Presented to the Midwest Mass Spectrometry Discussion Group at Washington University.
Approved for unlimited unclassified release SAND 2012-xxxxP.
SAND2012-3328P

April 25, 2012

Unknowns, Polymers, Bolts, and Beer, Oh My! Problem Solving with Mass Spectrometers and Microfabricated Devices at Sandia National Laboratories

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Materials Charaterization Dept. 1822

Acknowledgements:

SNL: Matthew Moorman, Amy Allen, Ted Borek, Mike Mangan, Mike Siegal, Ron Manginell

Univ. Wyoming: Dr. Franco Basile, Tamara Sibray, Sujit Kandar

Abstract

The Materials Characterization Department is Sandia's own "CSI" facility, where a variety of chemical analysis occurs. While we don't do forensic DNA work like in the television program, we test just about everything else. Gases, liquids, and solids are brought to our department for contaminant and impurity detection, composition analysis, elemental analysis, and more.

I will give some brief examples of how we have used mass spectrometry (MS) to address a variety of materials mysteries and problems, followed by a discussion on work combining Sandia's capabilities in microfabrication with mass spectrometry.

We have used microfabricated devices with low thermal mass and resistive heating functionality for the treatment and introduction of peptides and polymers into mass spectrometers. This allows us to thermally condition samples as well as measure calorimetric information about the sample. We are beginning to apply these methods to problems in polymer aging and characterization and protein/peptide analysis and I will discuss examples in both areas. I will also discuss Sandia's ongoing effort into building microfabricated ion traps.

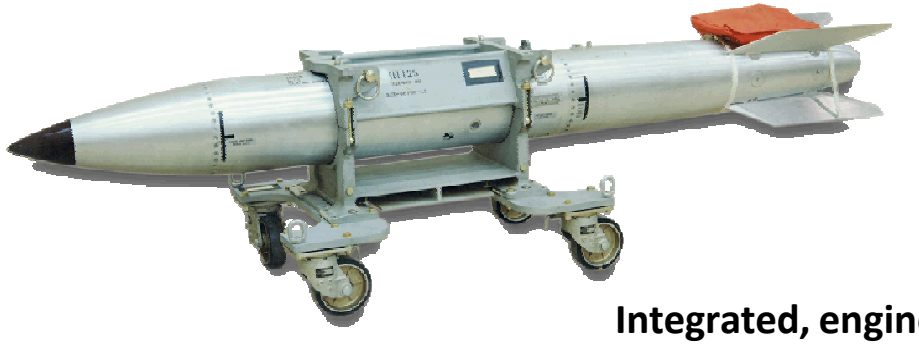
Sandia's History

1950s: Stockpile development (design, produce weapons).
1960s: Stockpile development; introduction of permissive action links. Development of space-based & seismic verification systems.
1970s: Additional missions in energy R&D
1980s: Department of Defense, Treaty verification technology, radioactive waste management, Technology transfer work all increase.
1990s: No new nuclear weapons systems, however life extension programs authorized. More international programs.
2000-2010s: Continuation of life extension programs. Enhanced activity with Department of Defense. Homeland security.

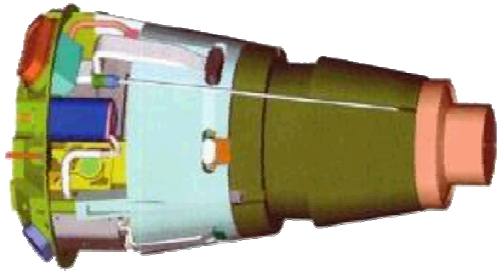
Sandia National Laboratories

Sandia's Mission

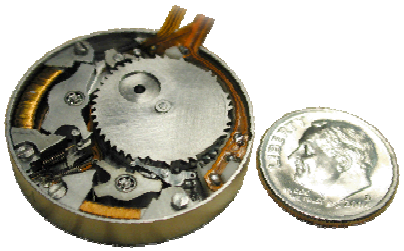
<u>Technical staff (4,277)</u>
Computing 16%
Math 2%
Chemistry 6%
Physics 6%
Other science 6%
Other fields 12%
EE 21%
ME 16%
Other engineering 15%



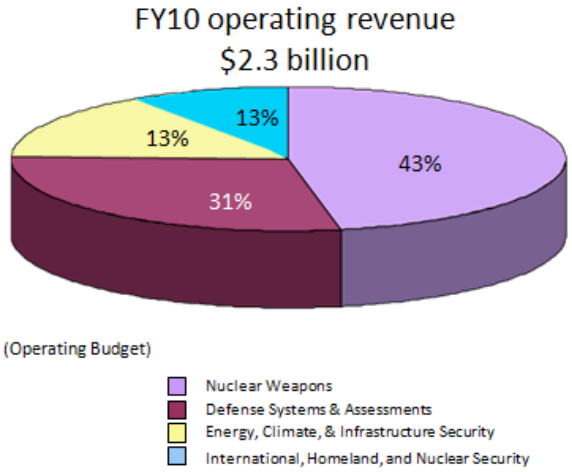
Integrated, engineered warhead systems



Arming, fuzing, and firing systems



Safety systems



1950 – 100% NW
2010 – 40% NW

Sandia National Laboratories

For Safety and Security, Aging and Composition of Polymers is Useful Knowledge

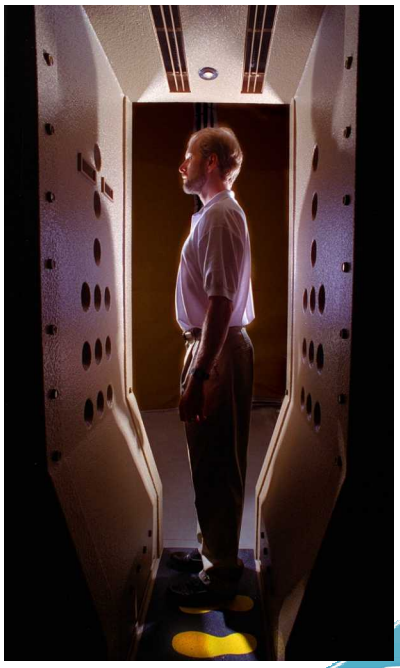
Seals / O-rings
Plastics
Binders
Wiring
Connectors
Circuit boards

When they come out of storage, you want them to work…..

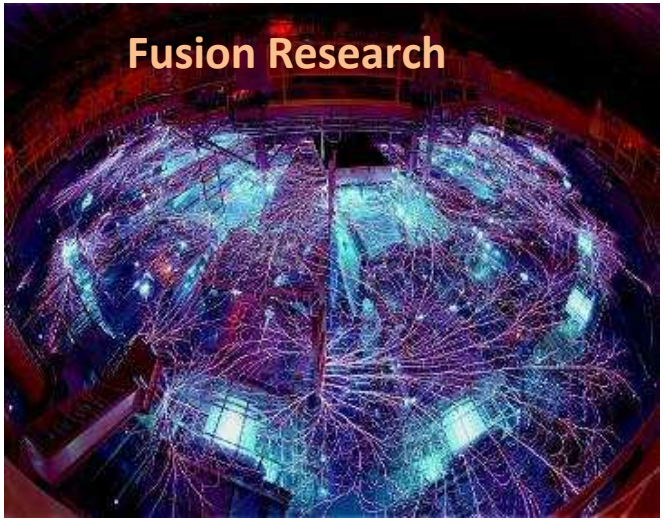
Sandia's Non-Nuclear Work

- Defense
- Satellites
- Energy, water
- Homeland security

Explosives Detection



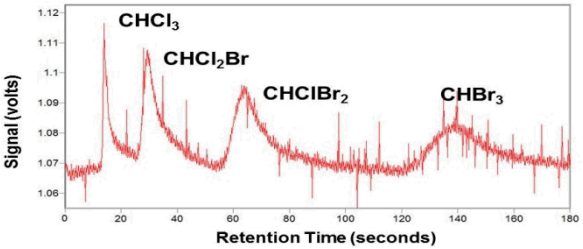
IED
Deactivation



Sandia's Non-Nuclear Work

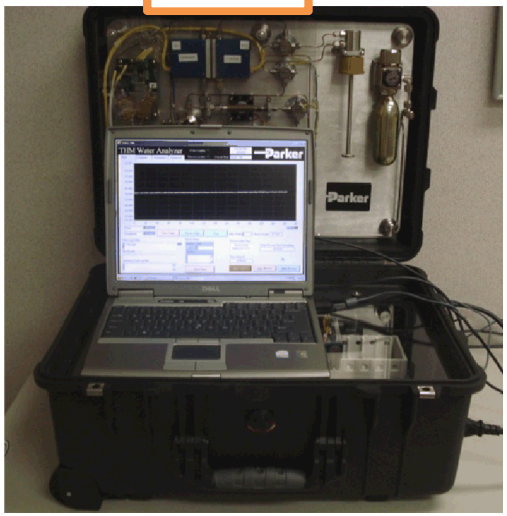
Disinfection Byproducts Detection

~2005

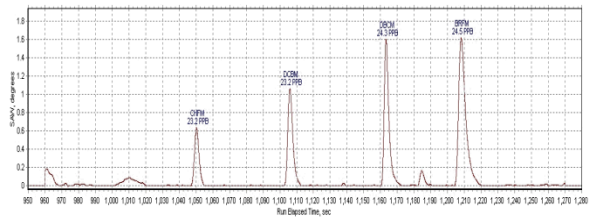


~100 ppm

~2009



2012



1 ppb

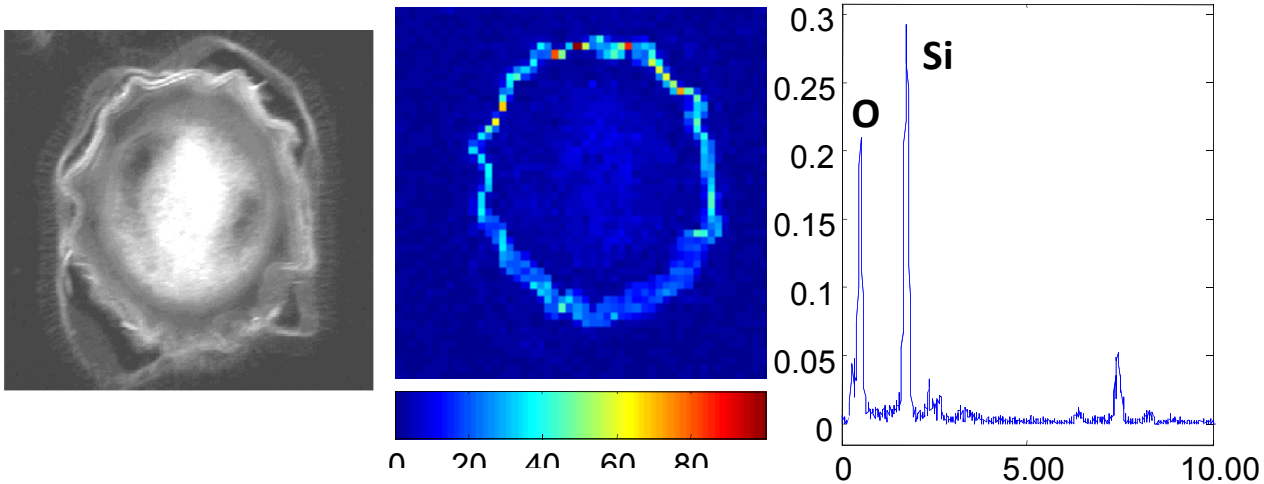
Improvement achieved through application of advanced materials (nanoporous carbon).

