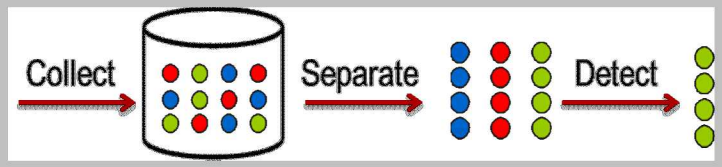
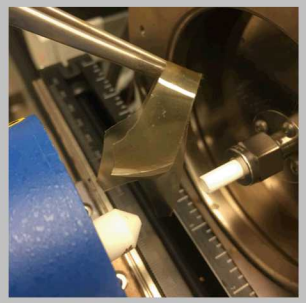
SAND2019-1180C





“Identification” of Unknown Outgassing Species Using Gas Chromatography-Mass Spectrometry

Curtis Mowry, Lance Miller, Adam Pimentel, Ray Fuentes
Sandia National Laboratories

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy’s National Nuclear Security Administration under contract DE-NA0003525.

Abstract

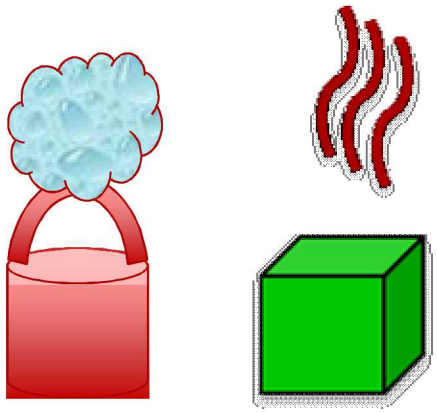
Sandia National Laboratories

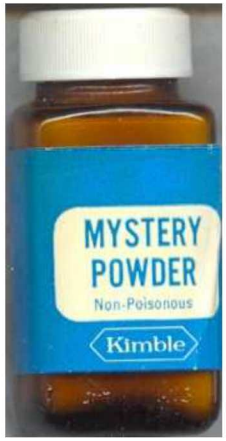
"Identification" of Unknown Outgassing Species Using Gas Chromatography-Mass Spectrometry

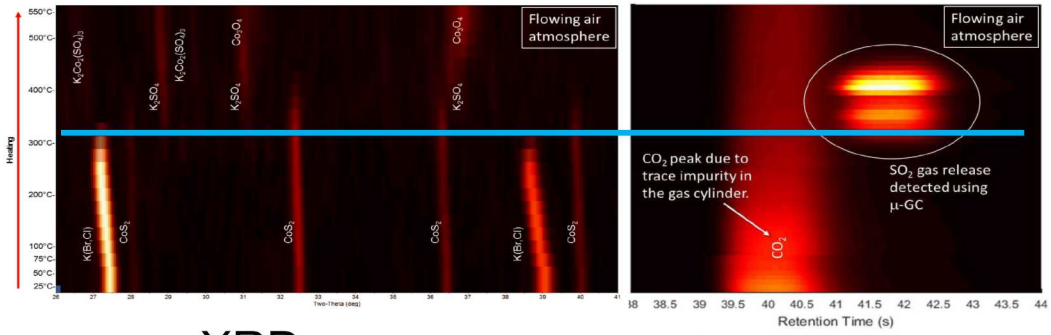
Chemical species can be released, or outgassed, from materials such as polymers, epoxies, or foams. These species can be unreacted starting materials or the product of complex decomposition reactions and once released can interact with other materials. A conformal coating was discovered to outgas which created concern regarding aging and interactions with other materials. To understand the risk, experiments were undertaken to identify specific products and quantities. Outgassing was assessed after various treatments (heat, vacuum, etc.) which would mitigate some source terms and is a common strategy for certification by manufacturers and those performing outgassing measurements. One major outgassed product detected in GC/MS (gas chromatography with mass spectrometry detection) experiments, however, was assigned with high confidence as two different species by two labs. Strange? Yes. In this situation it was possible for the measurement method to alter the measured species, so identification confidence based on library spectral matching was high. We will discuss the tools and process that demonstrates both labs were correct! This situation highlights the need sometimes to perform additional experiments to identify a true unknown species involved with critical materials and component investigations. We must remember that any analytical method is only detecting a small subset of the chemical space. Various authors are attempting to define the process of generating and communicate true "confidence" for GC/MS data [1,2]. Details and discussion of the Uvikote story are presented in this context of identifying unknown outgassed products.

1. Milman, B. L.; Zhurkovich, I. K., The chemical space for non-target analysis. TrAC Trends in Analytical Chemistry 2017, 97, 179-187.
2. Schymanski, E. L.; Jeon, J.; Gulde, R.; Fenner, K.; Ruff, M.; Singer, H. P.; Hollender, J., Identifying Small Molecules via High Resolution Mass Spectrometry: Communicating Confidence. Environ Sci Technol 2014, 48 (4), 2097-8.

Many Materials Outgas







XRD map

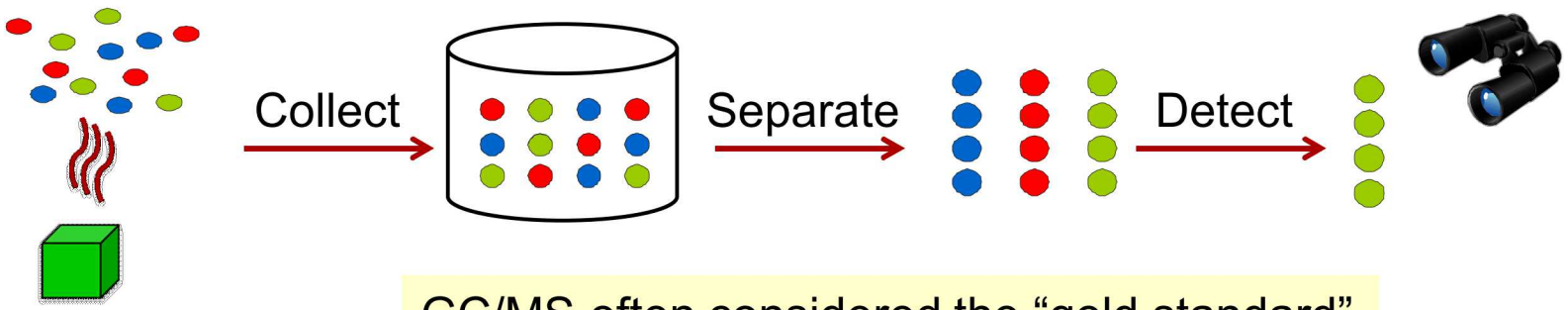
Gas data map

M. A. Rodriguez, E. N. Coker, J. J. M. Griego, C. D. Mowry, A. S. Pimentel, T. M. Anderson, Monitoring of CoS2 reactions using high-temperature XRD coupled with gas chromatography (GC). *Powder Diffraction* 2016, *31*. 7.

