



GC-TOF applications of accurate mass measurements

ASMS 2010

Flavor, Fragrance and Foodstuff Interest Group

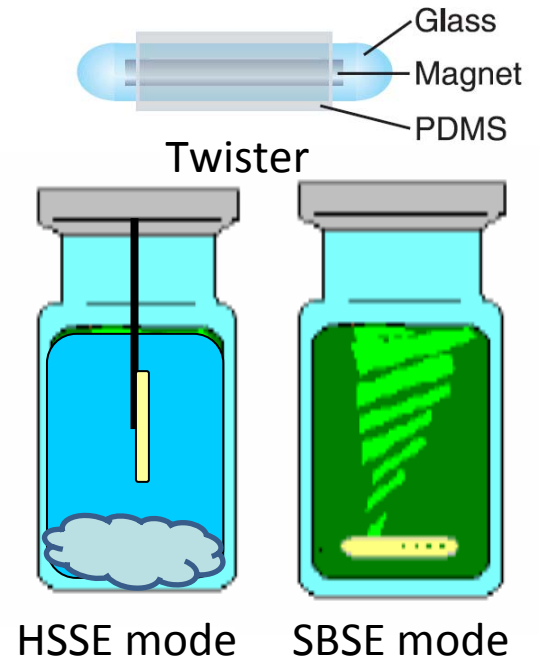
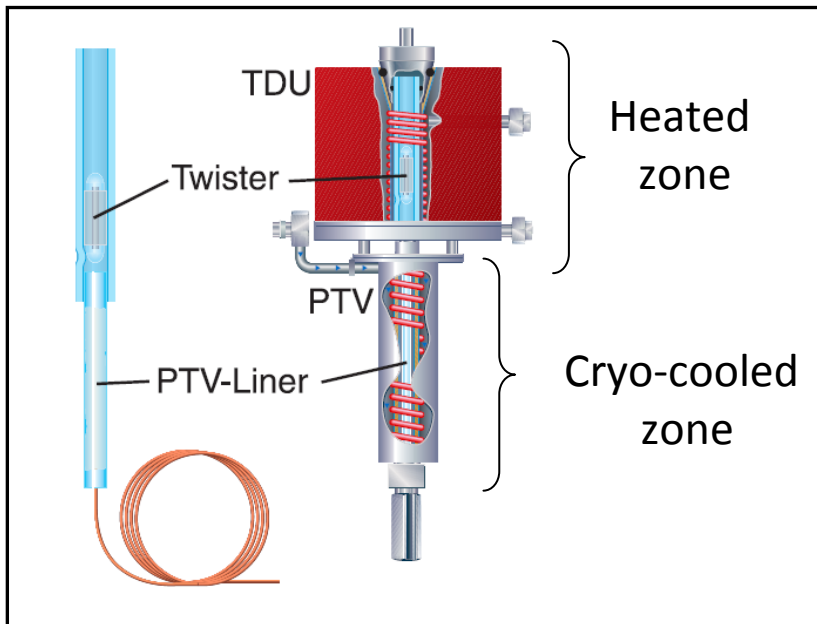
Tobias Kind

UC Davis Genome Center
FiehnLab - Metabolomics

High quality + high throughput VOC analysis

Twister stir bar (Gerstel)

- PDMS-based
- gaseous & liquid/homogenate sampling
- 100-fold more sensitive than SPME
- Thermal desorption / cryo-trapping



Automated + high throughput analysis of volatiles



Twister holder (sealed)