Sandia National Laboratories

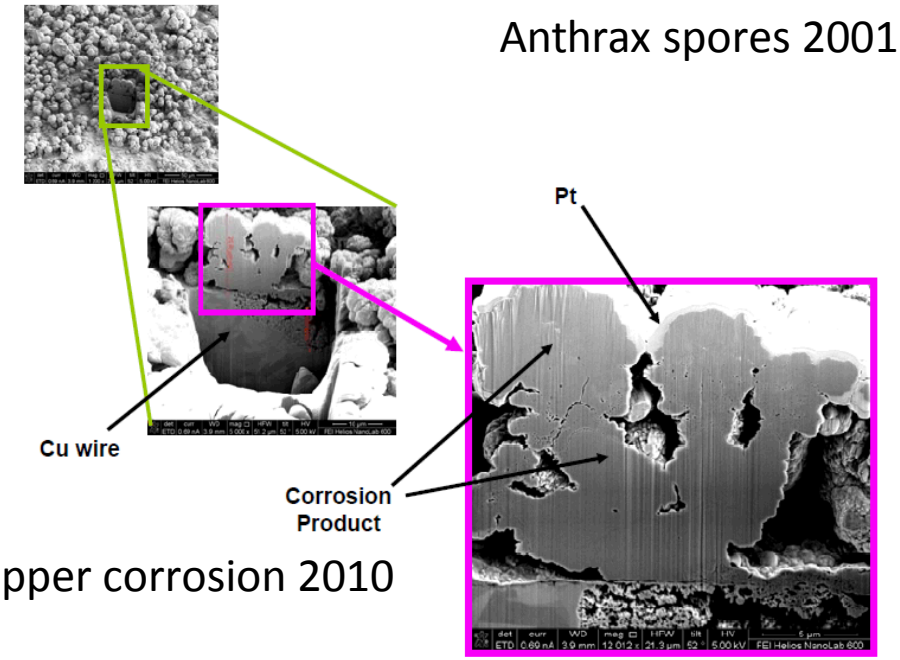
Materials Characterization Department

Experts in:

SEM
TEM
TOF-SIMS
Auger
XPS
AFM
XRD
XRF
LIBS
FTIR
MS



Anthrax spores 2001



Copper corrosion 2010

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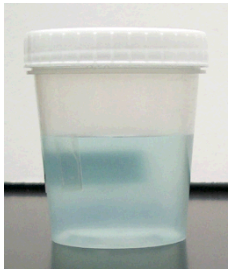
Organic / Inorganic Analysis

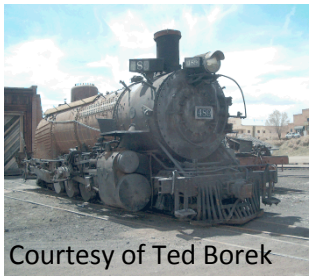
We Test:

GASES

LIQUIDS

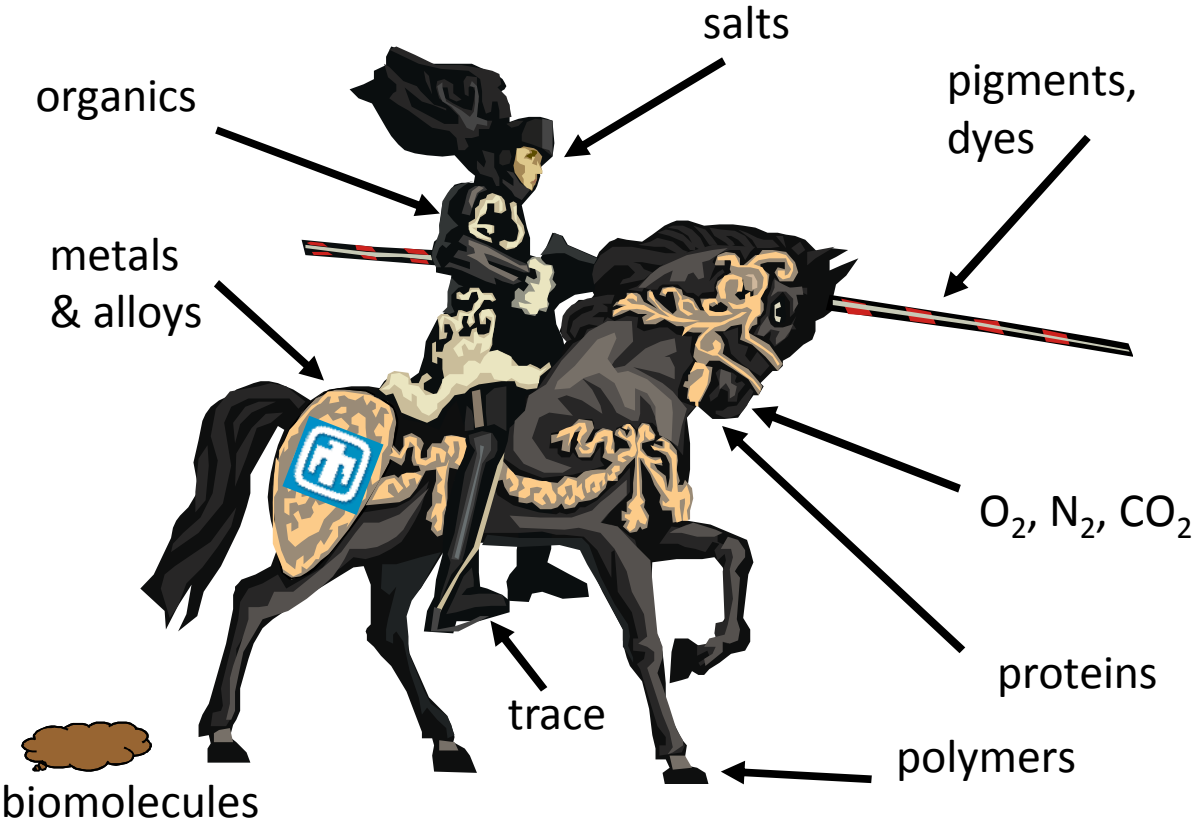


SOLIDS



Courtesy of Ted Borek

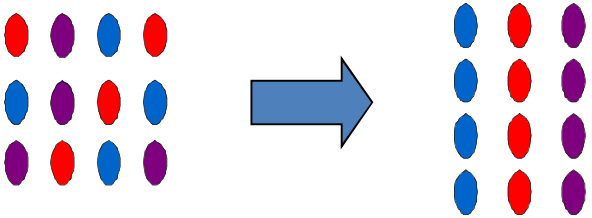
Looking for (for example):



We use methods for collection, separation, and detection.
We report on composition, impurities, quality control, validation, unknowns.

Analytical Chemistry in a Nutshell

- Collect/Prepare
  - liquids, solids, gases
- Separate
  - time, space, mass
- Detect
  - optical, mass, other properties



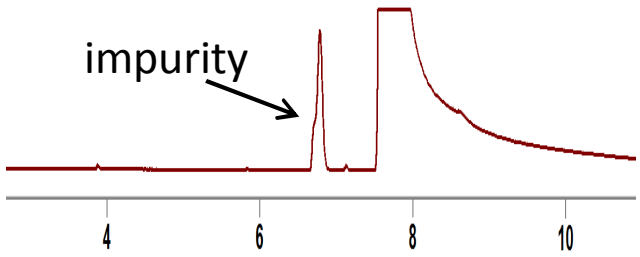
mix and match to find solutions

Mass spectrometry applied to unknowns:

Problem: solvent suspension of metal particles leaves residue

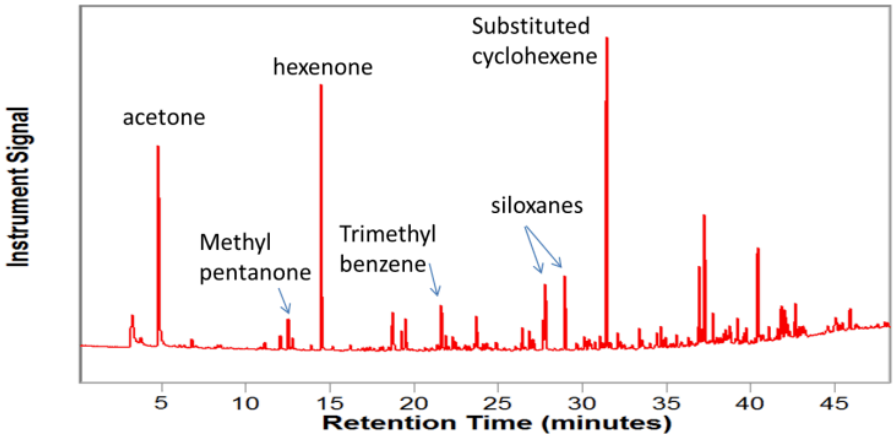
solvent?
vendor formulation?

GC/MS detects some
solvent impurities



solvent or semi-volatile
contamination of metal particles?

TD/GC/MS



<u>Issues that pop up:</u>
who has a control sample?
who else is testing?
is the customer asking right questions?
unclear/unspecified ingredients

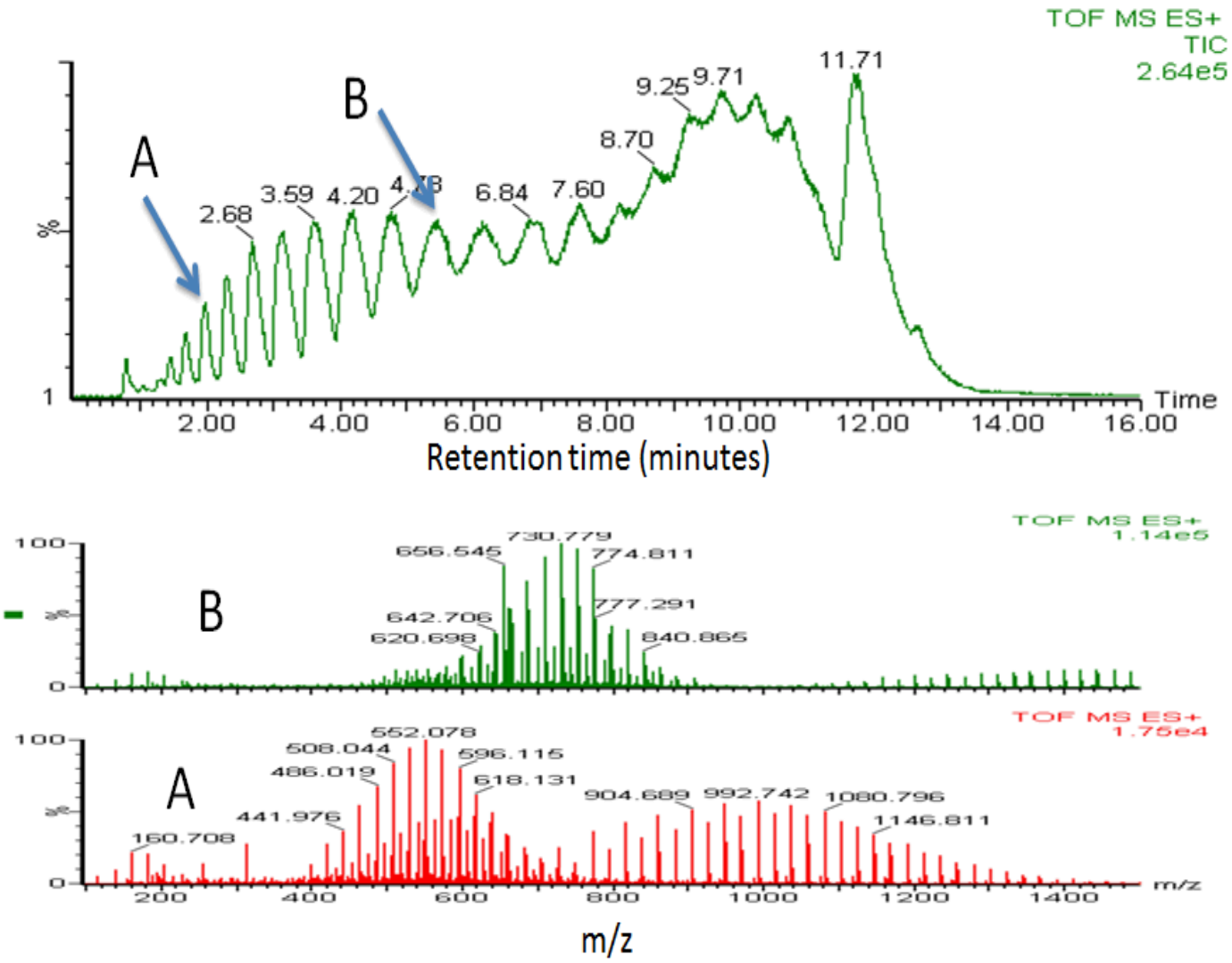
TD = thermal desorption

Mass spectrometry applied to unknowns:

non-volatile contaminant that won't show in GC/MS?

→ LC/MS

Yikes! Polymers in the solution!!



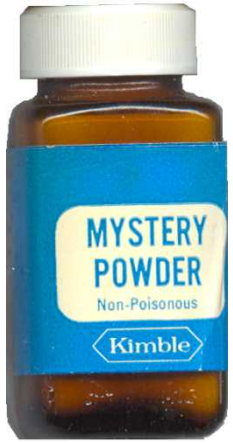
Mass spectrometry applied to bolts:

Using ICP/MS, what is composition of bolts?