There are many tools to measure outgassing

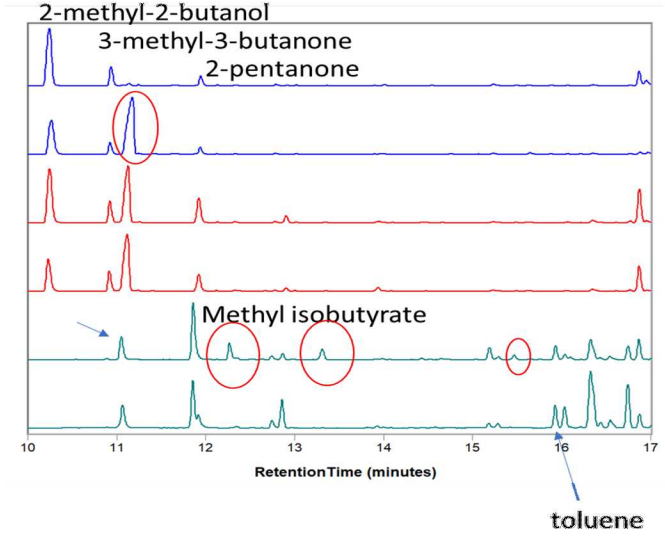
- Follow analytical chemistry trident

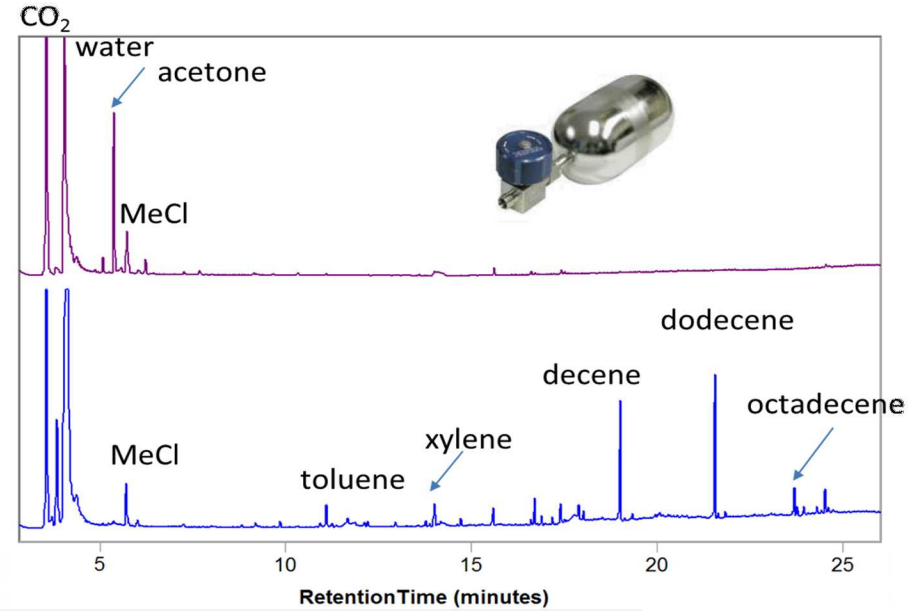
Sample preparation	**Separation**	**Detection**
Extraction Digestion Purge & trap Cryo-focus Preconcentration Thermal extraction Derivatization	Gas, Liquid or Ion chromatography thermal permeation	Electrochemical Spectroscopy (emission, UV/VIS) Mass spectrometry (QQQ, MS^n) FID, TCD, FPD, PDID, ECD

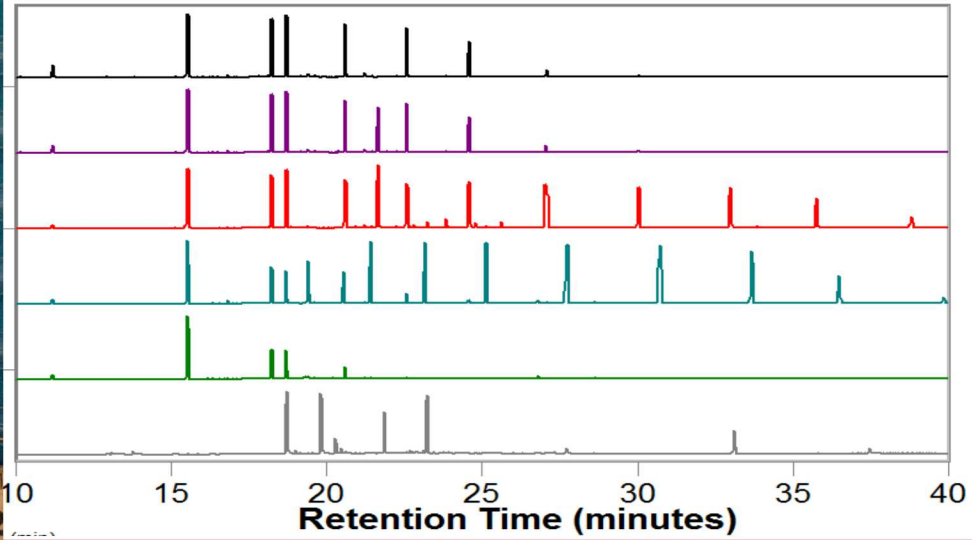


GC/MS often considered the “gold standard” because it provides “identification”