Thermal desorption unit
and GC injector

Automated sample loading



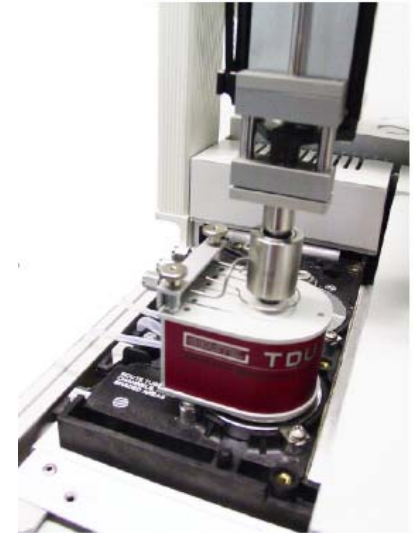
**Pick notched
liner on steel head**



**Transfer to
desorption unit**

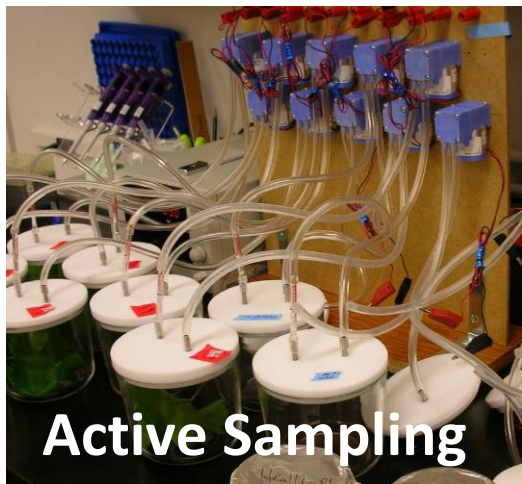


**Insert liner
with Twister**

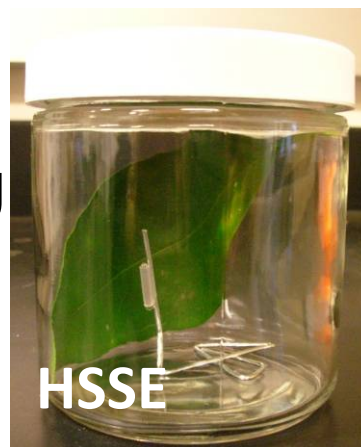


**Close and
go back**

Flexible sampling of volatiles with Twisters



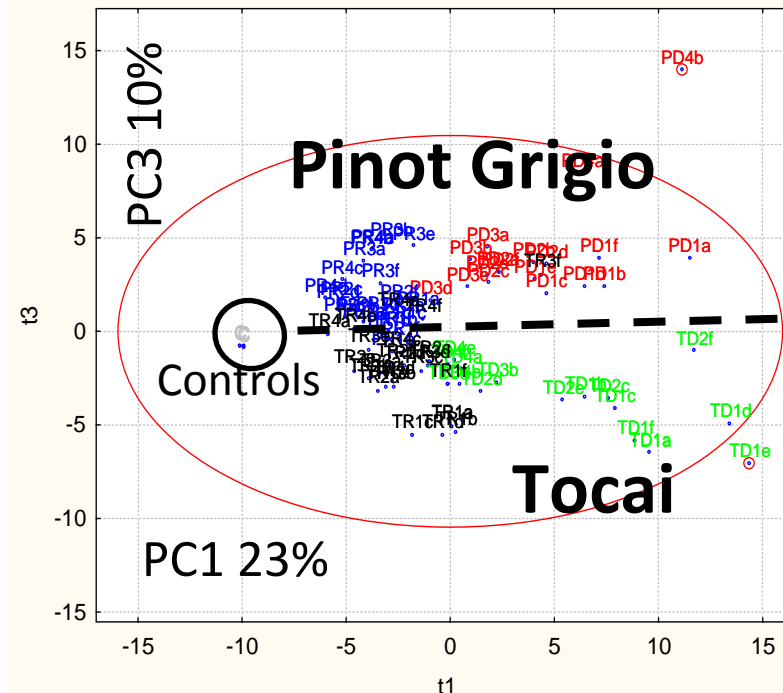
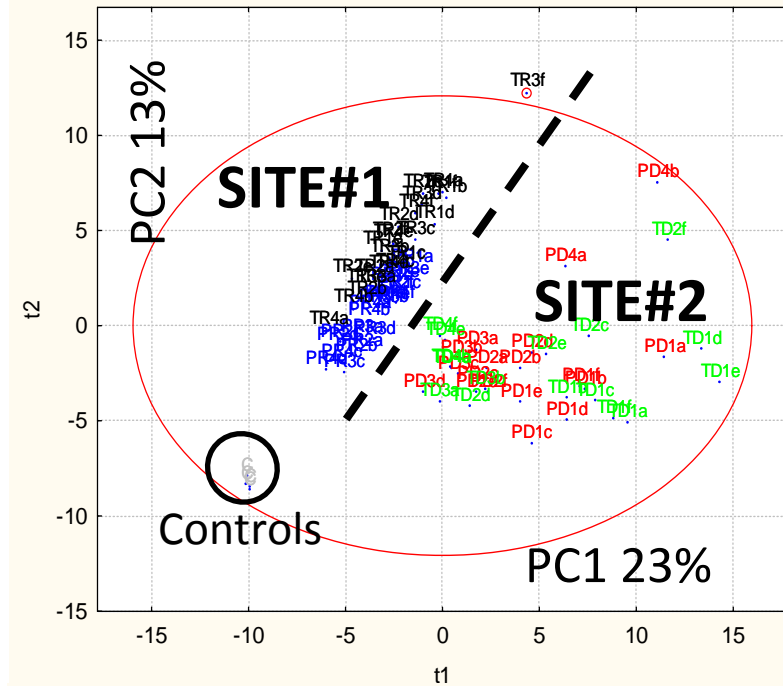