ICP	Ni	Mo	Co	Ti	Al	Hardness
Good Bolts	18.0	5.0	8.5	0.4	0.1	48
Failed Bolts	18.3	5.1	8.4	***0.54***	0.12	49

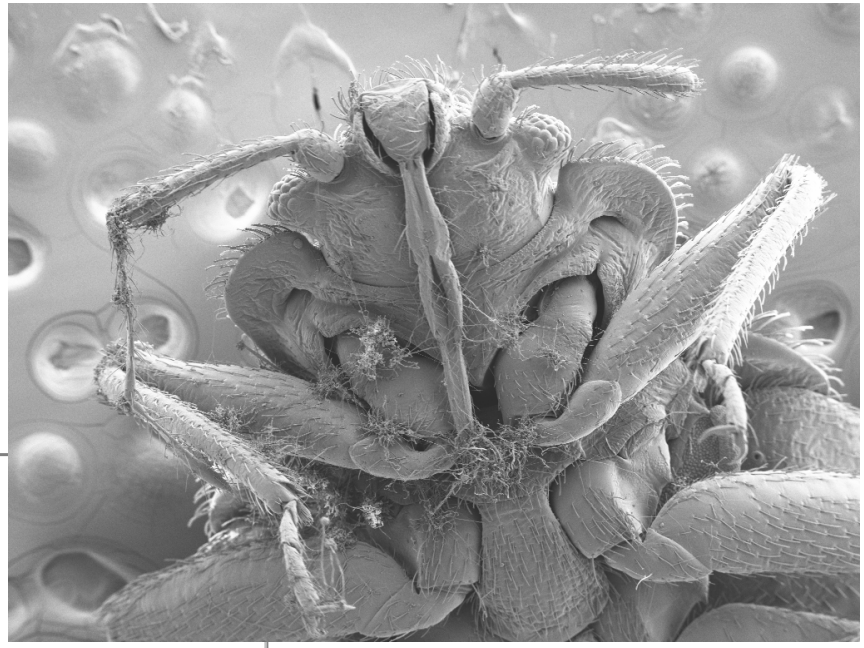
Issues that pop up:

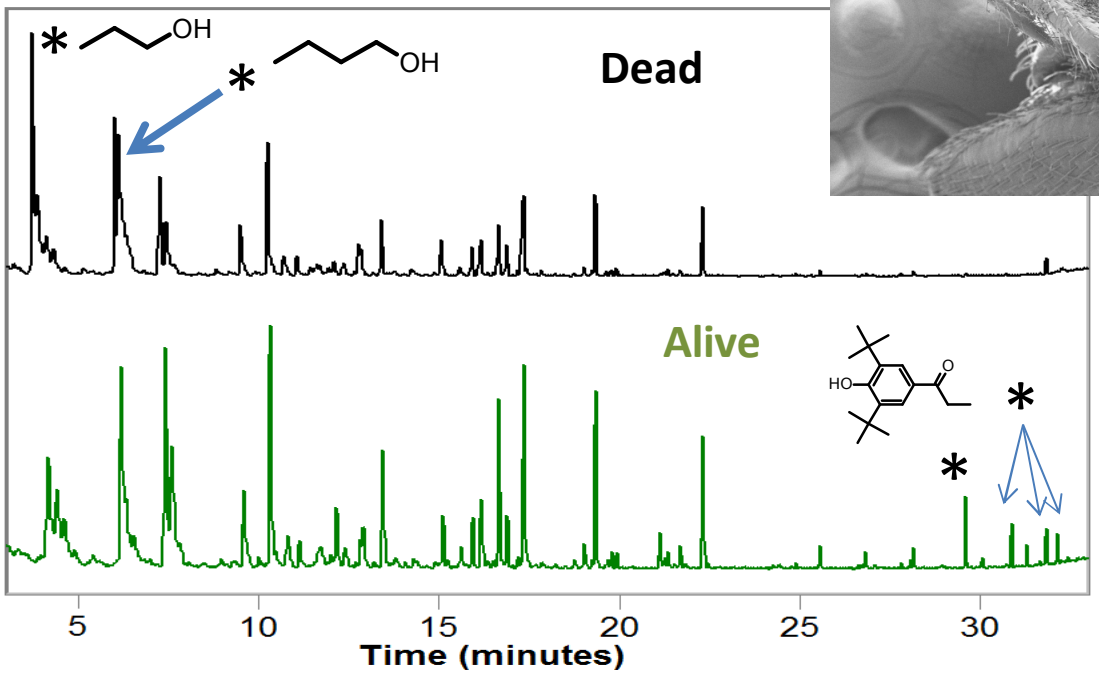
who has a control sample?
instrument confidence intervals?
digestion method? (instrument requires liquid)
dilution factors?
how long will the building last?
is the customer asking right questions?
unclear/unspecified ingredients



ICP = inductively coupled plasma

Mass spectrometry applied to bugs:





MS analysis provided customer with specific information for sensor development.

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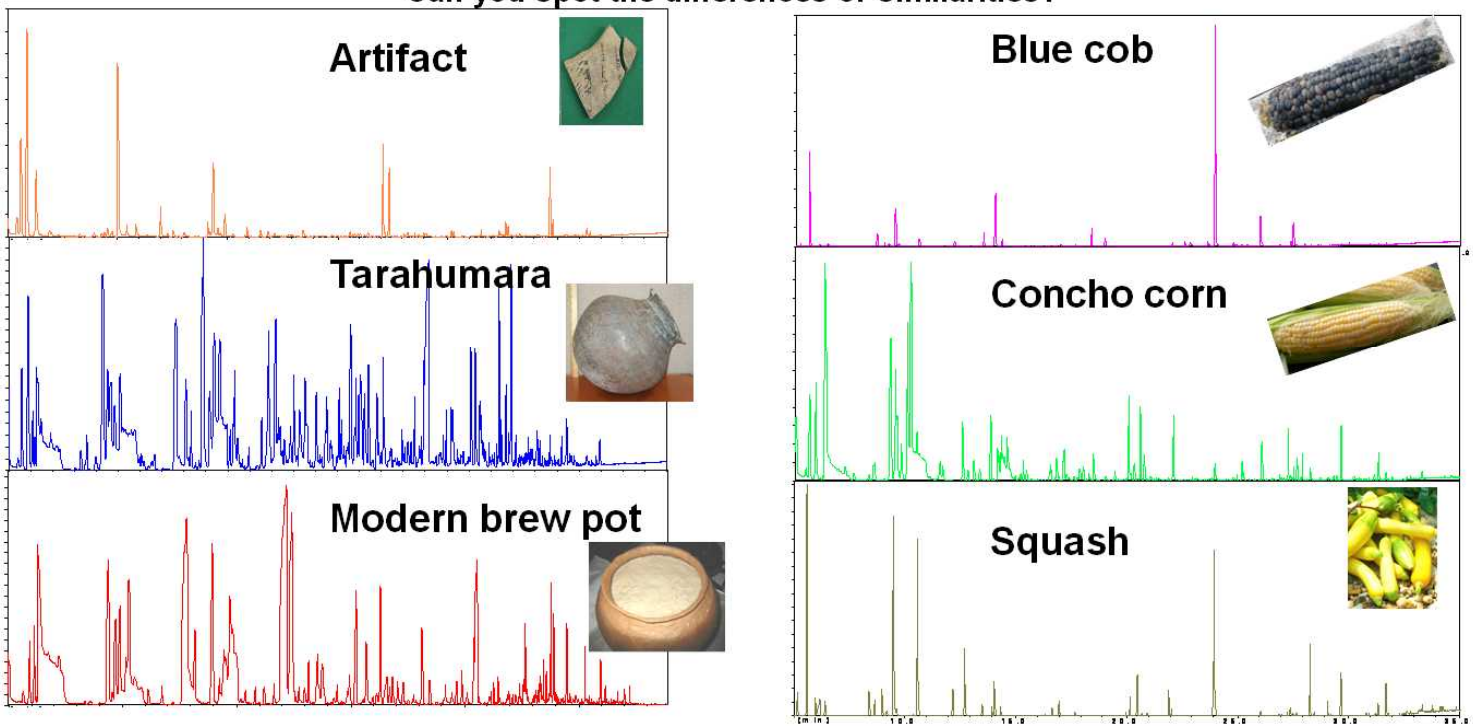
Mass spectrometry applied to beer:

Use TD/GC/MS

- **nondestructive**
- **no physical alteration of artifact**

Can you spot the differences or similarities?



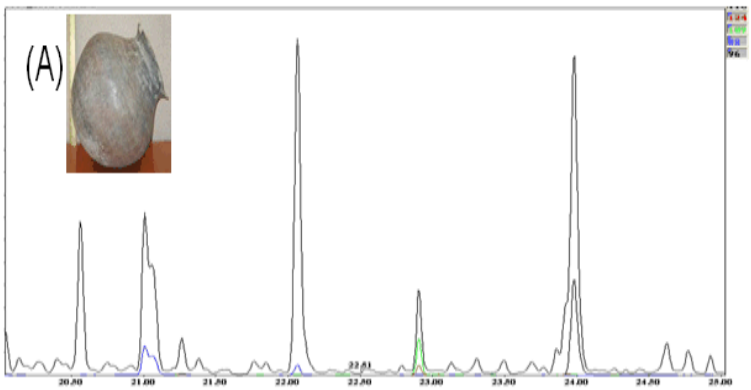
Issues:

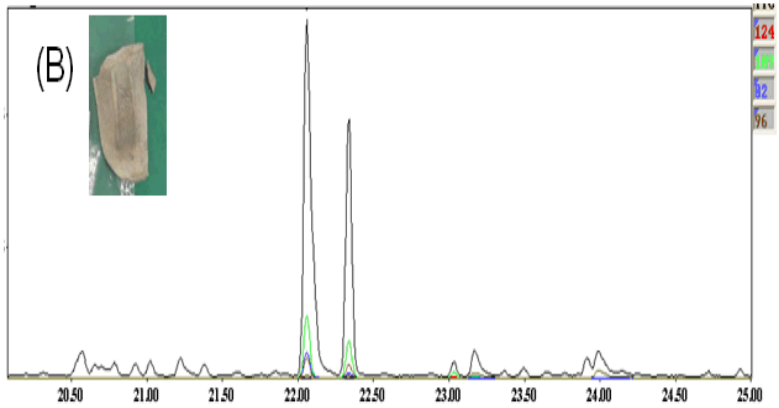
how do you define a control sample?

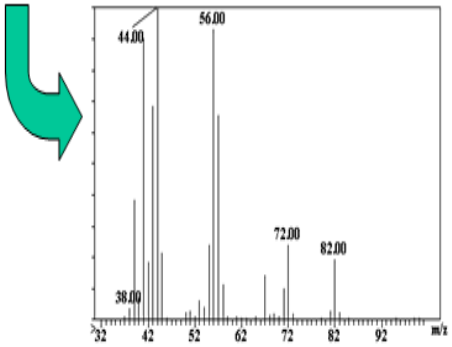
how do you account for instrument drift over years?

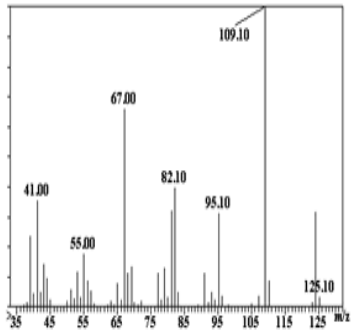
Mass spectrometry applied to beer:

Both Tarahumara (A) and Artifact (B) have a peak at 22.0 min. retention – are they the same compound?







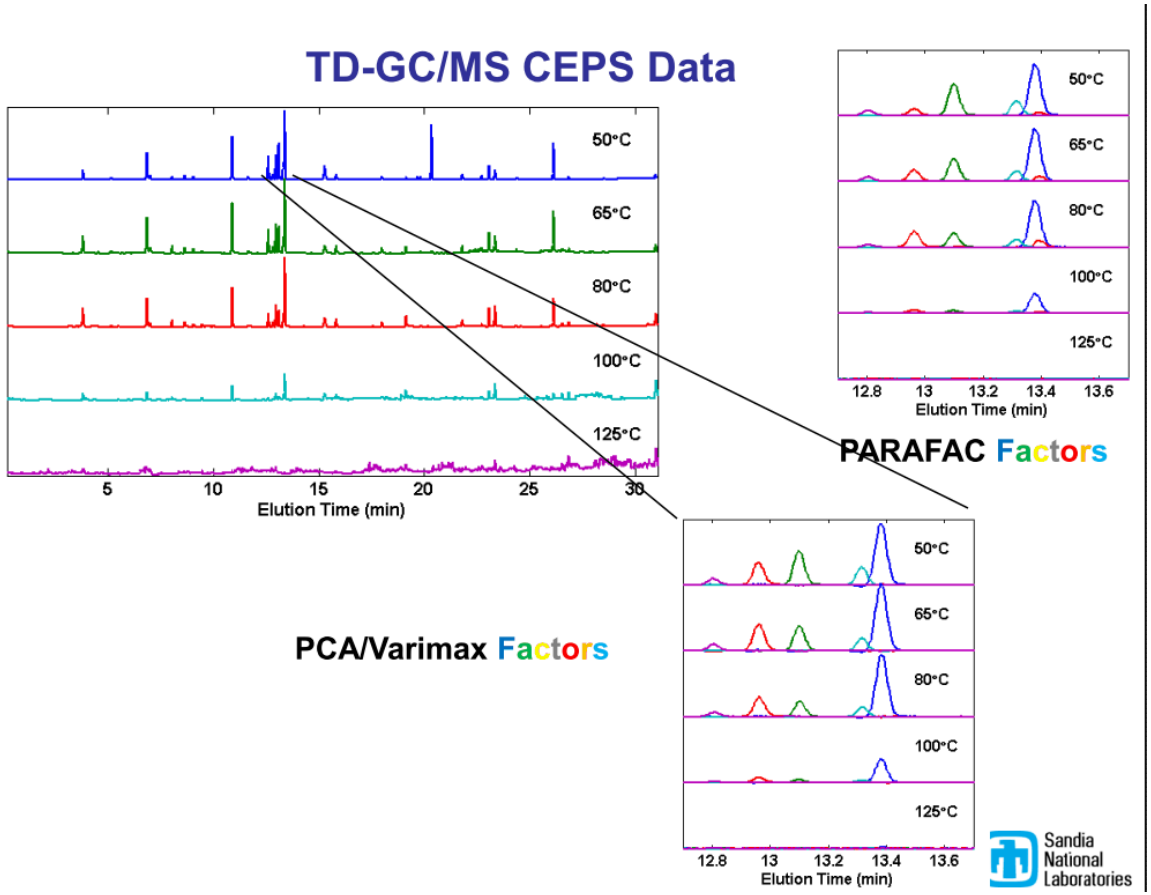


The mass spectrometer tells us this peak is not a match, HOWEVER there are many that do match!