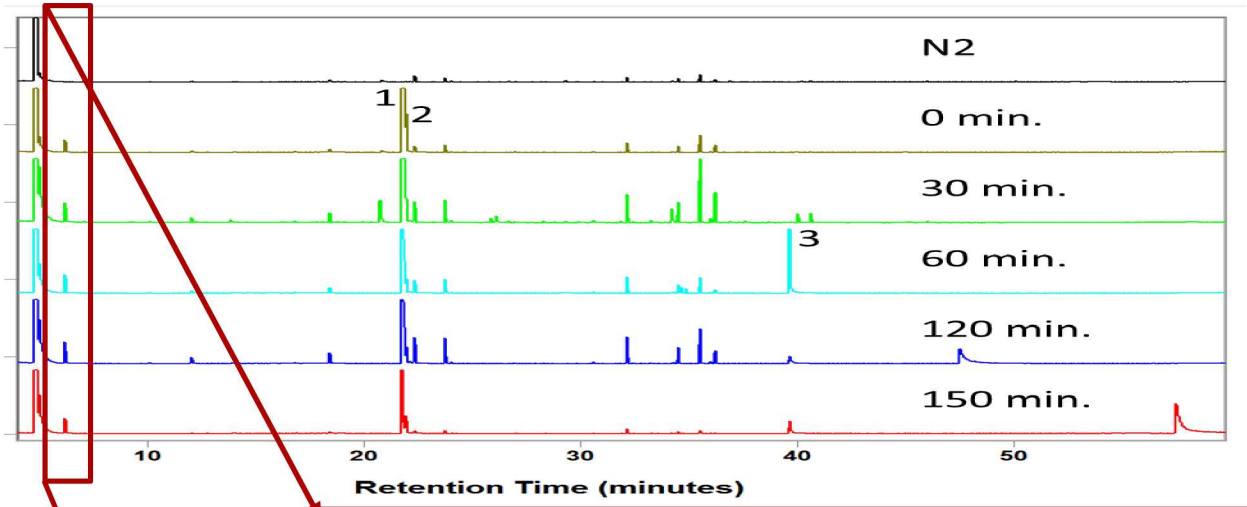
Outgassing and GC/MS – an easy fit



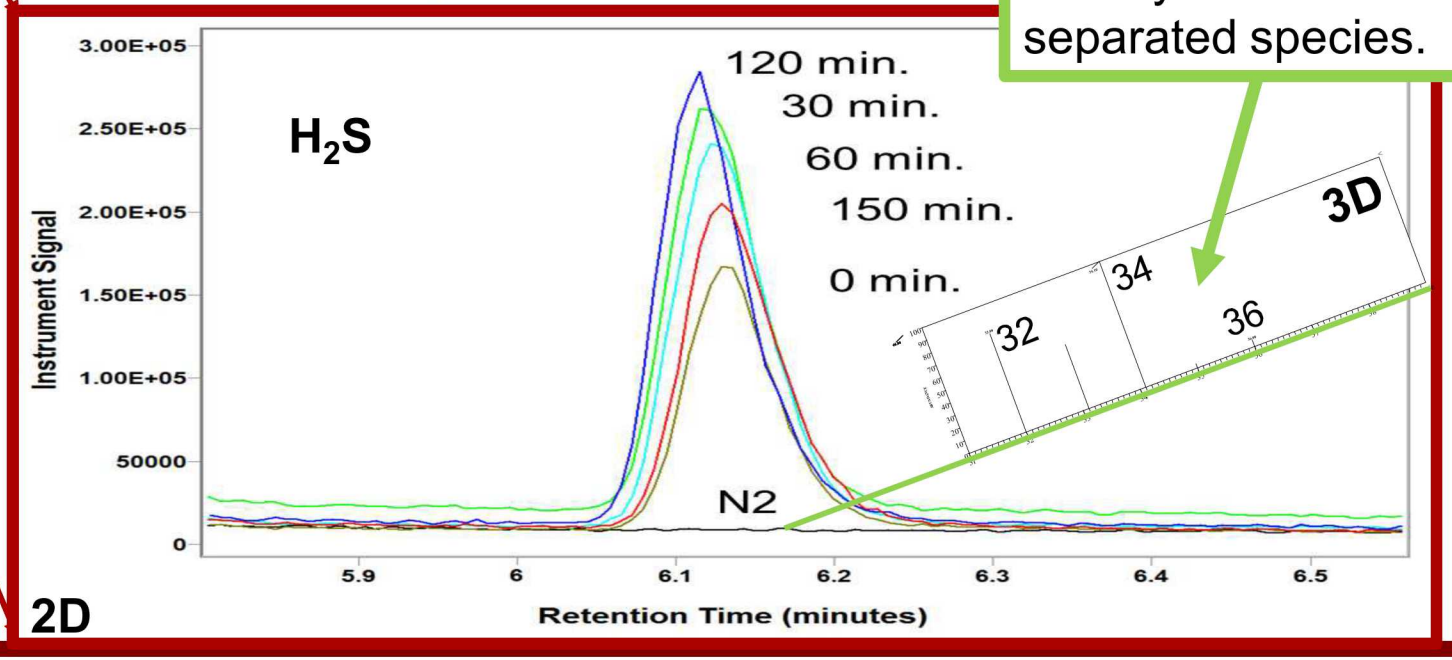




GC/MS, the "Gold Standard" for identification?

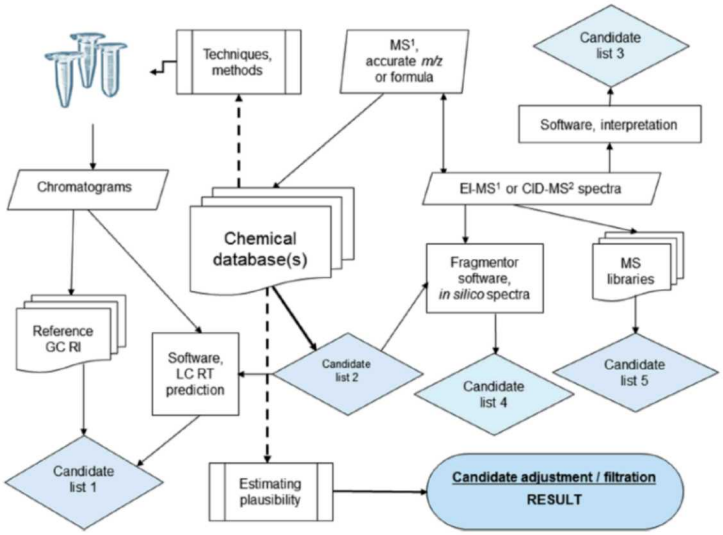


ZOOM



MS ion signal used to identify each separated species.

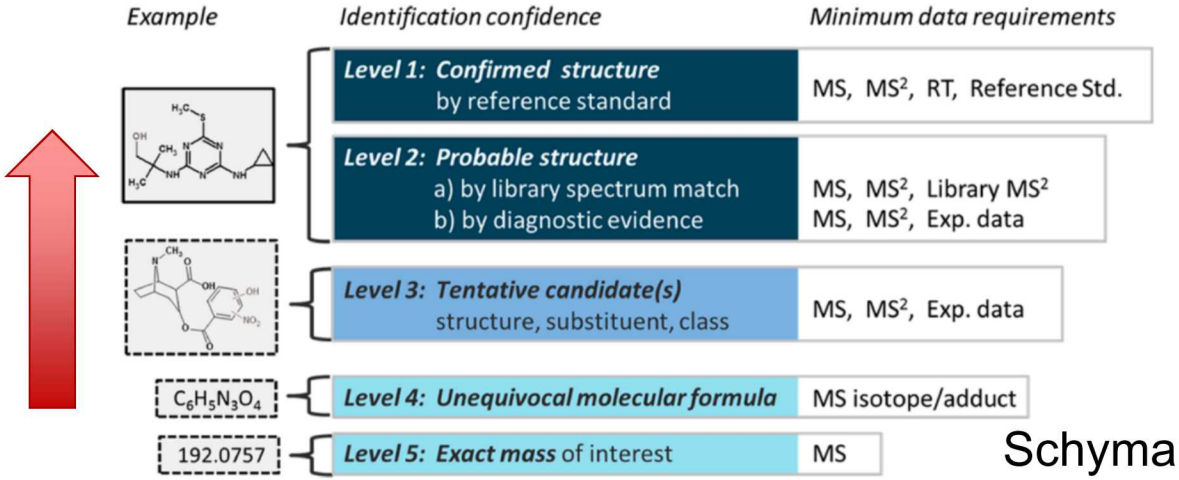
The confidence behind "identification" is subjective



Milman 2017

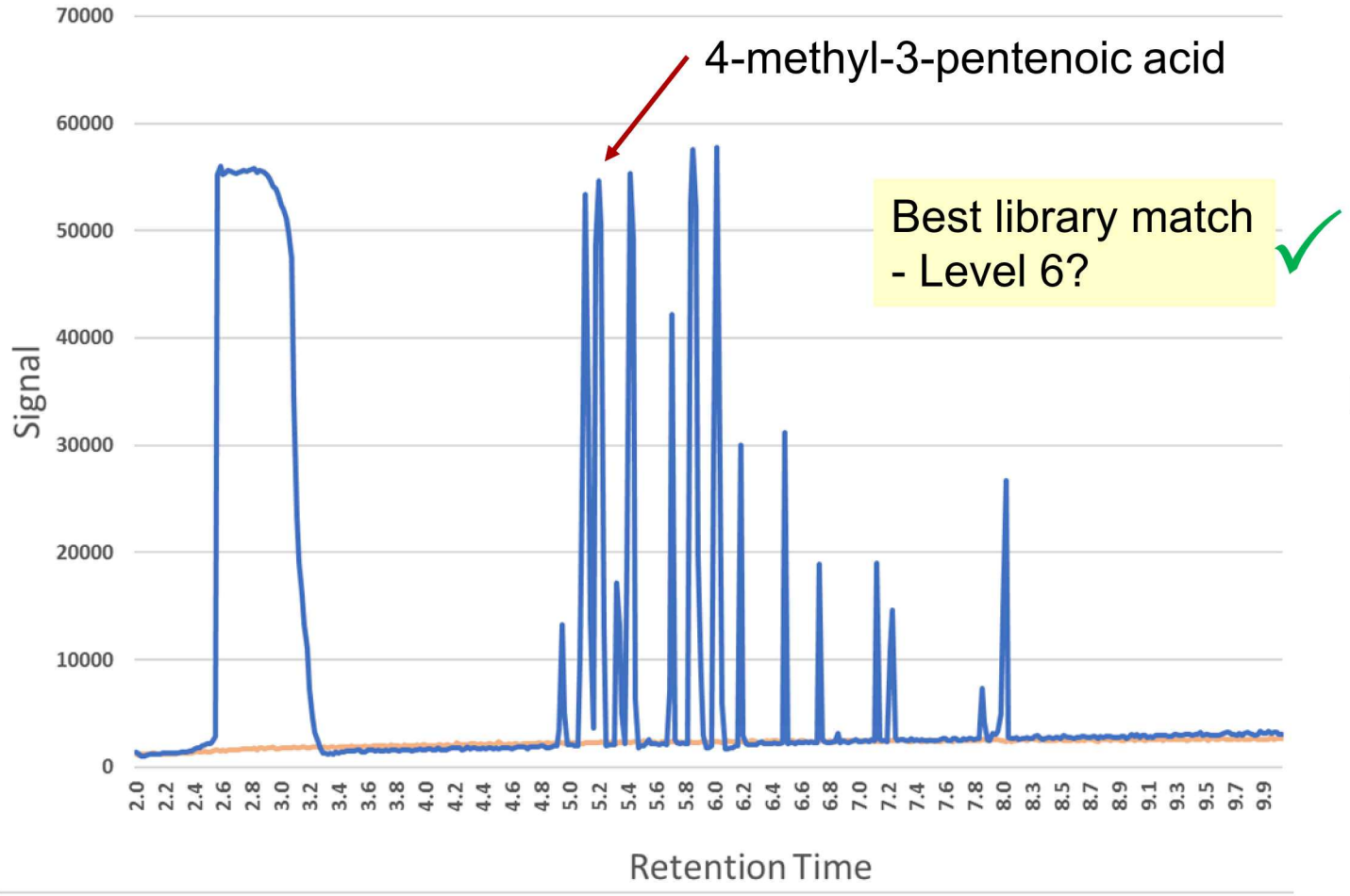
1. Compare w/authentic (RT,MS)
2. Compare w/libraries (RT,MS) (not same conditions)
3. HRMS, m/z, isotopes
4. Compare w/predicted (frags, loss)
5. Interpretation (software)