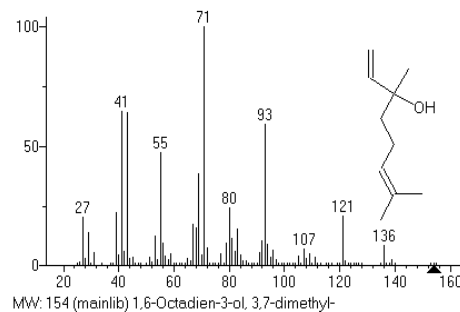
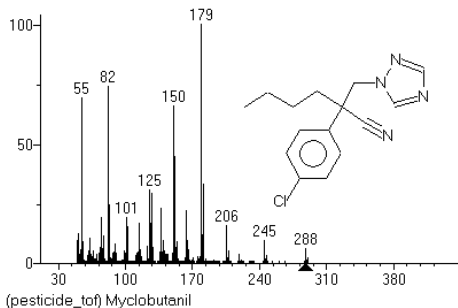
- Active & passive sampling
- Lab, greenhouse, field
- (Intact fruit)
- Easy to deploy off-site



Wine Grape Example

2 varieties, 2 vineyards, 4 harvest dates

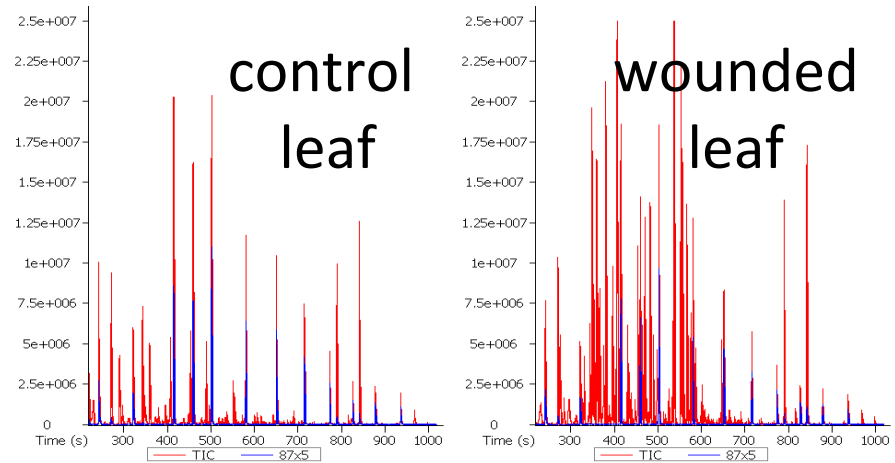
- PCA scores plots:
 - Site drives separation on PC1
 - Variety drives separation on PC3
- PCA loadings:
 - Pesticides are key in site differentiation
 - Terpenes key in varietal differentiation