MS analysis prevented incorrect assignment of coeluting compounds as markers.

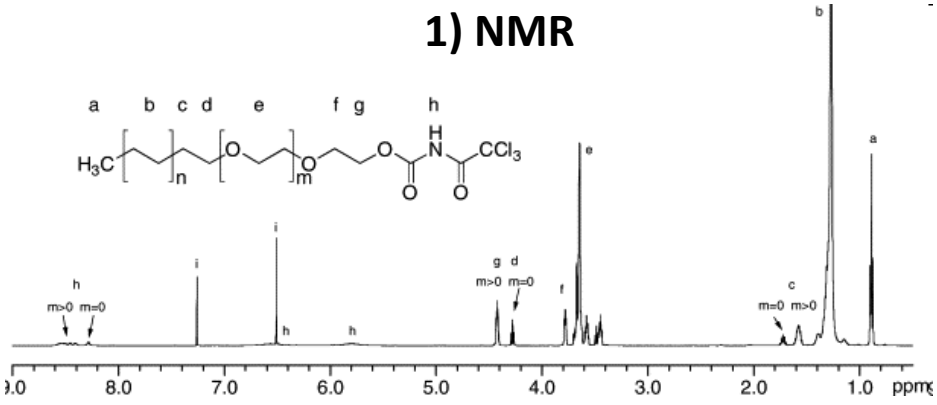
Advanced data methods

Rapid, PC-based algorithms enabled advanced analysis of complicated MS data.

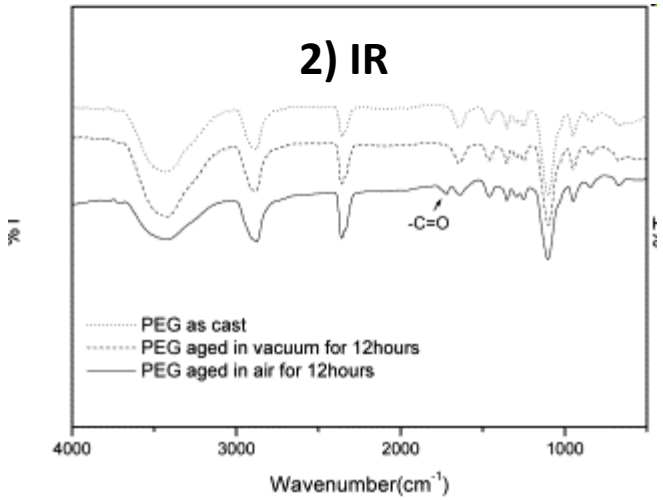


Tried and true methods for polymer analysis provide chemical information.

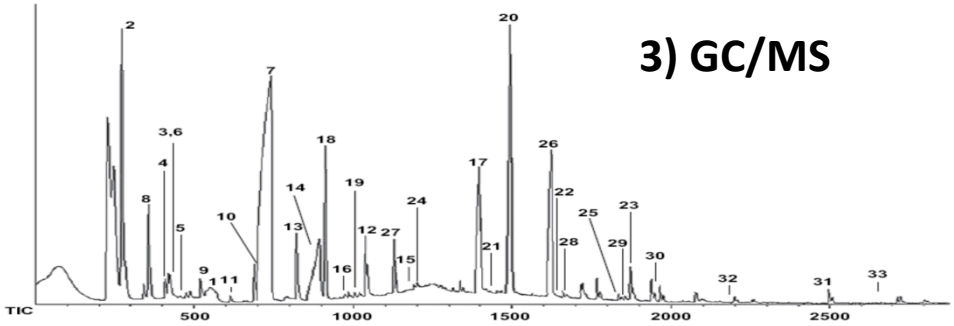
1) NMR



2) IR



3) GC/MS



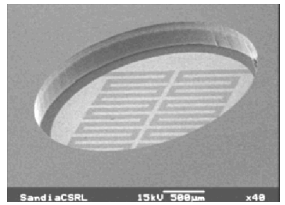
Useful
Predictable
Quick

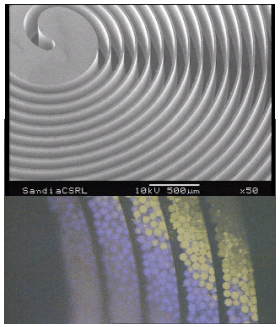
1) Postma, T.P. Davis, A.R. Donovan, G. Li, G. Moad, R. Mulder, M.S. O'shea, *Polymer*, vol. 47, pp. 1899-911, 2006.
2) W.-C. Lai, W.-B. Liau, Thermo-Oxidative Degradation of Poly(Ethylene Glycol)/Poly(-Lactic Acid) Blends, in *Polymer*, vol. 44, pp. 8103-09, 2003.
3) R. Bernstein, S.M. Thornberg, A.N. Irwin, J.M. Hochrein, D.K. Derzon, S.B. Klamo, R.L. Clough, *Polymer Degradation and Stability*, vol. 93, pp. 854-70, 2008.

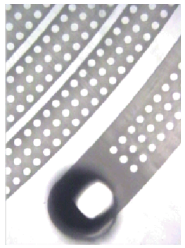
Sandia's microfabrication expertise is applied to each stage of analytical measurements

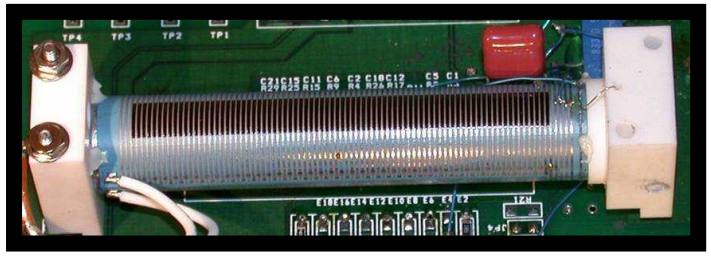
- Collect/Prepare
  - liquids, solids, gases
- Separate
  - time, space, mass
- Detect
  - optical, mass, other properties

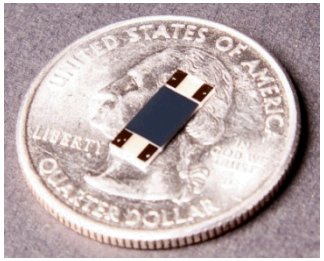
finned PC

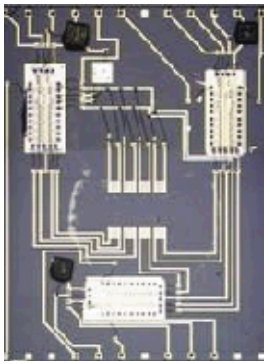


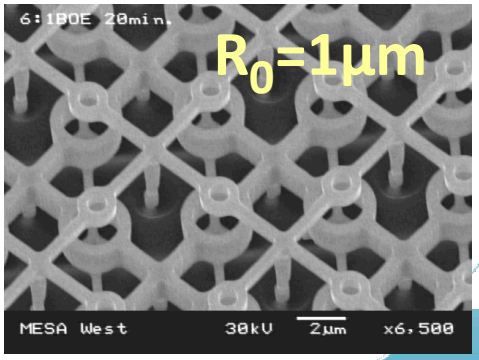












* Manginell et al. Review of Scientific Instruments, March 2012

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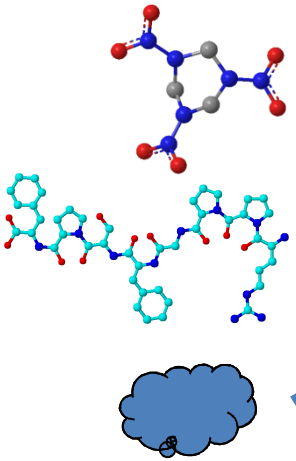
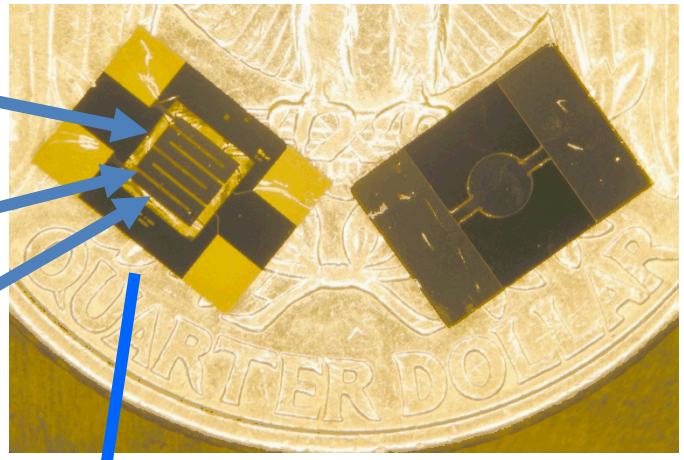
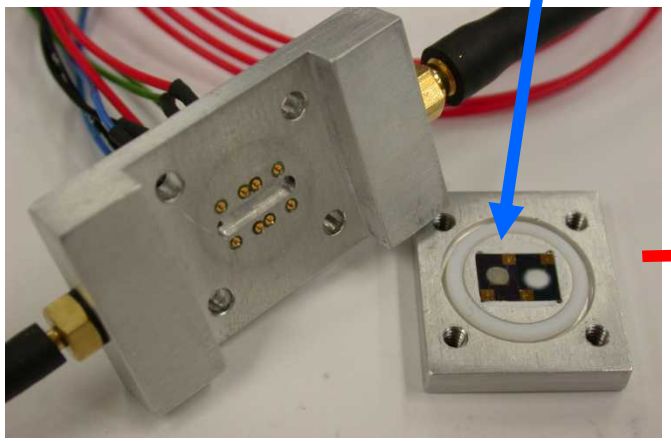
Sandia-fabricated micro-hotplates (μHP) perform sample collection and/or preparation.



or

or



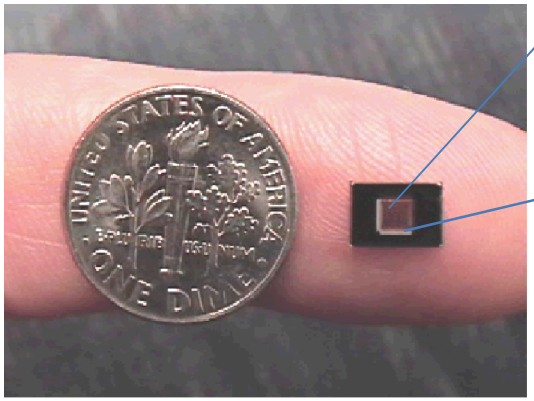


heat

measure

GC/MS
GC/???
TOF-MS

Sample collect/prep: controlling the environment and thermal profile.



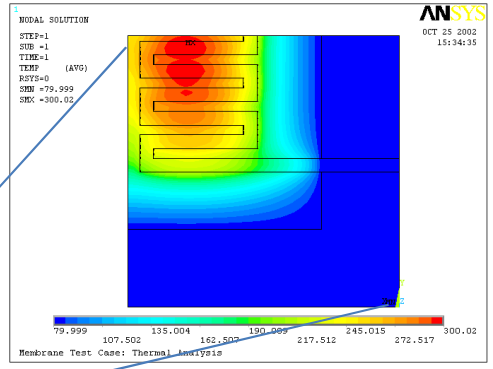


photo of new cup device

Applications:
vapor collection
vapor delivery

450 C in less than 100ms; <10V and <100mA
Pyrolysis derivatization reactions: <2.2Joule

$$T_{hot} = \frac{\left(\frac{R_{hot}}{R_o}\right) - 1}{TCR} + T_o$$

TCR = temperature coefficient of resistance

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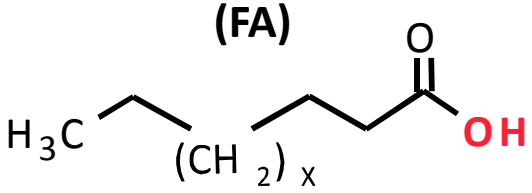
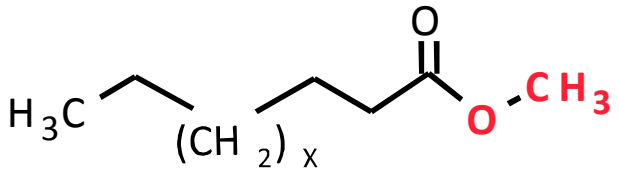
Sample prep: Microdevices provide measurement advantages by chemically converting samples with pyrolysis derivatization.

