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Mass Spectrometry and Microfabricated Devices for Materials Characterization at Sandia National Laboratories

Curtis D. Mowry

Materials Charaterization Dept. 1822

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NNSA National Nuclear Security Administration

Sandia National Laboratories

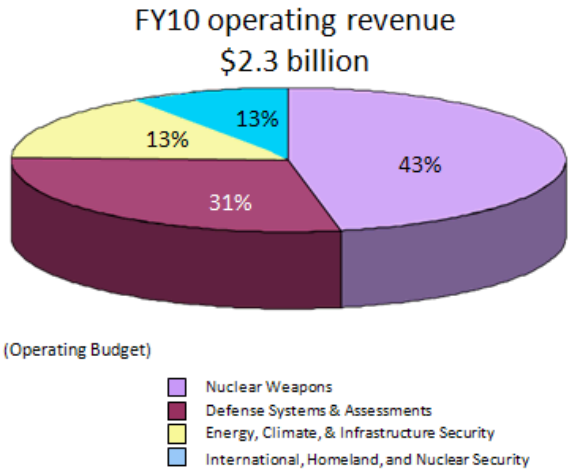
Sandia's History

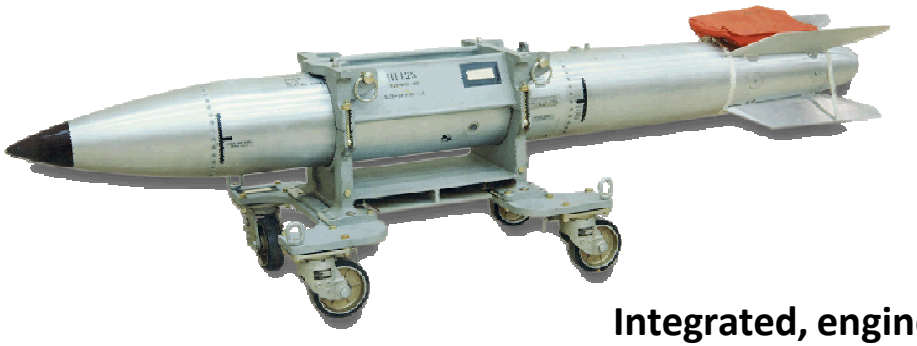
1950s: Stockpile development - design and produce nuclear weapons.
1960s: Continued stockpile development; introduction of permissive action links. Development of space-based and seismic verification systems.
1970s: Additional mission in energy research and development.
1980s: Department of Defense , 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.
2000s: Continuation of life extension programs. Enhanced activity with Department of Defense. Homeland security.