Track first - ID later: VOC BinBase

Current VOC database stats:

- 3600 samples (18 species)
- 1.3 million spectra
- 1500 unique spectra



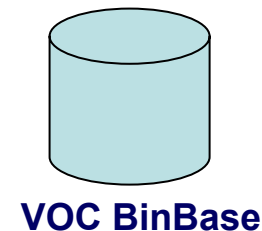
Annotation

- Adams MS+RI library 2000+
- Own standards

Red trace = sample TIC
Blue trace = FAME RI markers

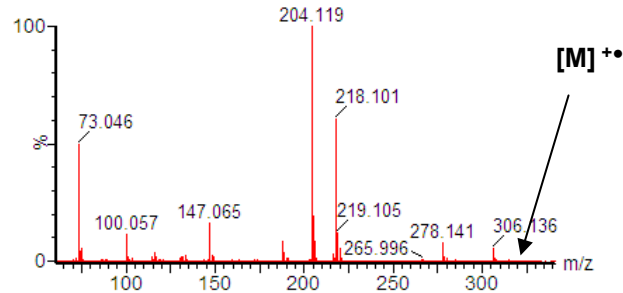
Millions of RIs
Millions of spectra

**Lesson learned: Do not throw away your data.
Ability to track & catalog unknowns critical in
area of complex volatile mixture analysis**



Accurate mass GC-MS with three reagent gases

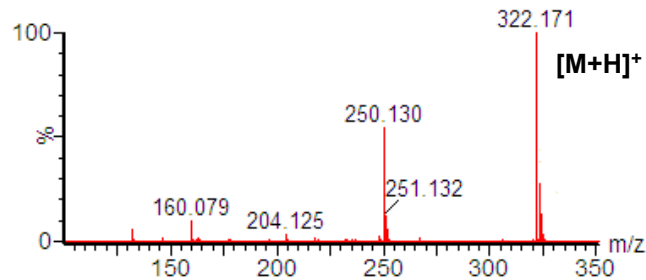
Electron ionization
accurate mass GC-MS (70 eV)



Molecular Ion Detection

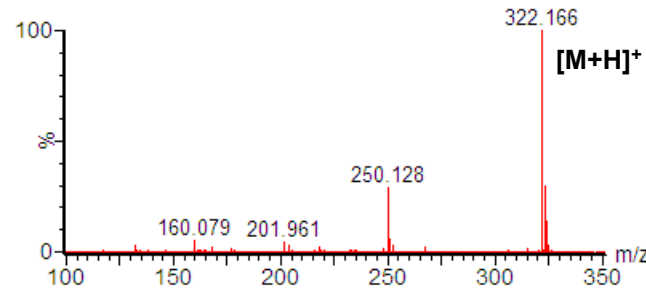
Fail

Chemical Ionization
accurate mass GC-MS (NH3)



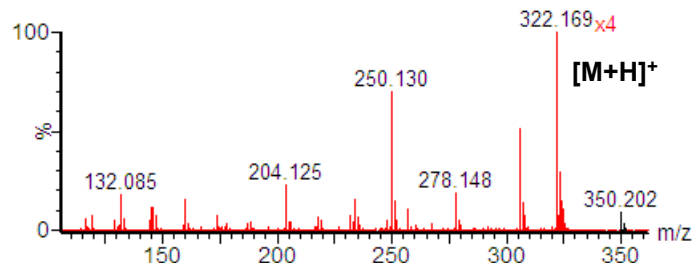
OK

Chemical Ionization
accurate mass GC-MS (Isobutane)