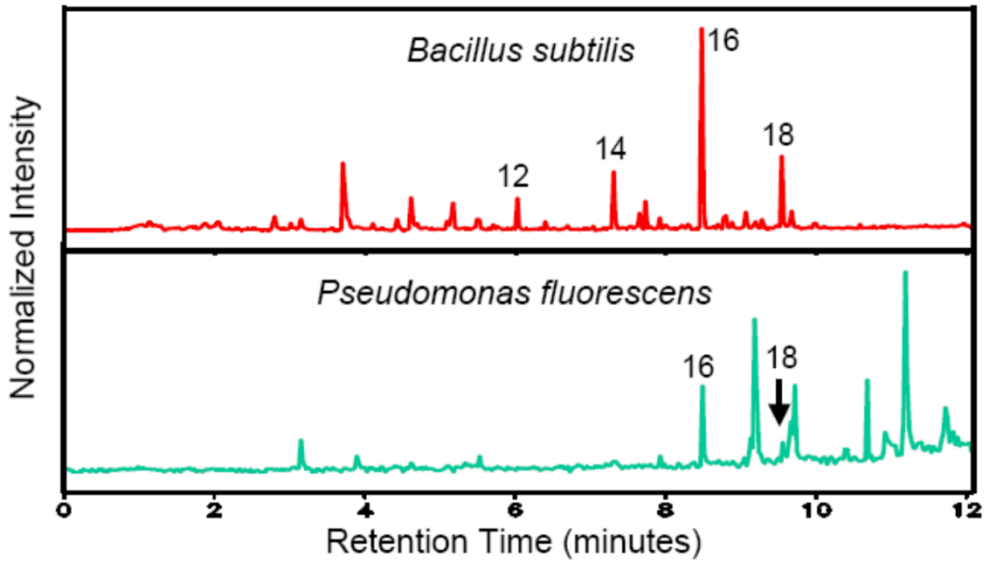
Fatty Acid (FA)



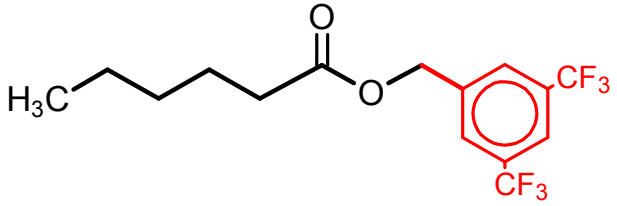
TMAH / pyrolysis

Fatty Acid Methyl Ester (FAME)





Also demonstrated:



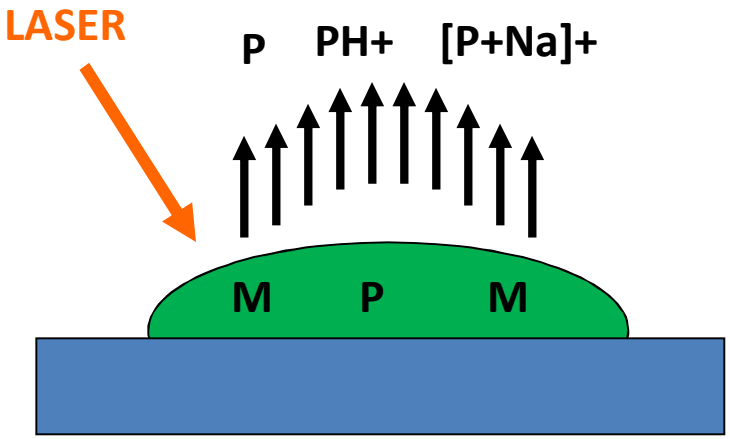
Applications:
edible oil adulteration
Biological warfare materials
Biofuels

Demonstrated applications:
Quantitative edible oil derivatization/analysis
Bacillus sp. whole cell / spore pyrolysis
Vaporization into GC/MS systems

Sandia National Laboratories

MALDI-MS is used for post heating measurements: shared 2002 Chemistry Nobel for good reasons.

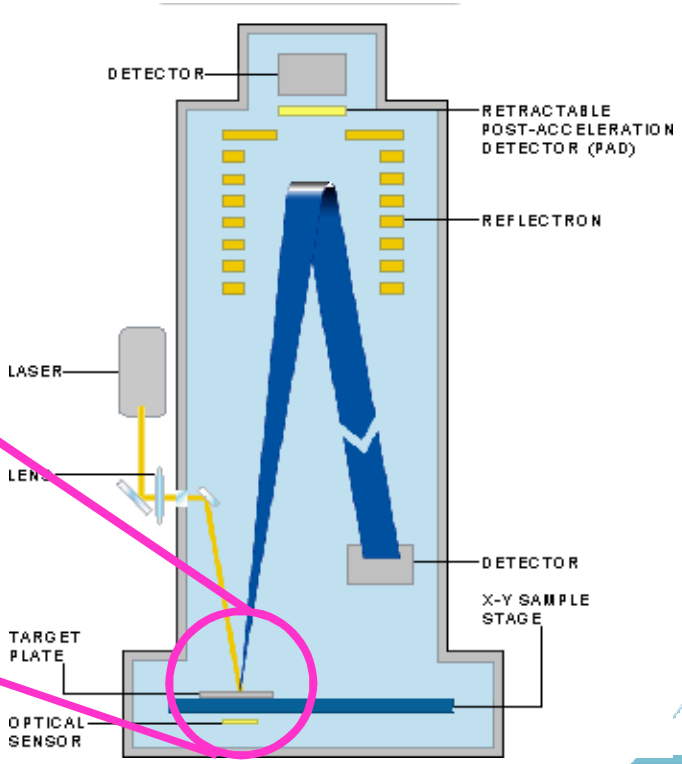
1. Generate ions



P=polymer, M=matrix

2. Measure flight time

$KE=\frac{1}{2}mv^2$



Simple, rapid
Intact molecules
High mass measurements

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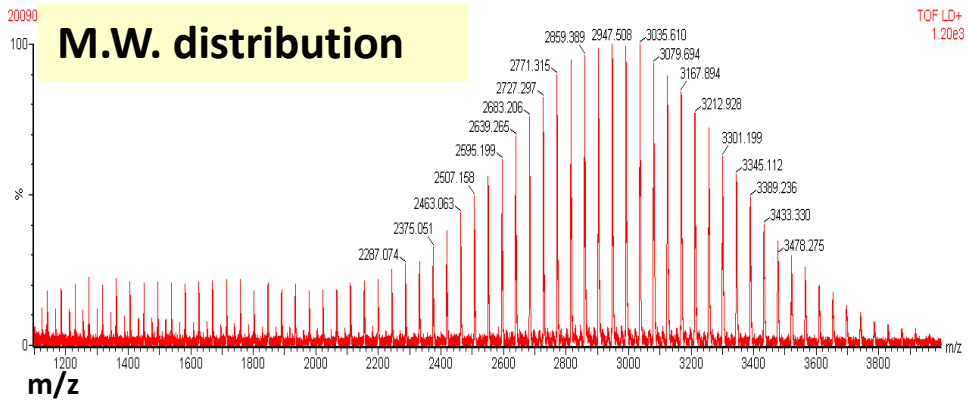
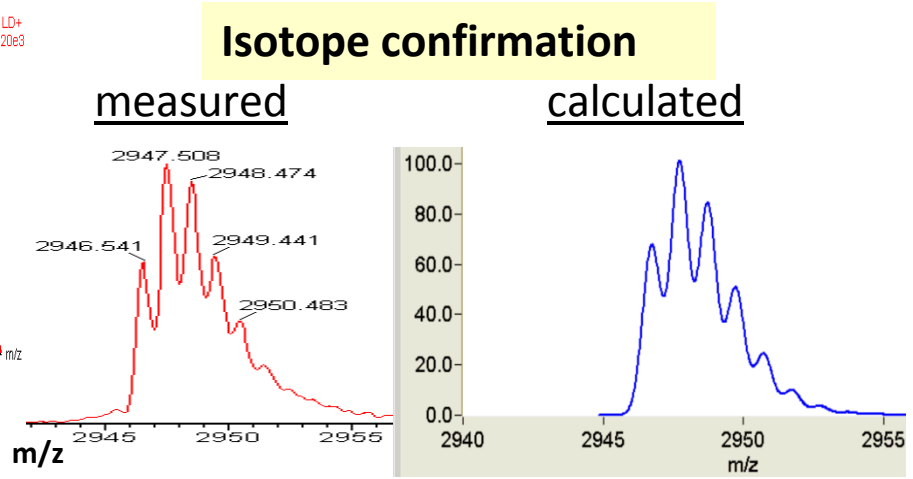
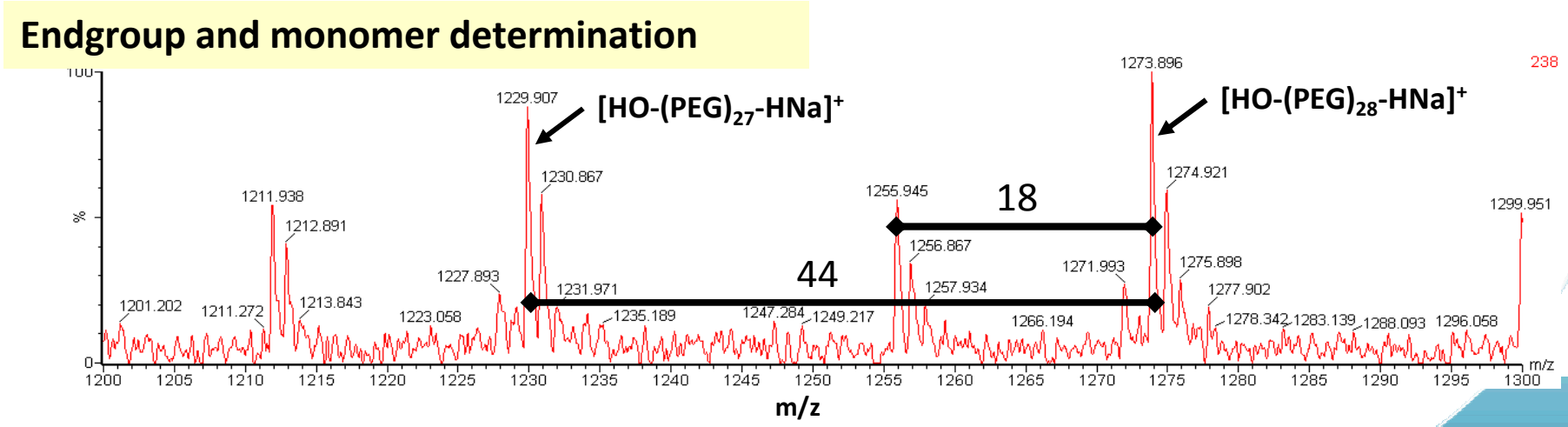
MALDI-MS provides rich information because polymers are measured fully intact.