Milman 2015



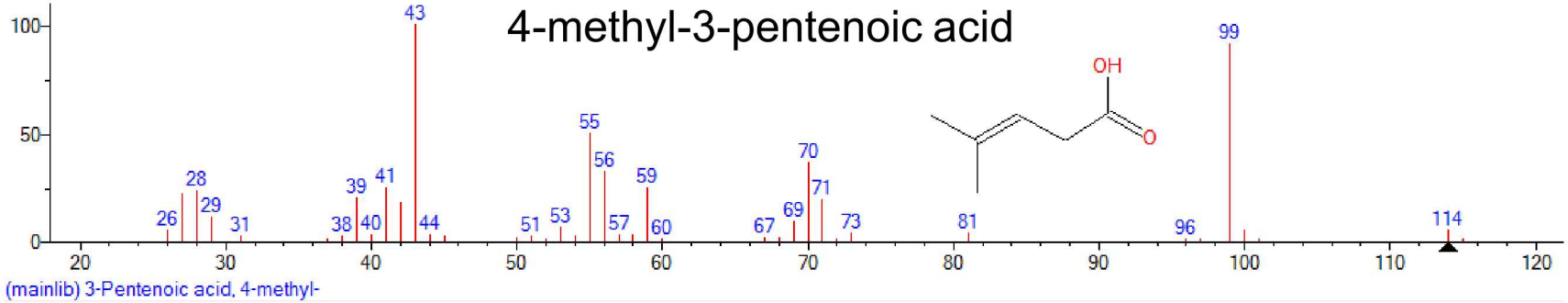
Schymanski 2014

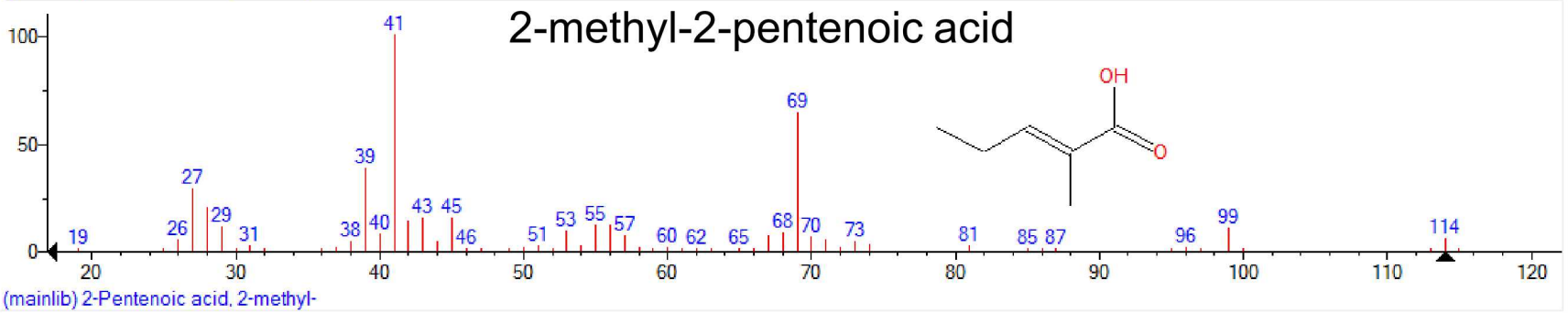
Many species were observed outgassing from conformal coating Uvikote

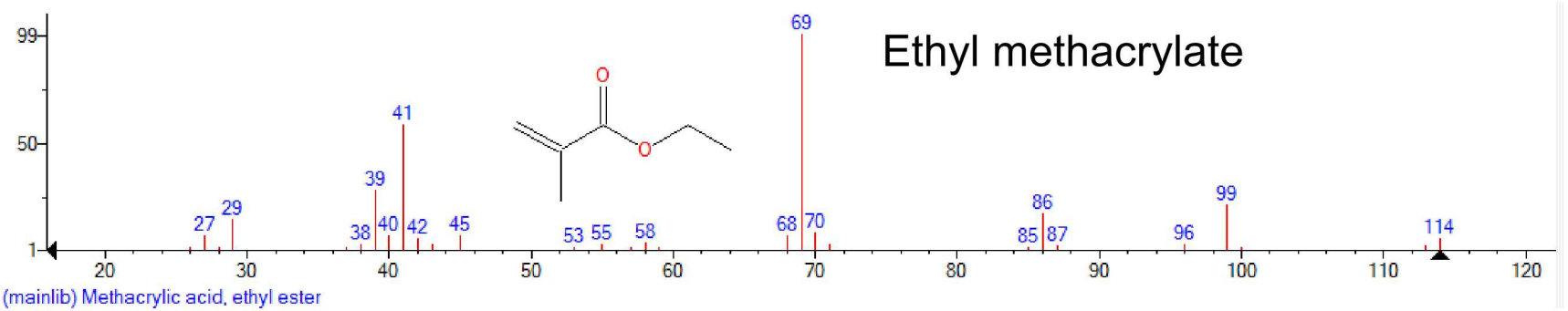


Finished?

