatively Identified Chemicals
Polar Extract	LC/MS		
Non-Polar Extract	GC/MS	No Data	no data No data
PAHs	SIM-GC/MS		
Volatile carbonyls in Field Air	HPLC	11	0
VOCs in Field Air	TD-GC/MS	67	0
This cell was purposefully left empty	**Total**	**78**	**0**

- Volatile carbonyls include formaldehyde, acetaldehyde, acetone and other low molecular weight aldehydes
- Not all compounds identified in lab experiments were detected in field air

Summary of VOC identification method

- Targeted analysis
  - Include chemicals of particular interest
  - Use analytical standard to “train” the instrument to look for specific (mass fragmentation pattern) at specific retention time
- Non-targeted analysis
  - Dominant peaks identified by mass spectral library match
  - Poorly resolved or complex peaks deconvoluted then compare to library
  - Confirm with pure standard matching spectra AND retention time on labs instrument
  - Approach typically identifies 80 - 90% of chemical mass (response area) in a given sample

Non-Polar Constituents in Crumb Extracts

Presenter: Randy Maddalena, Ph.D., LBNL

Overview of Non-Targeted Analysis for Semi-Volatile and Low Volatile Chemicals by GC

- Sample type and collection method
  - Manufacturer crumb rubber material
  - Installed crumb rubber material harvested from field
- Sample extraction and analysis
- Data analysis
  - targeted (example = PAHs)
  - non-targeted

Sample type and collection

- Crumb rubber collected from manufacturers
  - material from bulk bags
  - extracted and analyzed as received
- Installed crumb rubber material harvested from fields
  - location specific samples on field such as high impact areas and low impact areas
  - field specific composite samples
  - all samples analyzed as received (i.e., did not sieve or try to separate sand, cork or other environmental contaminants)

Sample Extraction and Analysis

Crumb Rubber - manufacturer, location specific or composite

Loaded into extraction cell as received with inert dispersant

optimize sample volume

Extraction cell run in Accelerated Solvent Extraction System (ASE Model 200)

Pressurized heated organic solvent (1:1 Acetone/Hexanes) **w/o additional cleanup or enrichment**

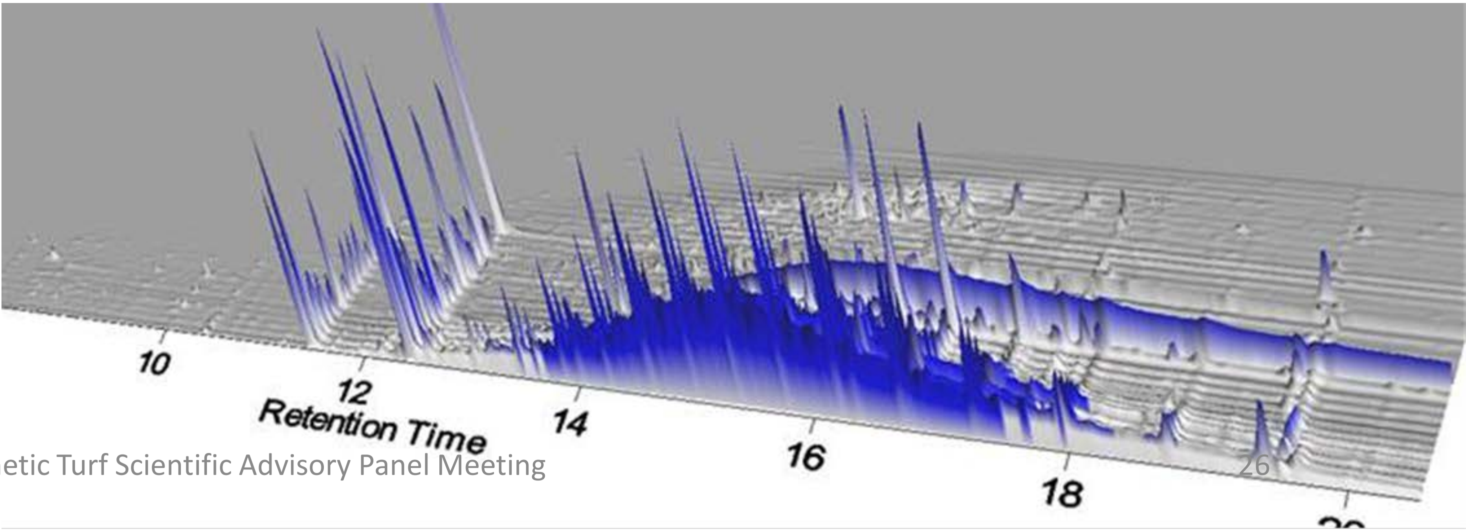
GCMS analysis Agilent GC 7890A with DB-UI 8270D column interfaced to 5977B Mass Selective Detector with High Efficiency Source **(typical detection < 1 pg on column**)