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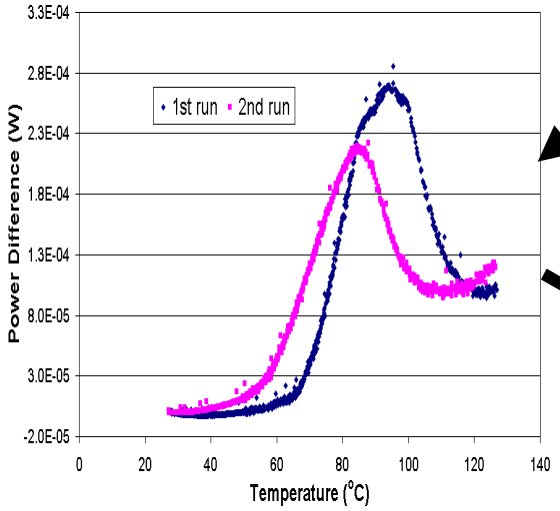
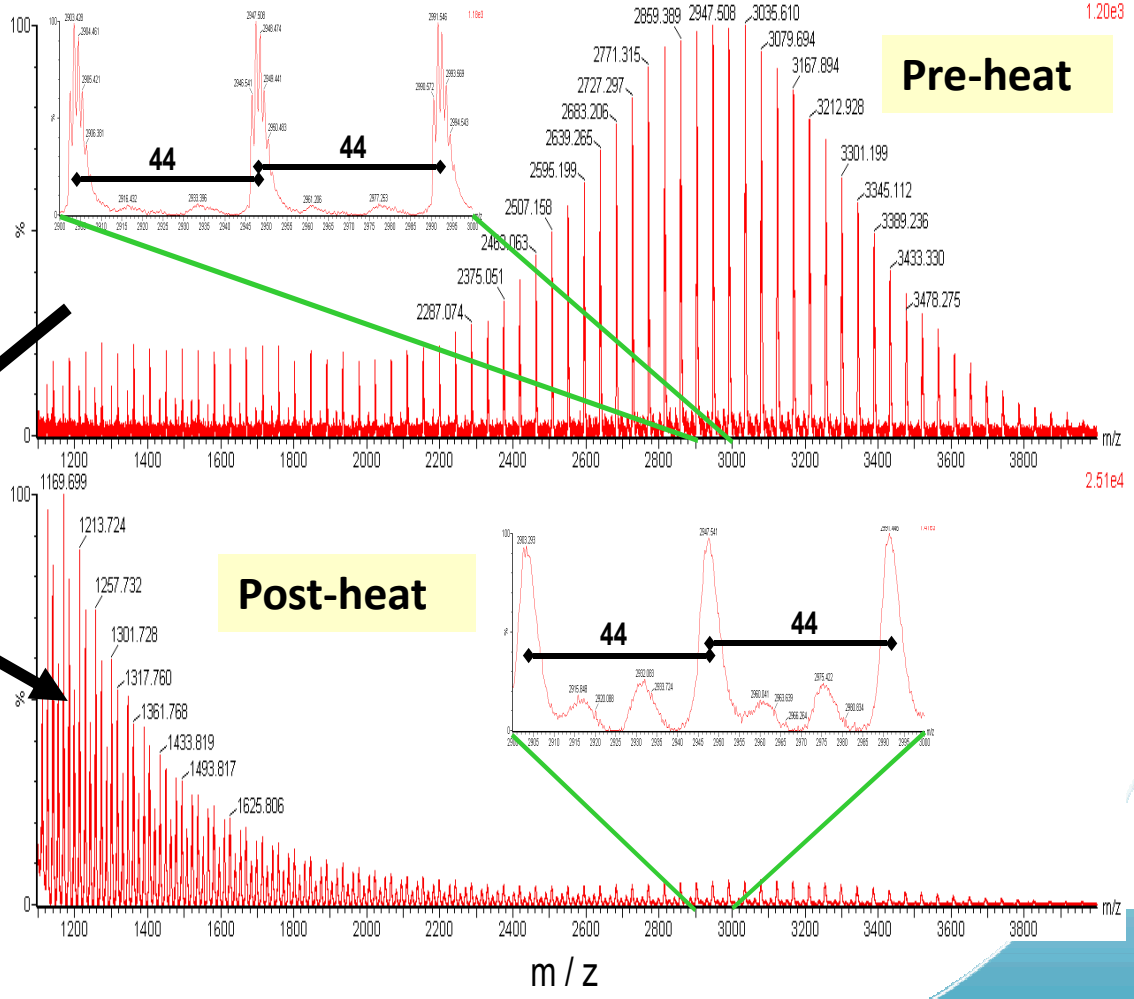
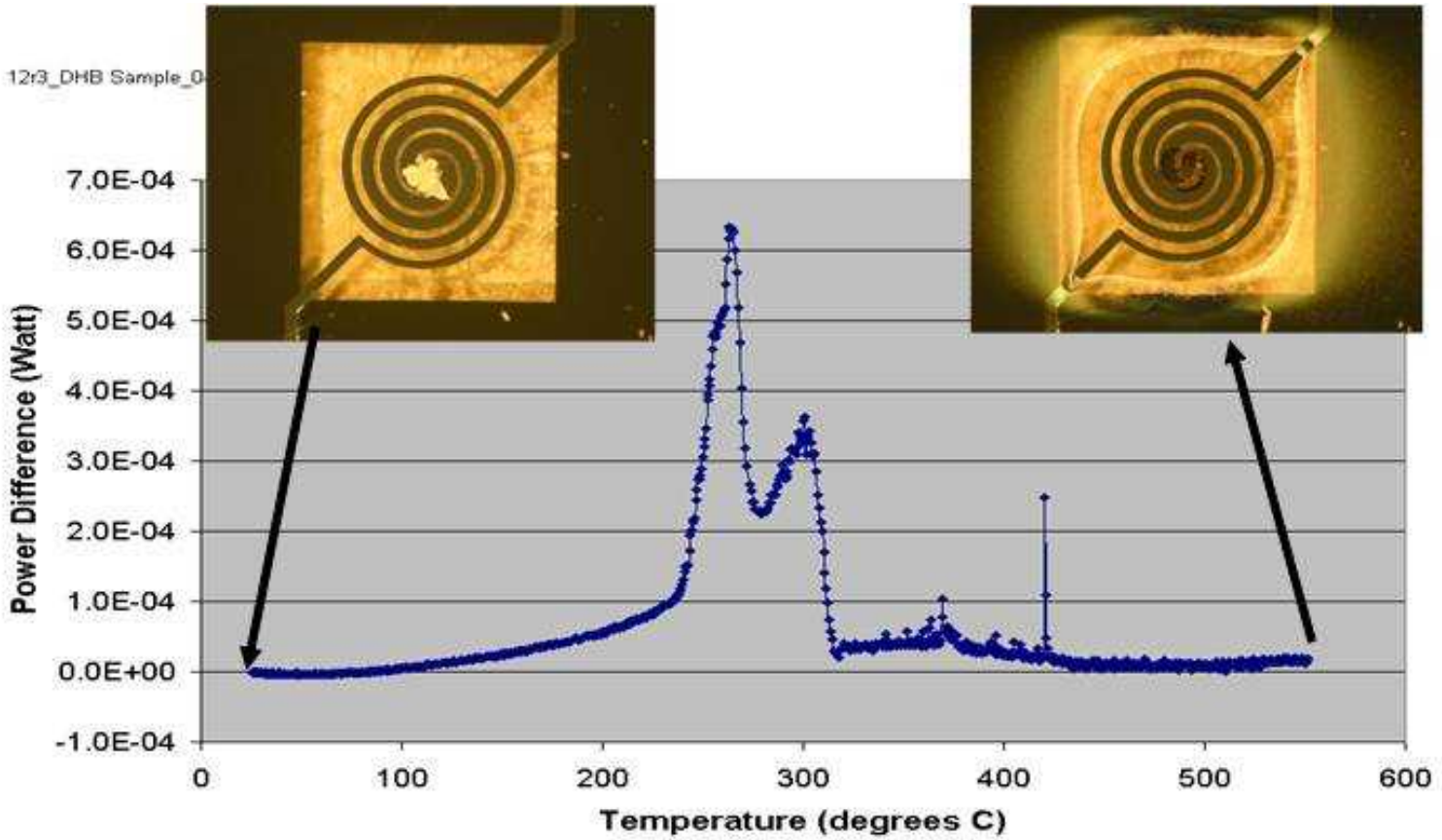
Sample prep: precise temperature ramping for aging studies for MALDI-MS directly from surface.

Consecutive heating ramps

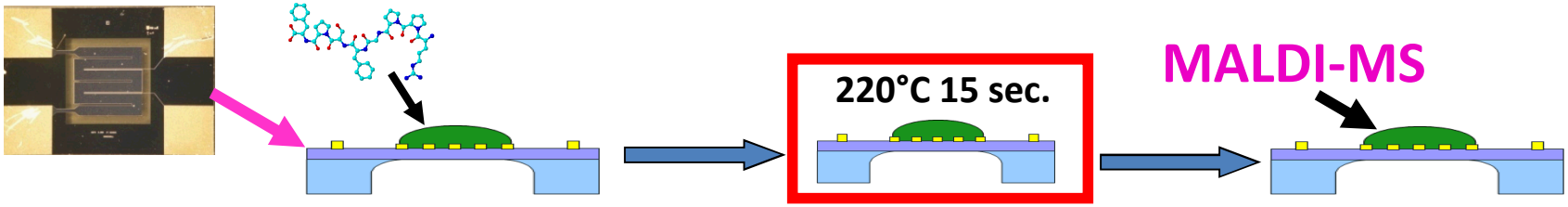




Microdevices applied to calorimetry



Sample prep: precise heating profile for thermal "digestion" for MALDI-MS directly from surface.



Pre-heat

RPPGFSPF

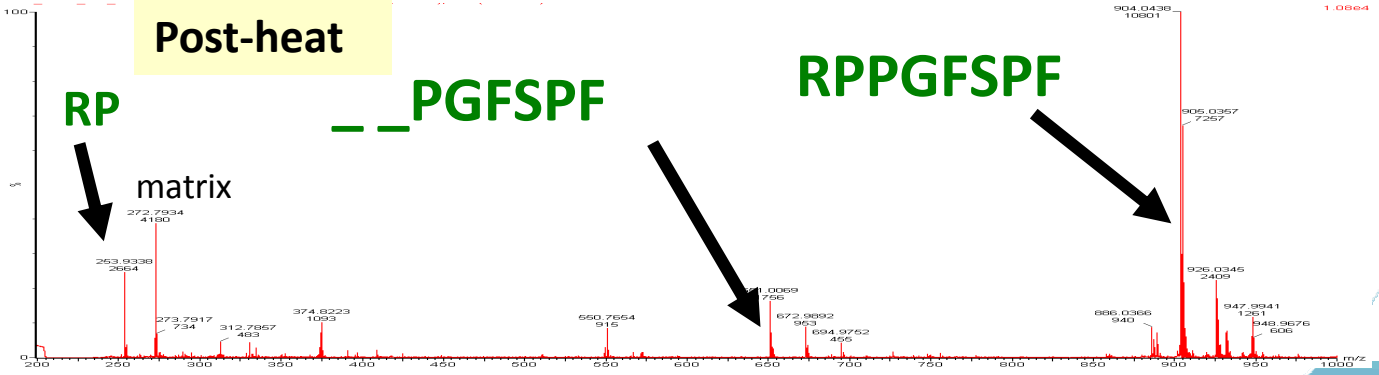
MALDI-MS detects intact and thermally degraded fragments.

Post-heat

RP

_ _PGFSPF

RPPGFSPF



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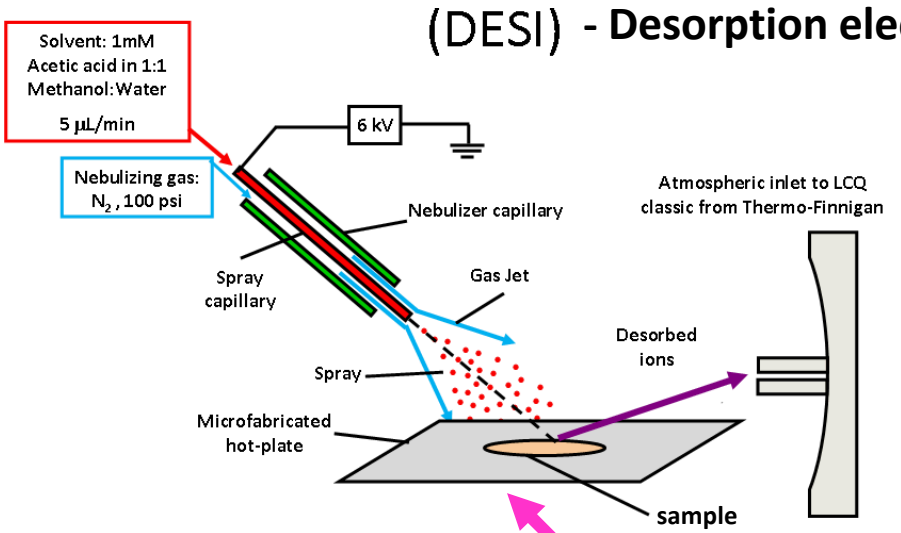
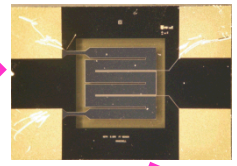
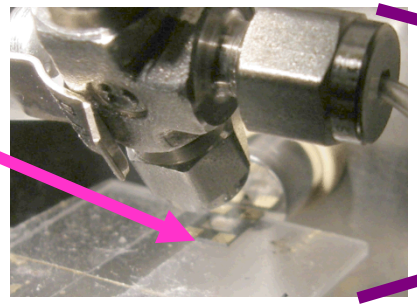
DESI-MS measures mass of molecules INTACT and without sample prep.

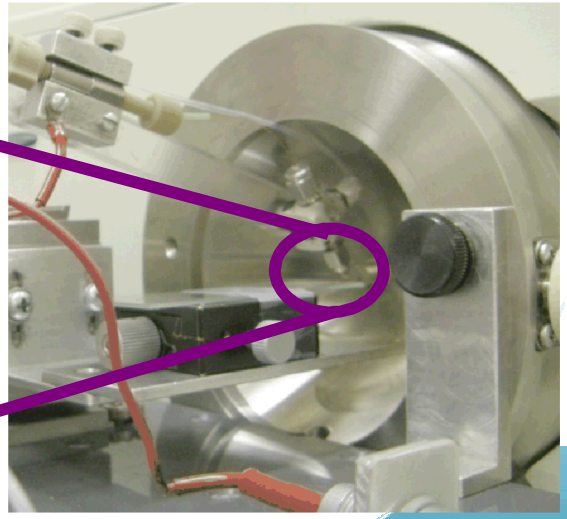


No sample preparation
in situ analysis
m.w. upper limit?