Library match requires good separations and/or deconvolution







Identification level 5, 4, and 3

Sandia National Laboratories

✓ **5: Exact mass**

$C_4H_8N_3O$ MW=114.0667338 dm=0.3 ppm

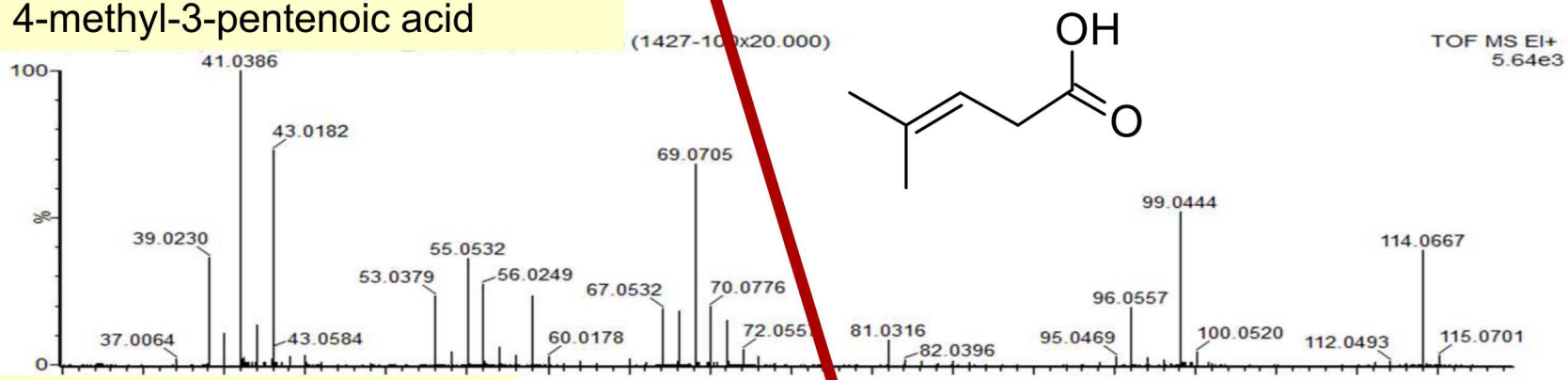
$C_6H_{10}O_2$ MW=114.068076 dm=12.1 ppm

X **4: Isotopic**

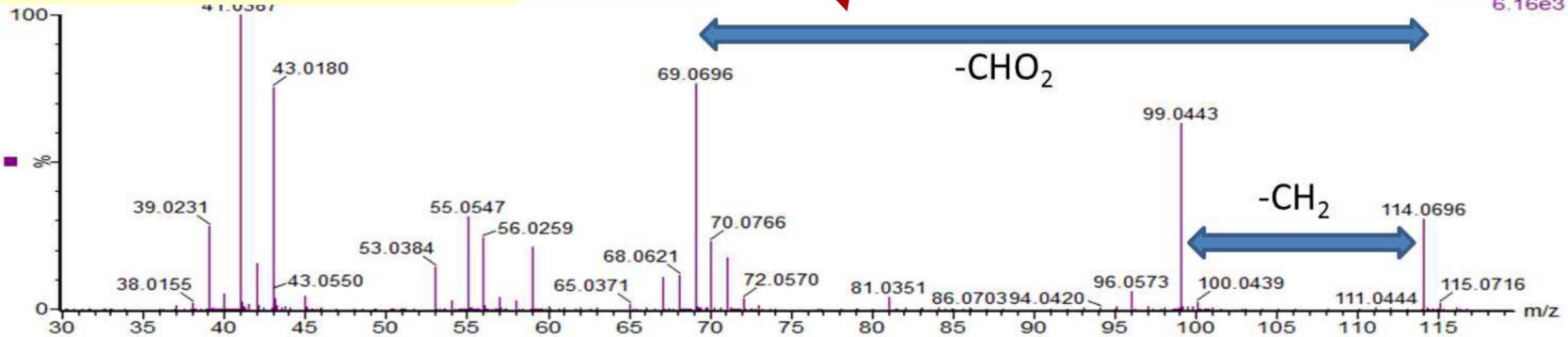
Same isotope ratio!!

✓ **3: structure or class**

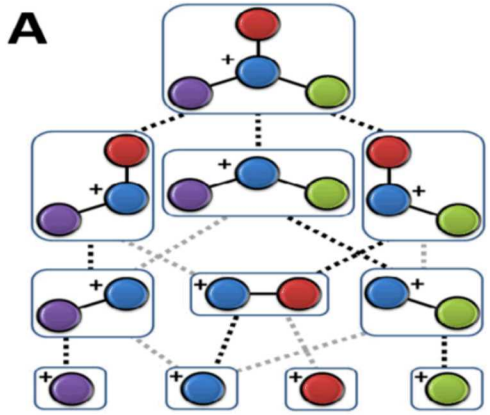
4-methyl-3-pentenoic acid

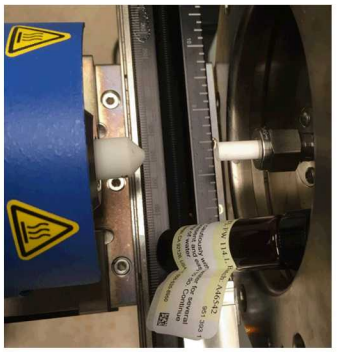


Uvikote



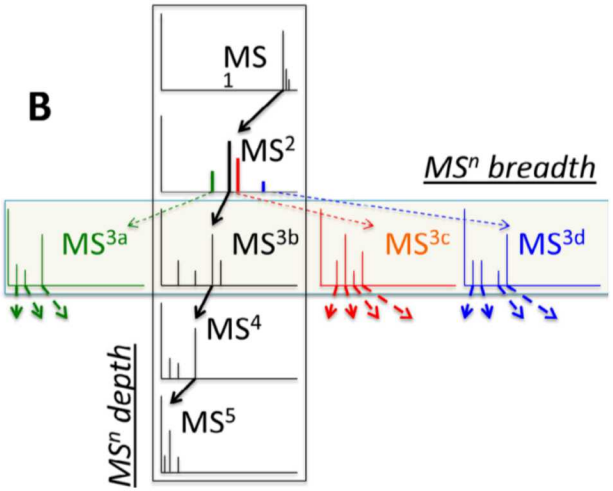
Level 2,1 : structural info from Fragmentation tree, compare to std.