Pressurized warm aqueous solvent (9:1 Water/Methanol)

LCMS (next presentation)

Data Analysis: Non-Targeted Analysis

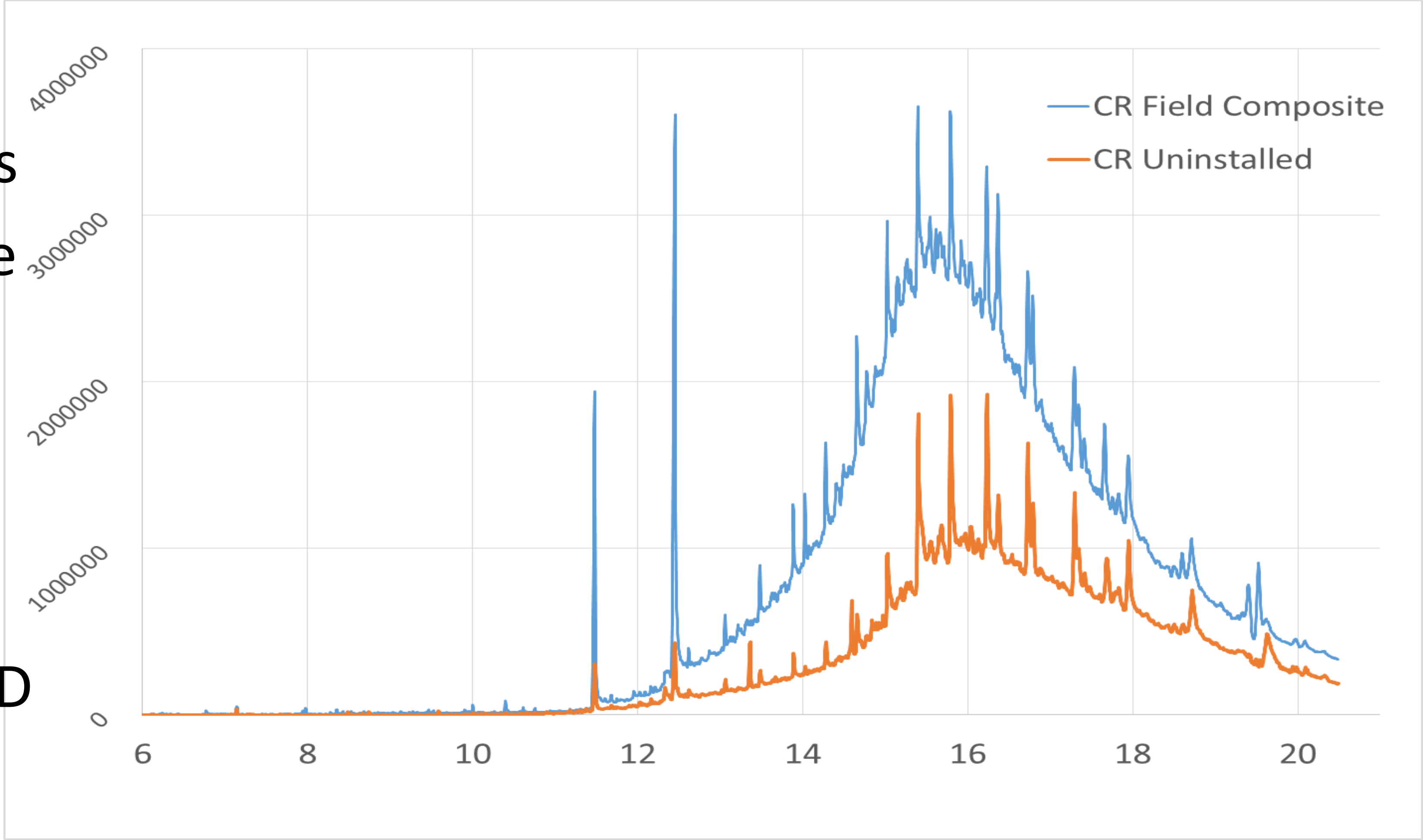
- Process is as described previously for VOCs but with the following differences
    1. Molecules typically larger with more complex mass spectra
    2. Detection limits several orders of magnitude lower than “full scan” VOC method (but not as low as SIM method used for targeted SVOC analysis)
    3. Chromatograms are much more complex (for the above reasons), particularly when aged