OK

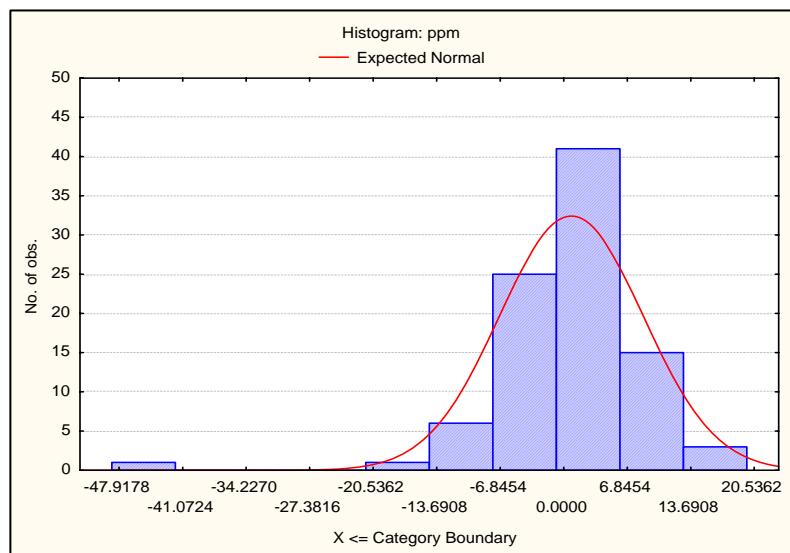
Chemical Ionization
accurate mass GC-MS (Methane)