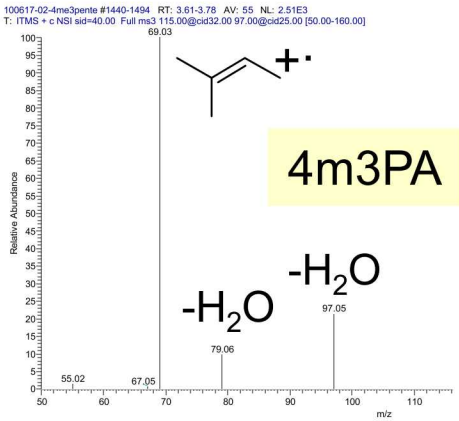


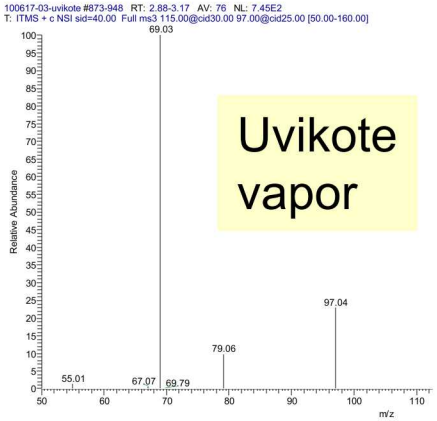
Vapor detection of chemical standard

Vapor from film



Vaniya 2015





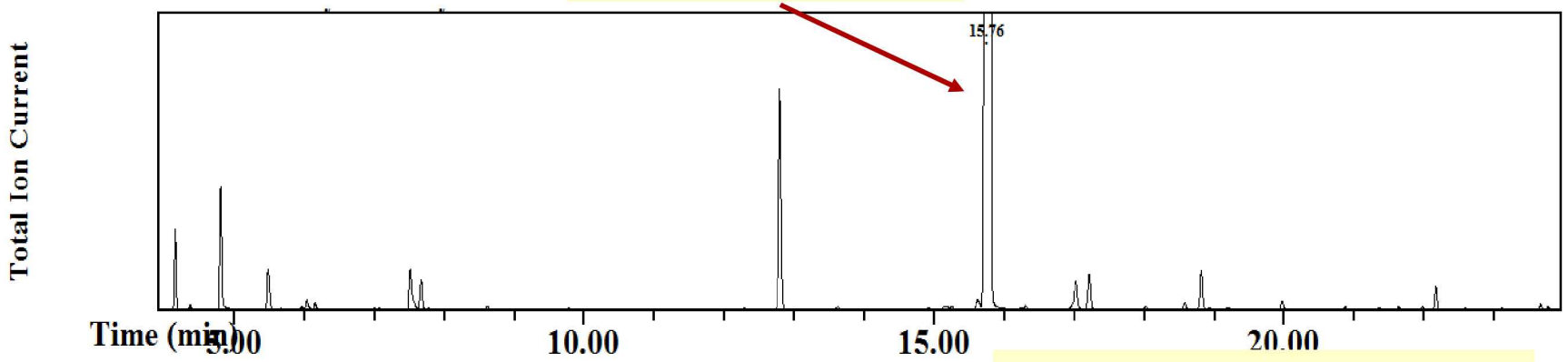
MS^3 115->97->scan products

note film was NOT introduced directly into hot gas

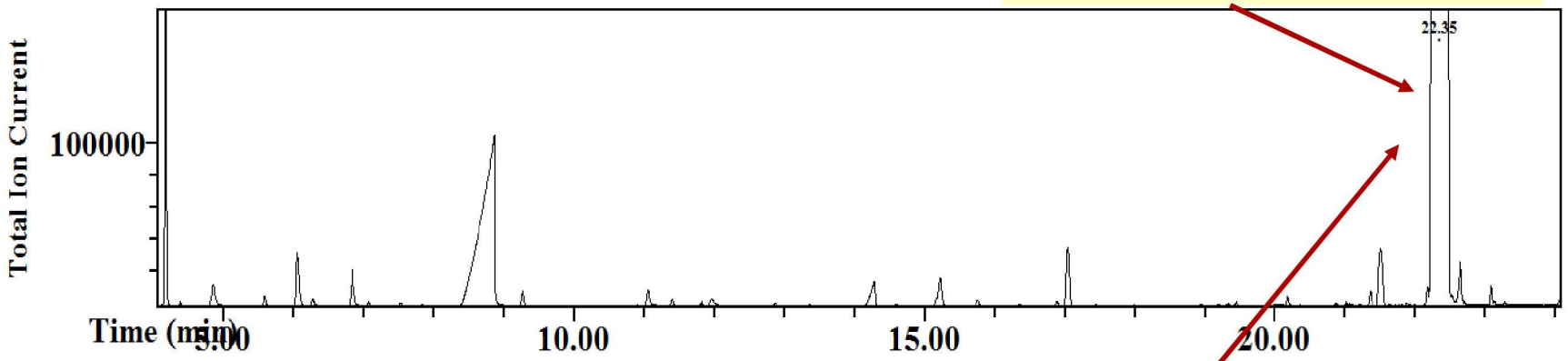
More Level 1: confirm retention time

Sandia National Laboratories

Ethyl methacrylate



4-methyl-3-pentenoic acid

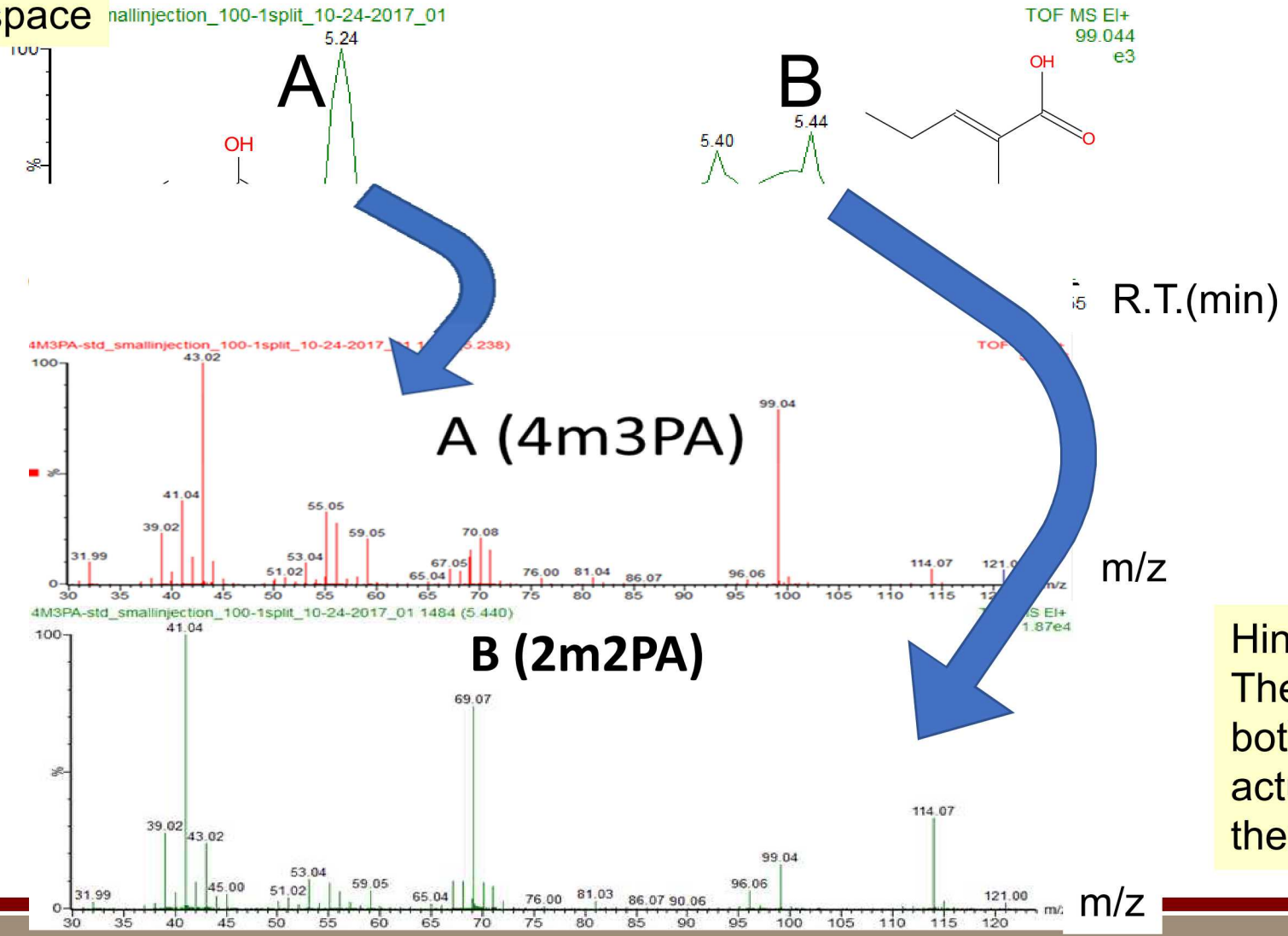


✓ Uvikote retention time (major peak) = 22.3 minutes

So how do we get great library matches for both 4m3PA and 2m2PA?