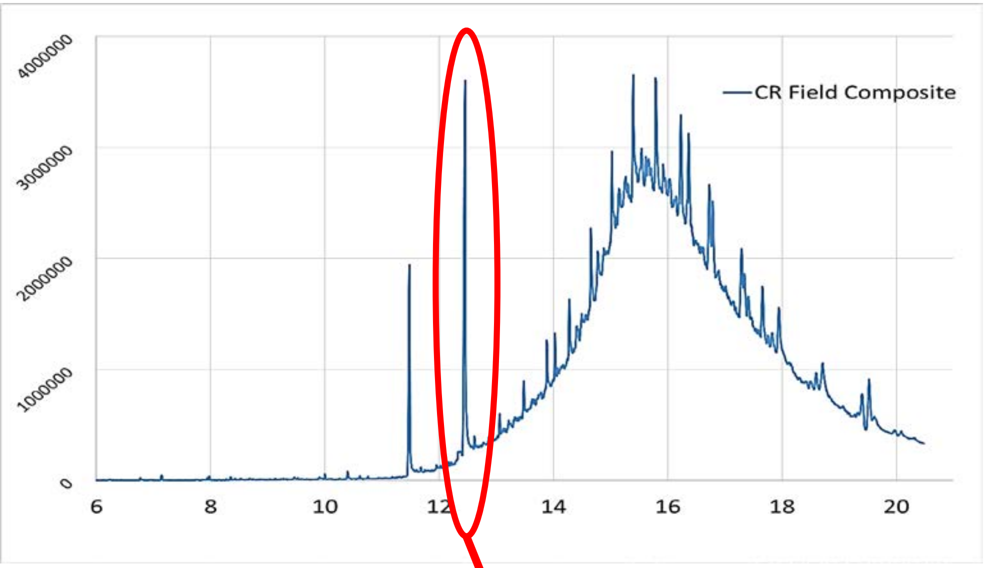
Data Analysis: Non-targeted Analysis

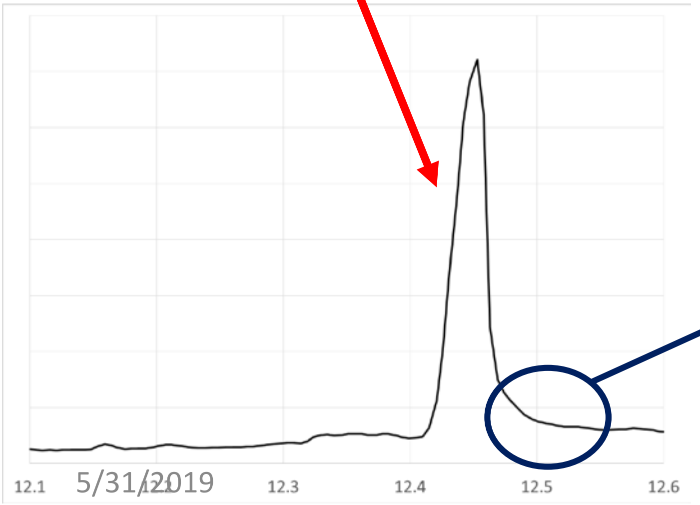
- Raw extracts have complex chromatograms
- Field samples have more unresolved