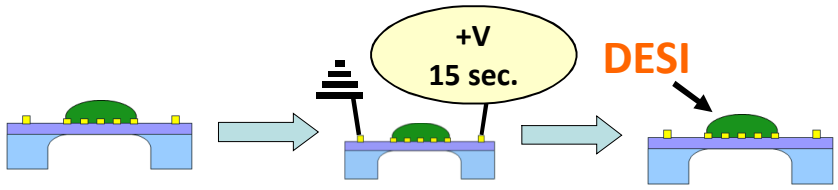
Examples:
Explosives
Drugs
Polymers
Oils



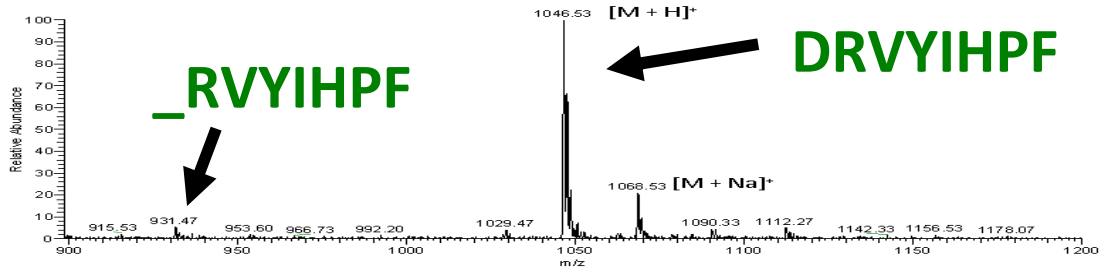




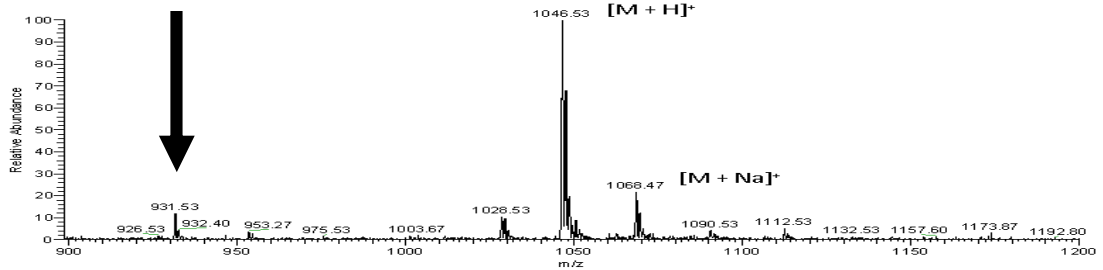
Sample prep: thermal “digestion” of polypeptide for DESI-MS directly from surface



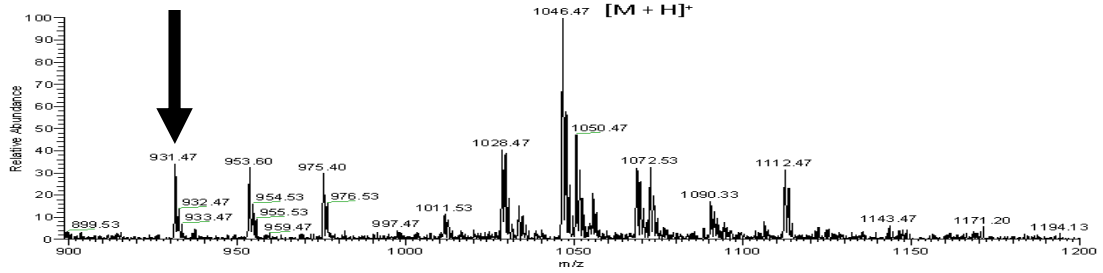
218°C



240°C



259°C



Sample heated by µHP ⇒ effects of heat detected without sample manipulation.

Precise control over heat and heating profile.

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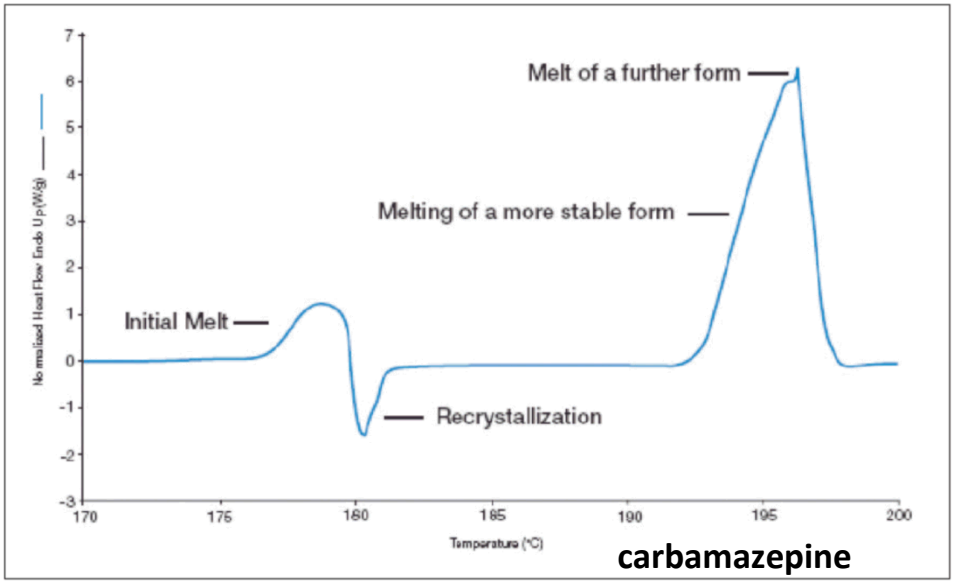
Typical calorimetry provides insight into chemical processes.

Perkin Elmer DSC 8500
scanning rates to 750ºC/min



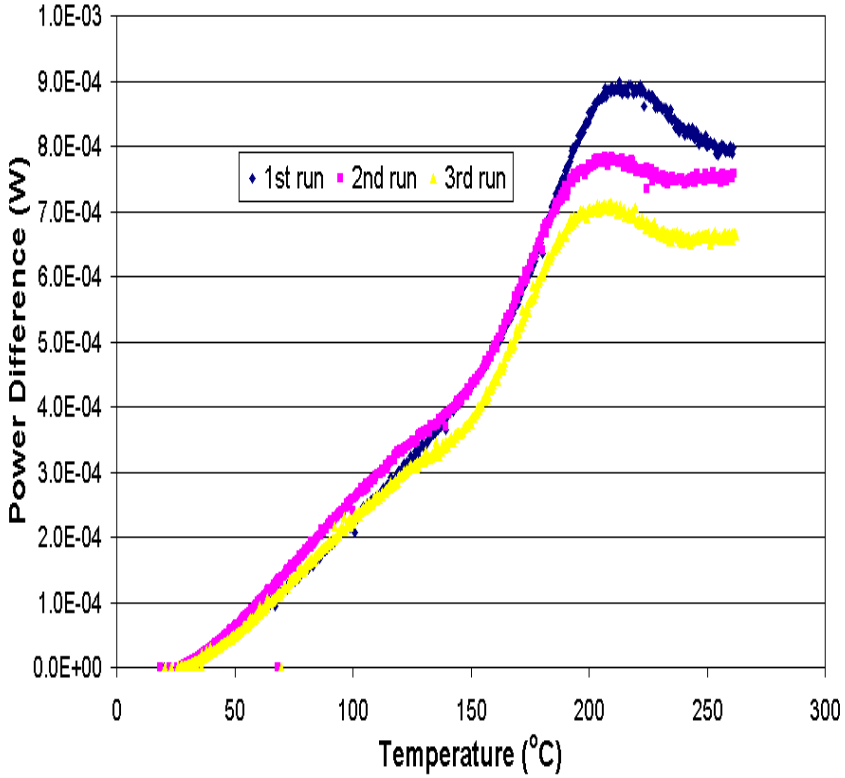
Measurements: shape/width of curve, onset temp, variation w/ ramp rate, energy flow

Applications: heat capacity, purity, energetics, crystal phase

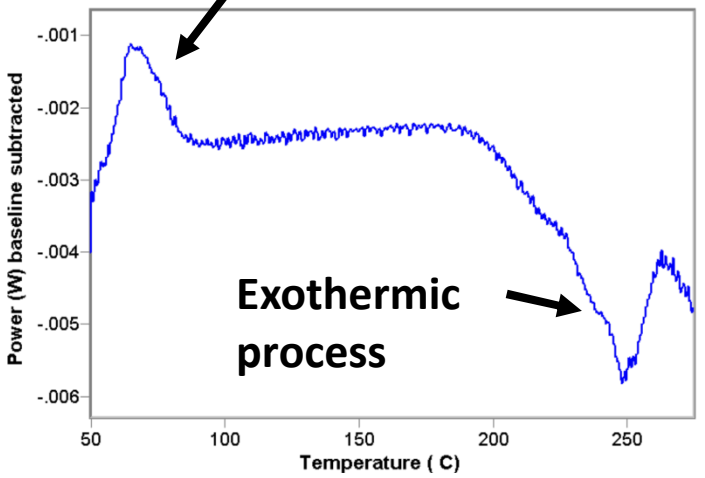
Perkin Elmer sales literature data shown.

Sample prep: μHP calorimetry has same features and control as traditional calorimetry.

Consecutive heating polypropylene.



Endothermic melting



Control:
Scan rate
Temperature range
Atmosphere

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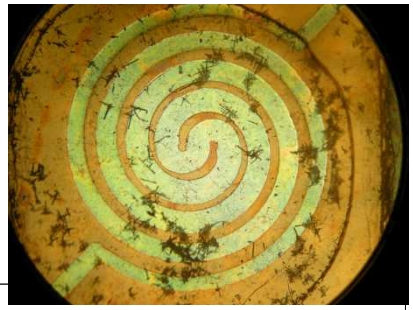
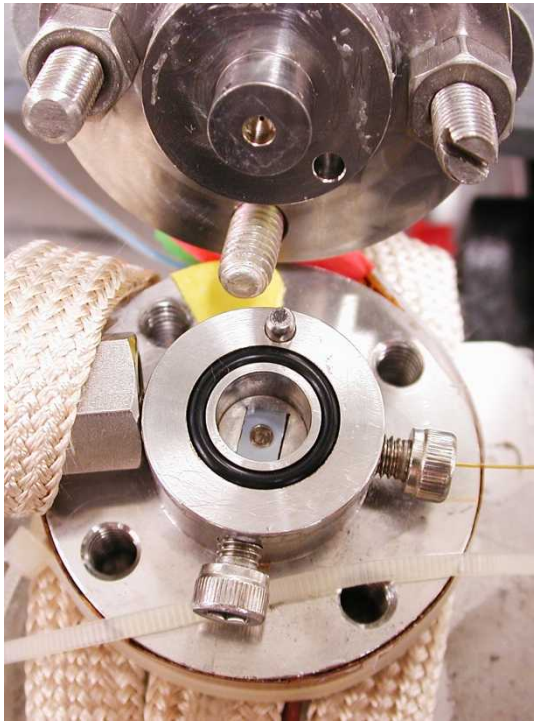
Challenges for microdevice calorimetry MALDI

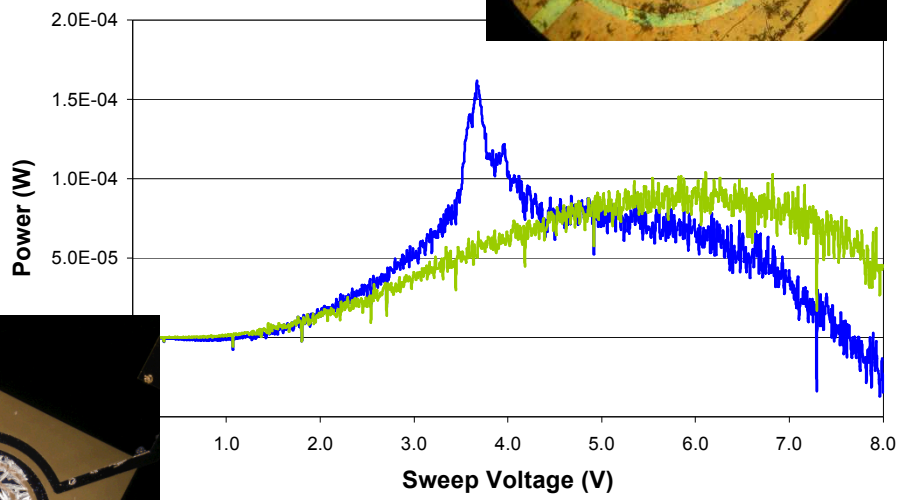
- Temperature calibration
- Sample deposition
- Matrix deposition
- Electrical hardware

Scan rate ~3200 °C/min. !