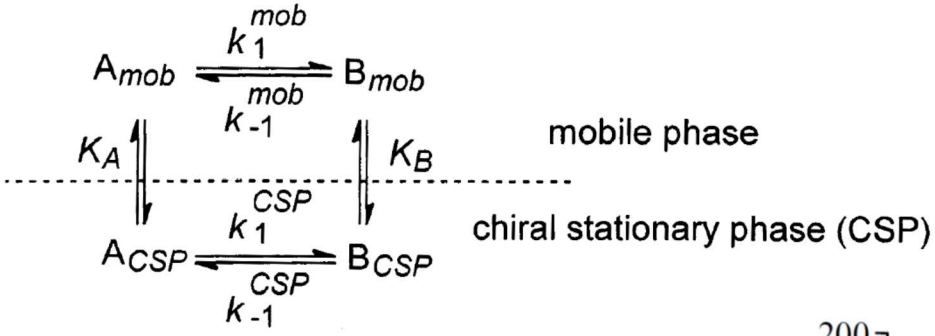
Sandia National Laboratories

Headspace



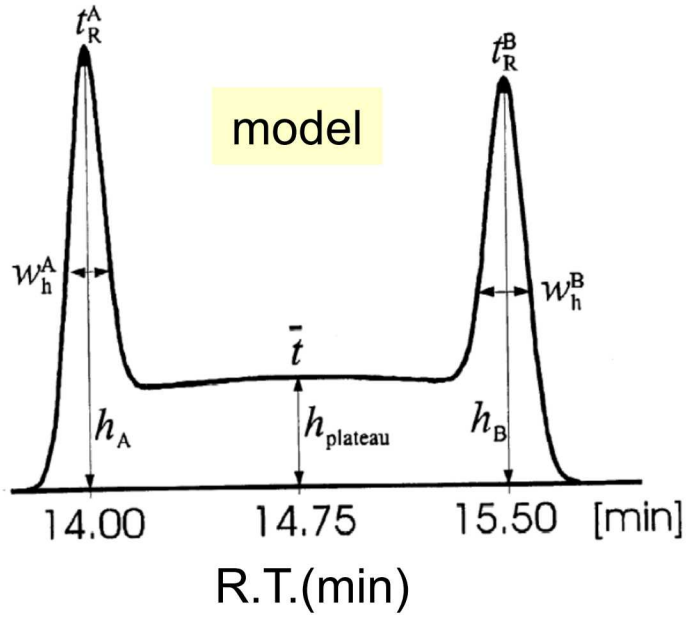
Hint: They're both actually there

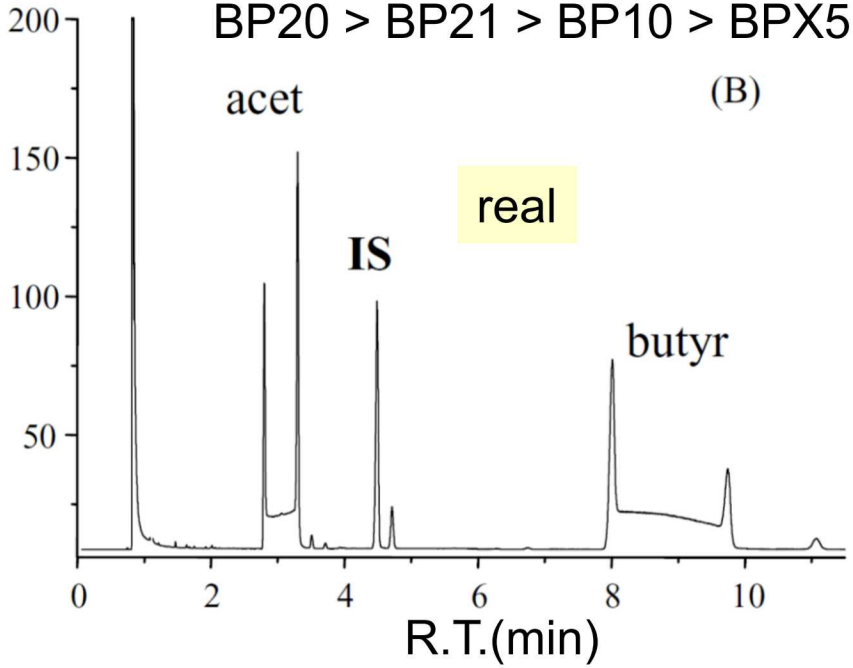
Thermal rearrangement in-column!



Time, temperature, and column phase dependent!

Phase effect:
BP20 > BP21 > BP10 > BPX5



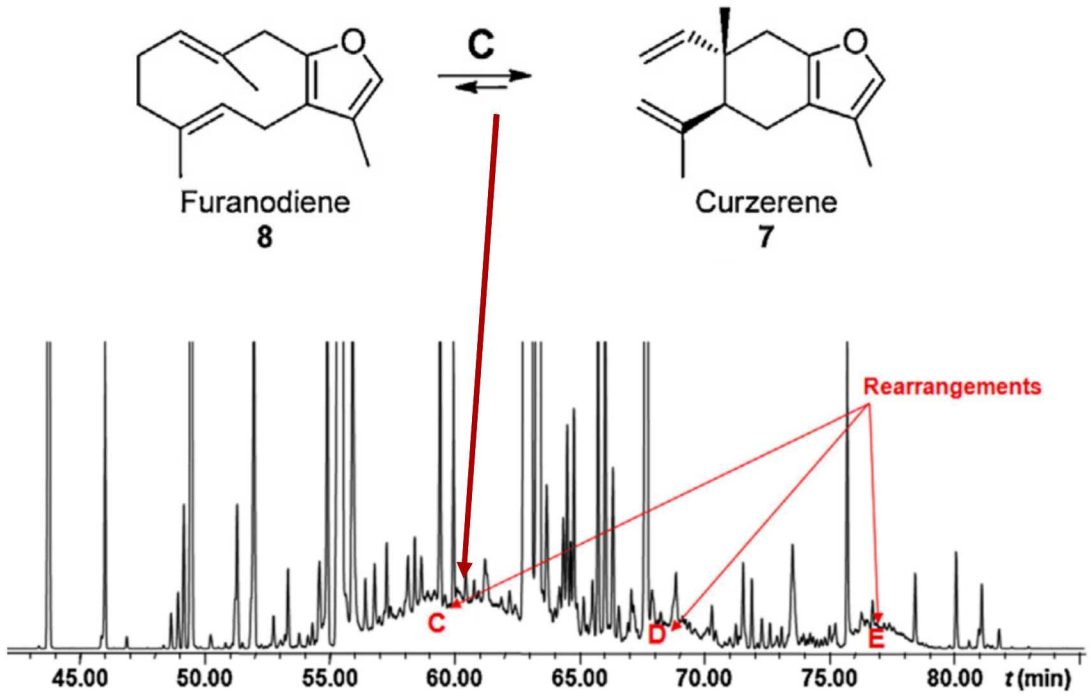


Trapp 2001

Mariott 2004

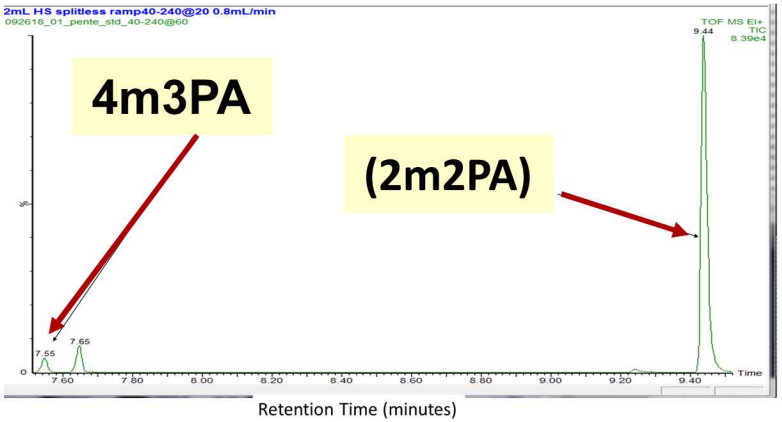
Thermal rearrangements often not noticed.

- Thermal labile compounds – Amirav labile steroids “injector is the place where most dissociation can occur...”