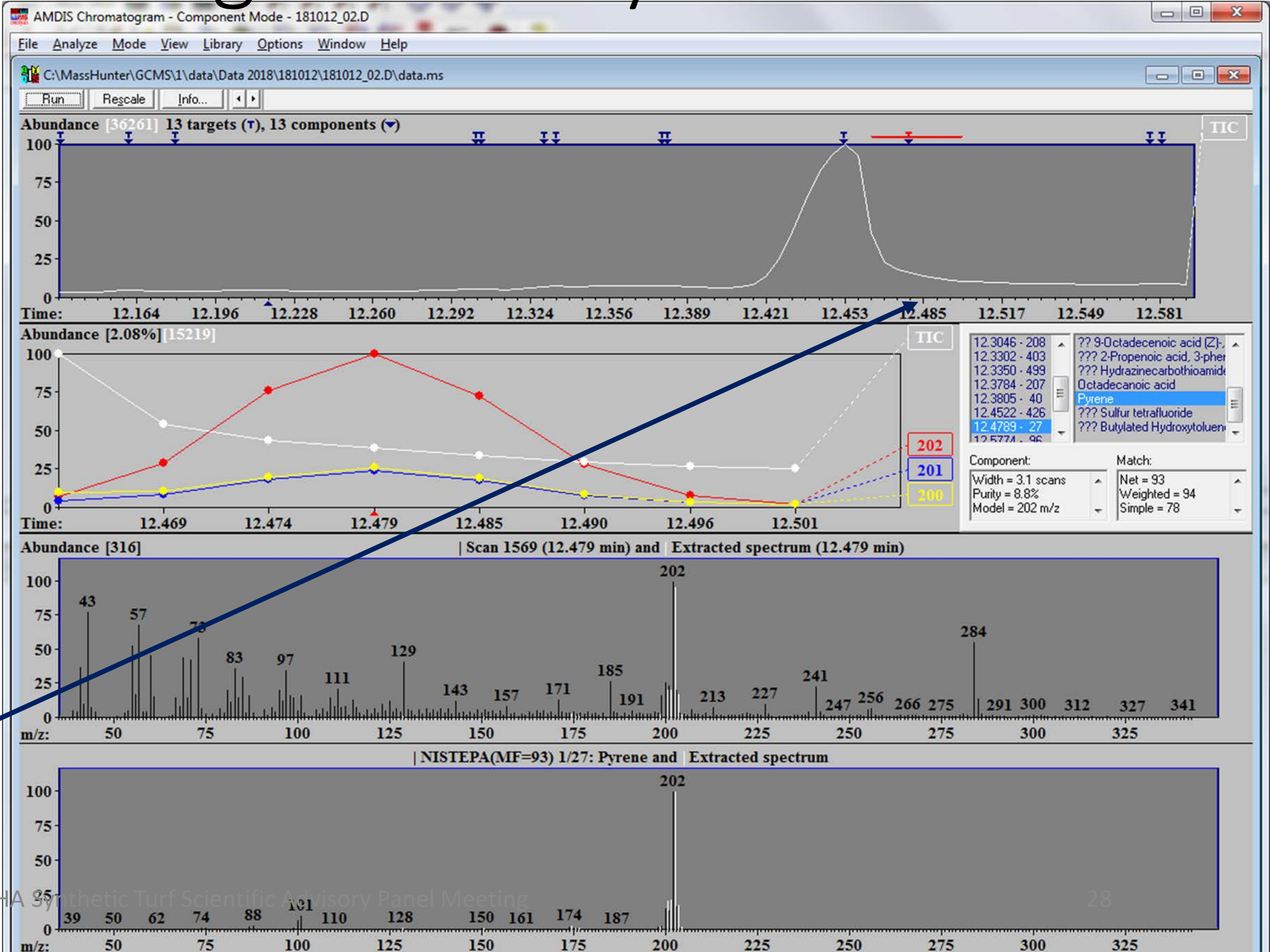
  (i.e., chromatographic hump)
- The humps make for highly complex mass spectra (see previous 3-D illustration)



Data Analysis: Non-Targeted Analysis







C:\MassHunter\GCMS\1\data\Data 2018\181012\181012_02.D\data.ms

Abundance [36261] 13 targets (T), 13 components (▼)

Abundance [2.08%] [15219]

12.3046 - 208
12.3302 - 403
12.3350 - 499
12.3784 - 207
12.3805 - 40
12.4522 - 426
12.4789 - 27
12.5774 - 96

?? 9-Octadecenoic acid (Z)-,
??? 2-Propenoic acid, 3-pher
??? Hydrazinecarbothioamide
Octadecanoic acid
Pyrene
??? Sulfur tetrafluoride
??? Butylated Hydroxytoluen