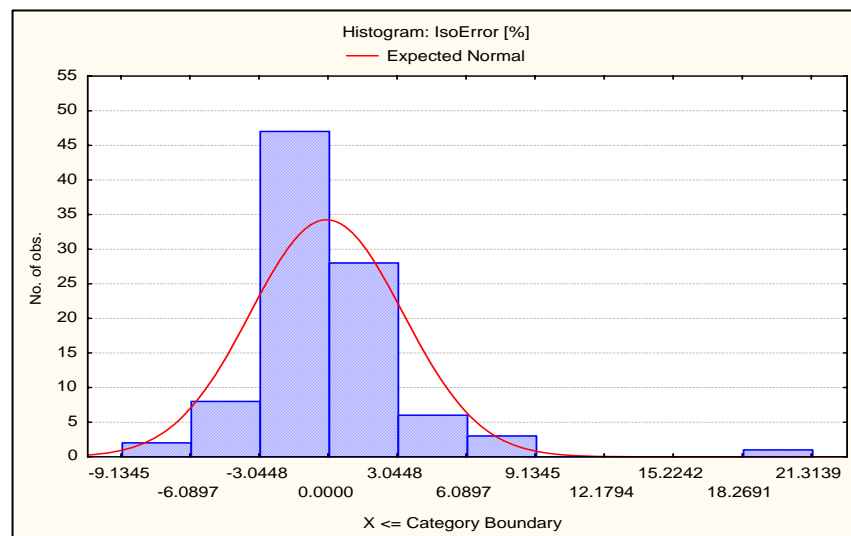
OK

Figures of merit for accurate mass GC-TOF

Accurate Mass Error



Isotopic Abundance Error

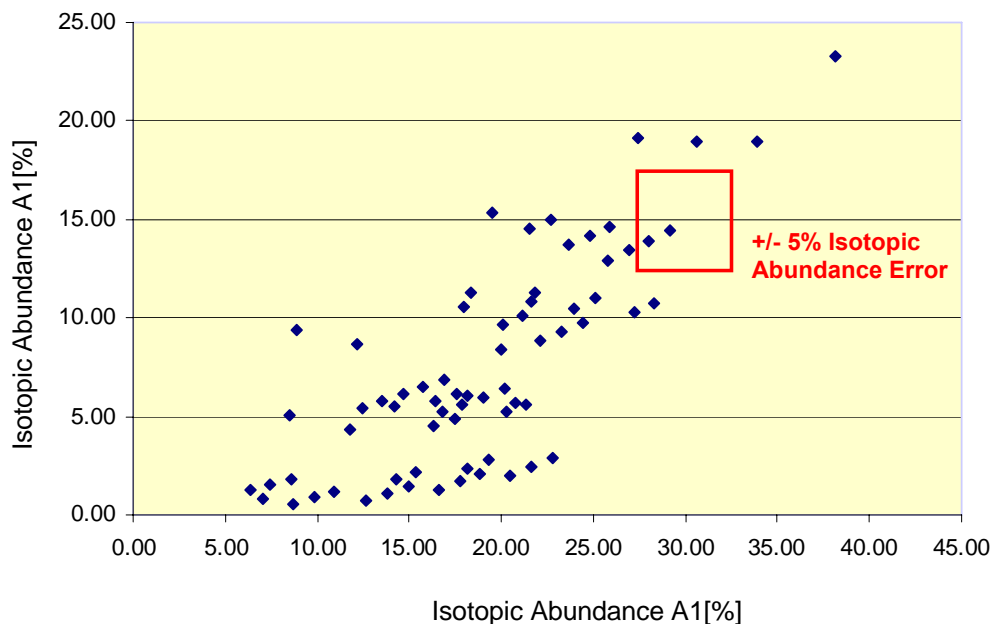


Average mass error = 5.7 ± 5.3 ppm (n=90)
Isotopic abundance ratios $A+1/A = 2.1 \pm 2.6$ %
Isotopic abundance ratios $A+2/A = 1.6 \pm 2.0$

Seven Golden Rules
(open access software)

Isotopic abundance (sometimes) more important than mass accuracy

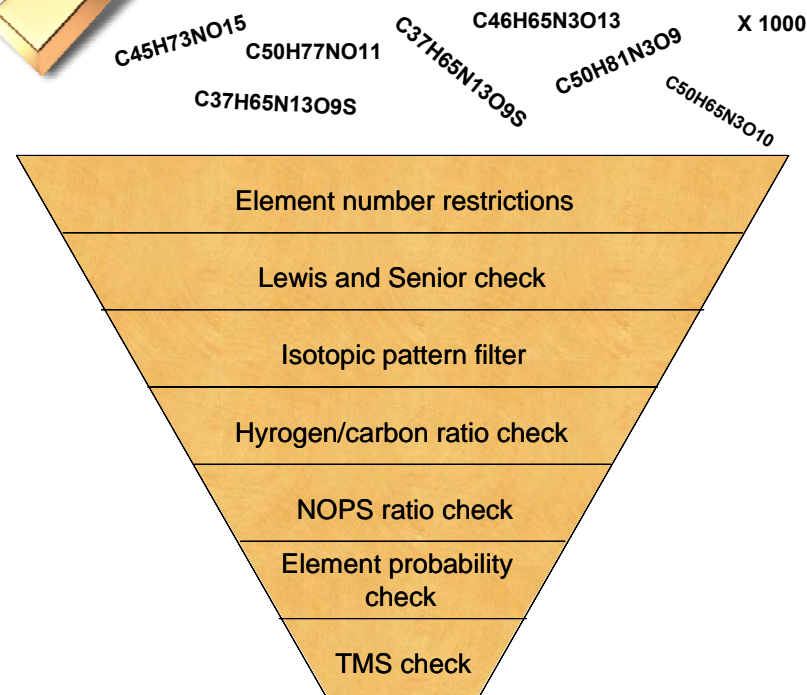
70 formulas @ 10 ppm



2 formulas left after Seven Golden Rules



Seven Golden Rules



- 1) C45H73NO15
- 2) C46H65N3O13
- 3) C46H82N3O10P
- 4) C44H69N9O9
- 5) C47H65NO14

Thank you!



Fiehn Lab

Sponsors Fiehn Lab

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Kristie Cloos (Lipids, MS, GC-MS)

Dr. Pierre Ayotte (Docking)

John Meissen (UPLC, LC)

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Kirsten Skogerson

+ Doug Stevens (Waters)