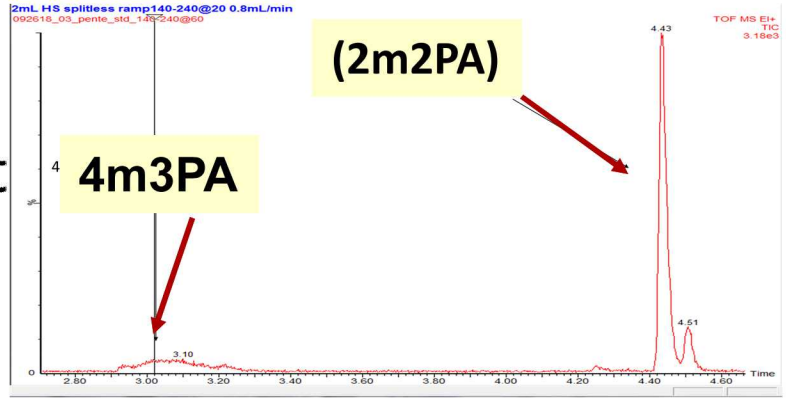


Filippi 2015: cope rearrangement

Can get both 2,2 and 4,3 with column temperature ramps (ffap) but not inlet temperature



Heat



Temp °C	RT 4-3 (min)	RT 2-2 (min)	Area 4-3	Area 2-2	Ratio 4-me-3-pent : 2-me-2-pent
40 - 240	7.54	9.45	8.44	0.4	21:01
60 - 240	6.55	8.45	10.42	2.52	4.1:1
80 - 240	5.54	7.46	9.14	2.42	3.8:1
100-240	4.58	6.45	6.97	2.75	2.5:1
120 - 240	3.68	5.44	2.69	1.53	1.75:1
140 - 240	2.96	4.45	0.27	0.93	1 to 3.4

Conclusions

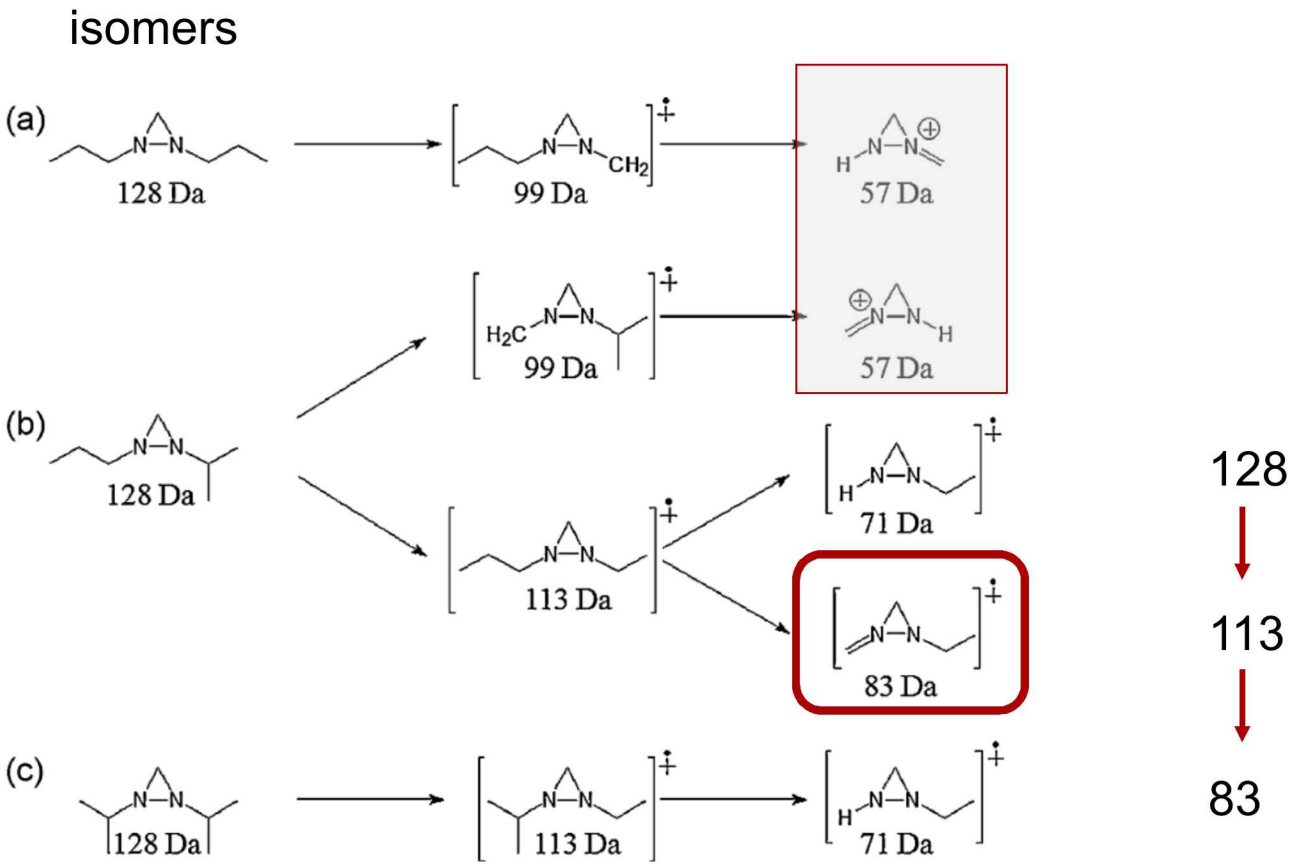
Sandia National Laboratories

- Many materials outgas
- Spectral libraries are very useful but should not replace experienced data interpretation
- No single technique can measure the universe of molecules
- “True” identification is a multi-step process
  - Effort should match data objectives
- For the Uvikote outgassing – the method can transform and affect the measured products.

References

- Filippi, J.-J.; Cocolo, N.; Meierhenrich, U. J., Peak-bridges due to in-column analyte transformations as a new tool for establishing molecular connectivities by comprehensive two-dimensional gas chromatography–mass spectrometry. *J. Chromatogr. A* **2015,** *1383*, 134-143.
- Dagan, S.; Amirav, A., Fast, very fast, and ultra-fast gas chromatography-mass spectrometry of thermally labile steroids, carbamates, and drugs in supersonic molecular beams. *J. Am. Soc. Mass Spectrom.* **1996,** *7* (8), 737-752.
- Trapp, O., Chromatographic peak deconvolution of constitutional isomers by multiple-reaction-monitoring mass spectrometry. *J Chromatogr A* **2010,** *1217* (7), 1010-6.
- Milman, B. L.; Zhurkovich, I. K., The chemical space for non-target analysis. *TrAC Trends in Analytical Chemistry* **2017**, *97*, 179-187.
- Milman, B. L., General principles of identification by mass spectrometry. *TrAC Trends in Analytical Chemistry* **2015,** *69*, 24-33.
- Schymanski, E. L.; Jeon, J.; Gulde, R.; Fenner, K.; Ruff, M.; Singer, H. P.; Hollender, J., Identifying Small Molecules via High Resolution Mass Spectrometry: Communicating Confidence. *Environ Sci Technol* **2014,** *48* (4), 2097-8.
- Vaniya, A.; Fiehn, O., Using fragmentation trees and mass spectral trees for identifying unknown compounds in metabolomics. *TrAC Trends in Analytical Chemistry* **2015,** *69*, 52-61.
- Trapp, O.; Schurig, V., Approximation function for the direct calculation of rate constants and Gibbs activation energies of enantiomerization of racemic mixtures from chromatographic parameters in dynamic chromatography. *J. Chromatogr. A* **2001,** *911* (2), 167-175.

Fragmentation can provide info



Trapp 2010