Component:
Width = 3.1 scans
Purity = 8.8%
Model = 202 m/z

Match:
Net = 93
Weighted = 94
Simple = 78

Abundance [316] | Scan 1569 (12.479 min) and | Extracted spectrum (12.479 min)

| NISTEPA(MF=93) 1/27: Pyrene and | Extracted spectrum

Data Analysis: Targeted Analysis

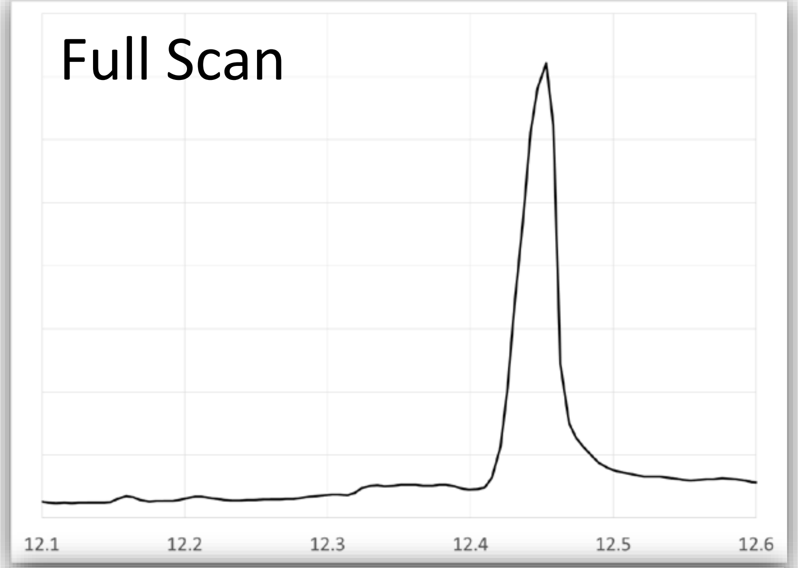
- Add isotopically labeled internal standards prior to extraction
- Liquid injection of extract (without cleanup or enrichment)
- Eighteen component mix of Polycyclic Aromatic Hydrocarbons with internal and recovery standards
- Selected ion monitoring (i.e., look only for targeted compounds)
- Compounds range from naphthalene (MW = 128 g/mol) to dibenz[a,h]anthracene (MW = 278 g/mol)
- Data analysis automated with performance review by analyst (basically we train the instrument what to look for)

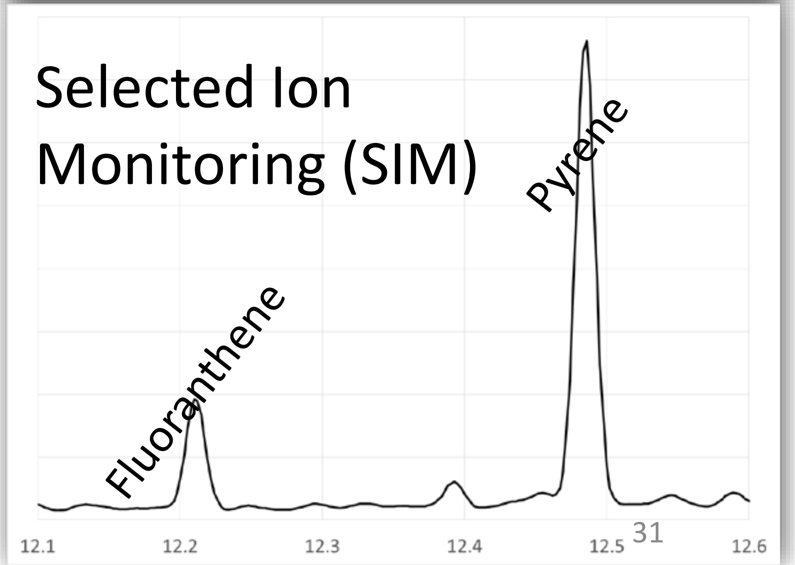
Identified Chemicals in Field Air

Chemical Class/Matrix	Instrumental Analysis	No. of Confirmed Chemicals	No. of Tentatively Identified Chemicals
Polar Extract	LC/MS		
Non-Polar Extract	GC/MS	32	182
PAHs	SIM-GC/MS	20	
Volatile carbonyls in Field Air	HPLC	11	0
VOCs in Field Air	TD-GC/MS	67	0
This cell was purposefully left empty	**Total**	**130**	**182**

Summary of SVOC (non-polar) ID method

- Targeting chemicals allows us to “see” at much lower levels in complex chromatograms
- The trade-off is that you only see what you are looking for
- Sample enrichment (i.e., concentration of extract) not needed because we optimize the mass of crumb extracted
- Not using “cleanup” steps on extract insures that all chemicals are included but many of these chemicals are of little interest (branched alkanes) and it is much harder on the instrument


Full Scan


Selected Ion Monitoring (SIM)