Less than
2.8 micrograms
RDX

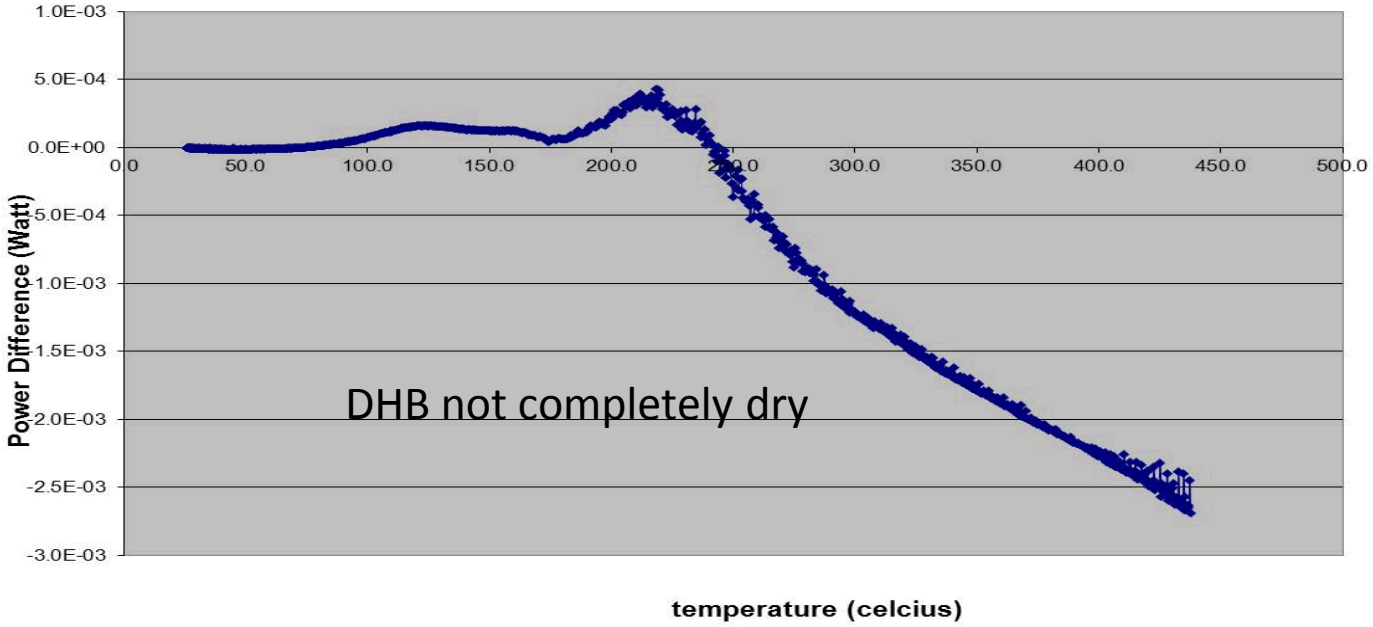






More challenges and future work for calorimetry

- Thermal behavior of matrices
- Other devices (structures, heater materials0
- MALDI mapping
- Calorimetry of biological samples
- Processing of MALDI samples
- Temperature ramp & hold



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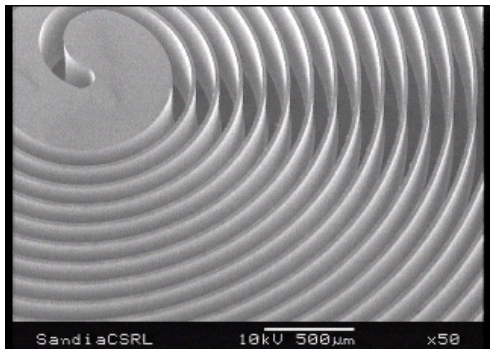
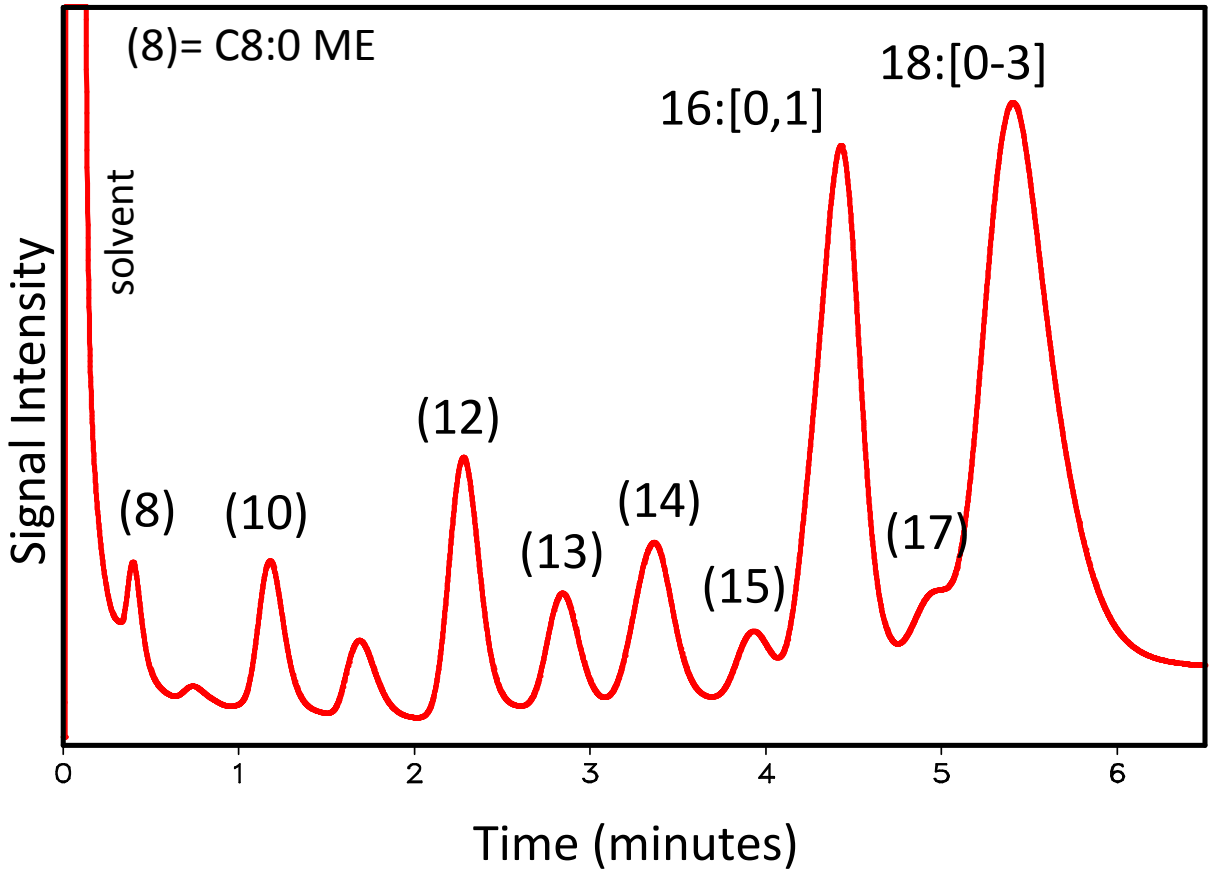
Microdevices applied to separation

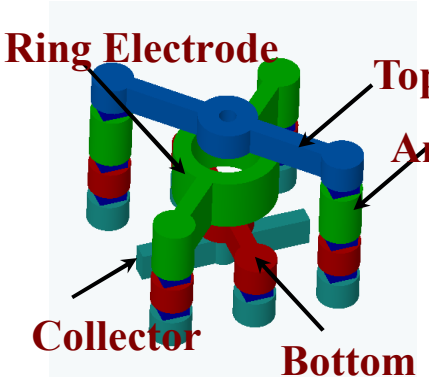


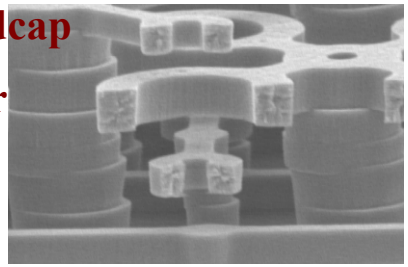


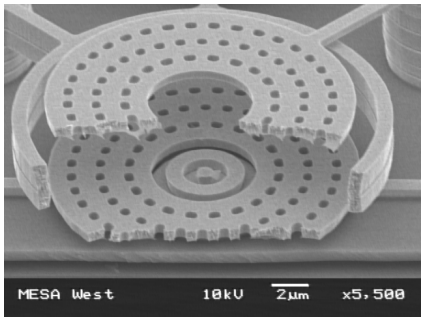
GC079, OV-101 coated 100µm x 86 cm, N2 carrier, temperature ramp 60-150 @20°C/min.

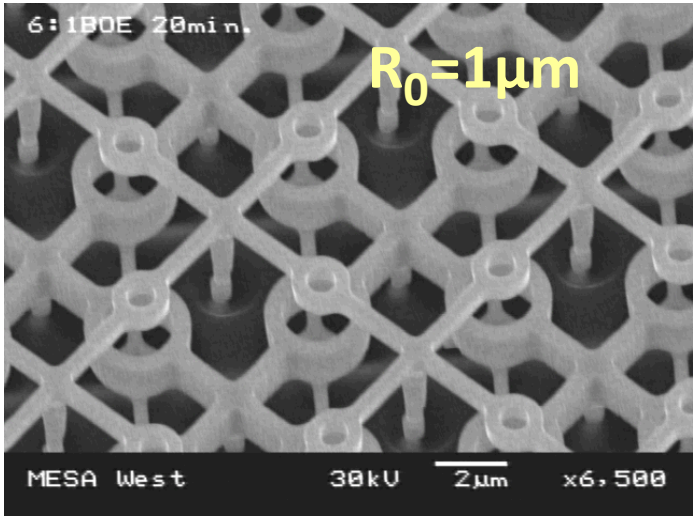
Microdevices applied to detection

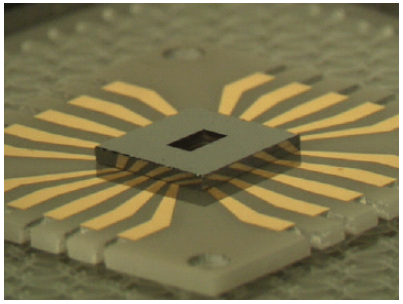
- Arrays of linear traps
  - range in number and size from 3 trapping regions of 0.97 mm (lateral electrode to electrode distance) to 39 trapping regions of 90 micrometers in size.
  - Each of these trap arrays occupies a 4 mm X 3.5 mm trapping zone and
  - resides within a 64 mm^2 trap chip packaged onto a 1 $inch^2$ AlN carrier.











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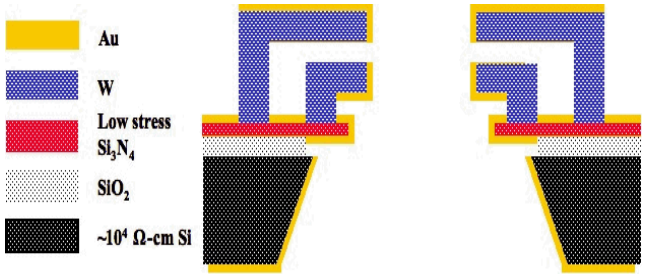
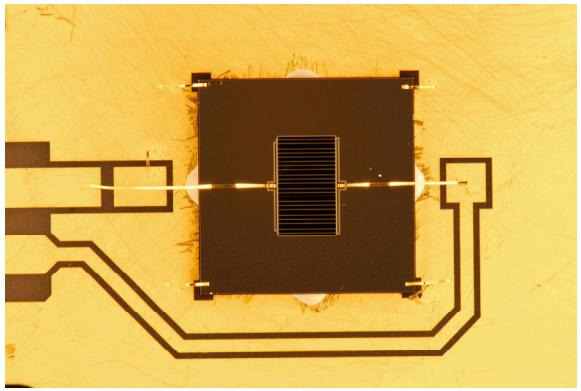
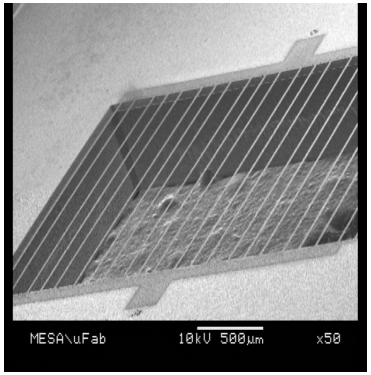
Microdevices applied to detection

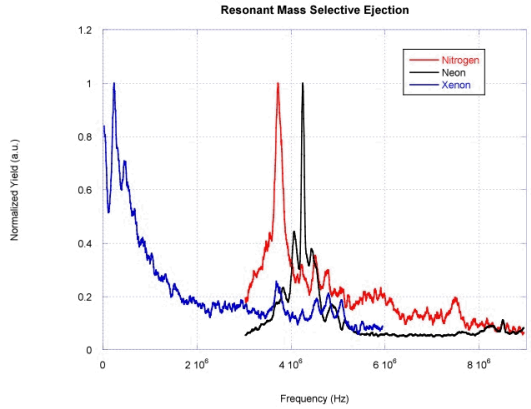
1st Generation: Array of Paul-Straubel Traps in Trap/ejection/Time-of-Flight operation mode

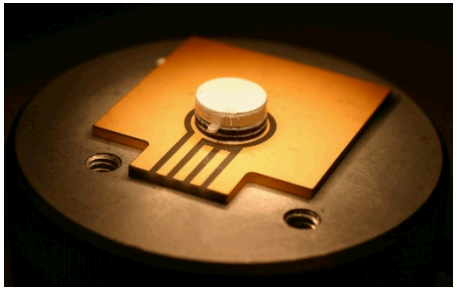


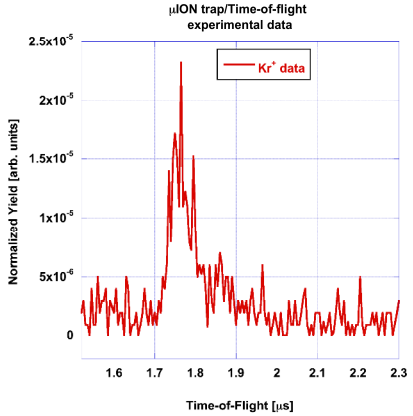




2nd Generation: Array of cylindrical ion traps in Trap/resonant mass ejection operation mode







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Conclusions

Materials characterization
- Never a dull moment
- Talk with customer
- Apply the right tools

Sandia micro-hotplates
- Versatile, low mass
- Low heat capacity and capable of high temperature,
- Inert to many chemicals, and
- robust for heating and mass spectrometry sample introduction.

Sandia Microdevices
- Useful for sample collection, preparation, separation, and detection applications
- Have benefits and tradeoffs