Sandia National Laboratories

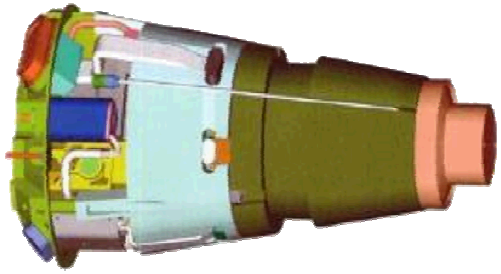
Sandia's Mission

<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%

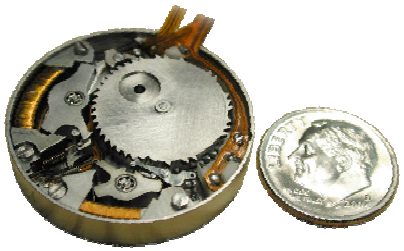




Integrated, engineered warhead systems



Arming, fuzing, and firing systems



Safety systems

1950 – 100% NW
2010 – 40% NW

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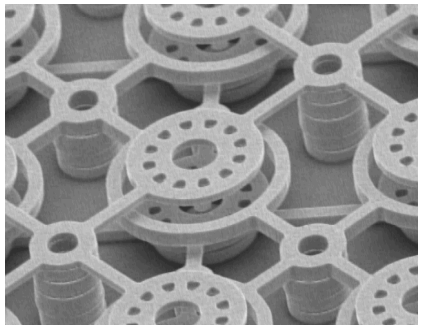
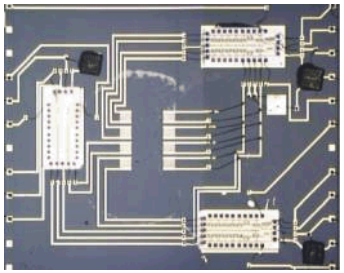
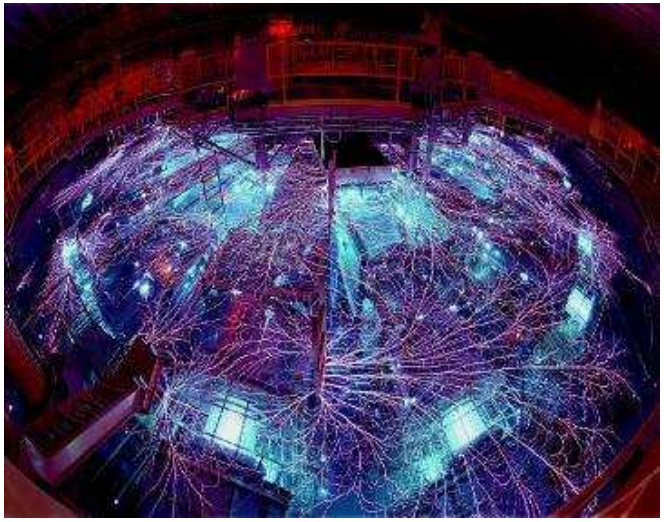
Sandia's Non-Nuclear Work

- Defense
- Satellites
- Energy, water
- Homeland security



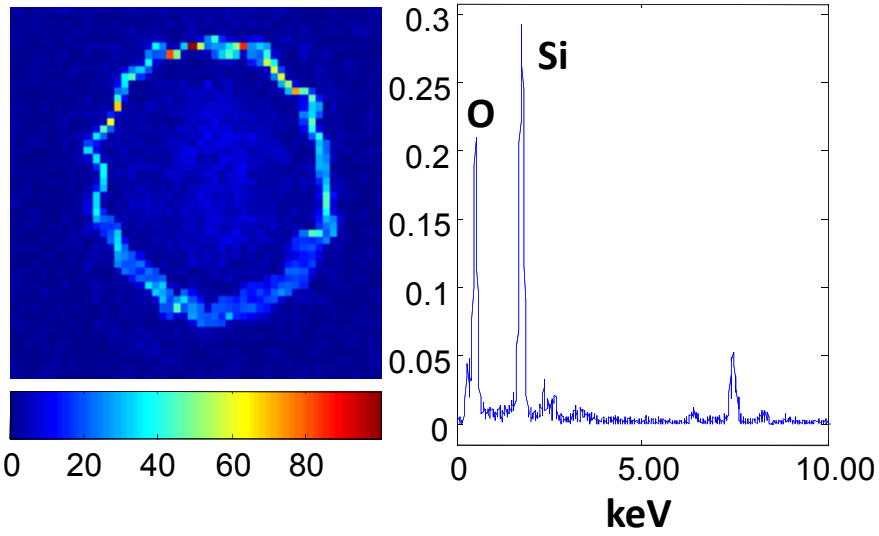


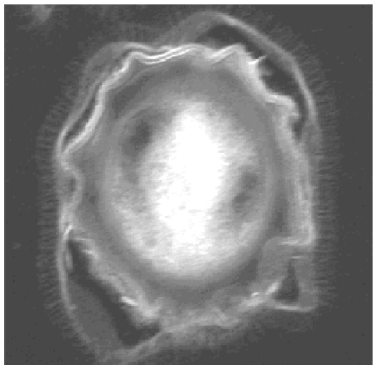


Materials Characterization Department

Experts in the following techniques:

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



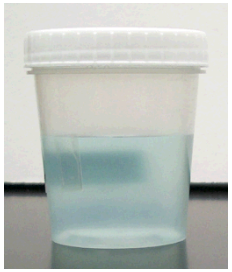


Organic / Inorganic Analysis

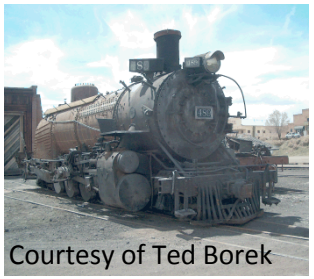
We Test:

GASES

LIQUIDS

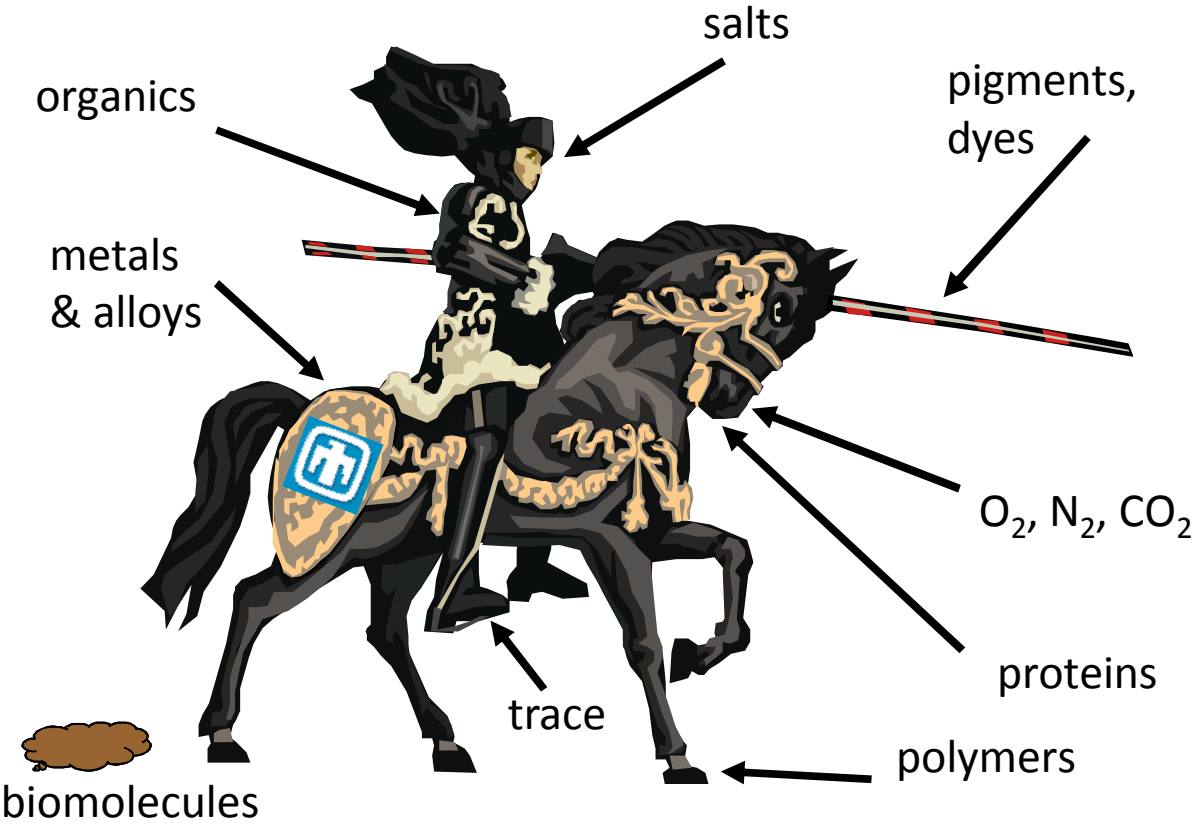


SOLIDS



Courtesy of Ted Borek

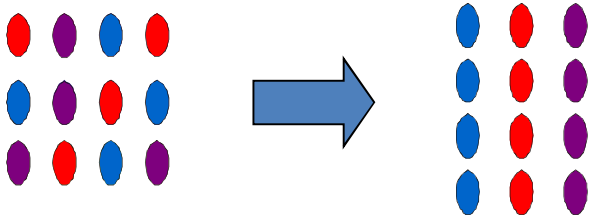
Looking for (for example):



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

Analytical Chemistry in a Nutshell

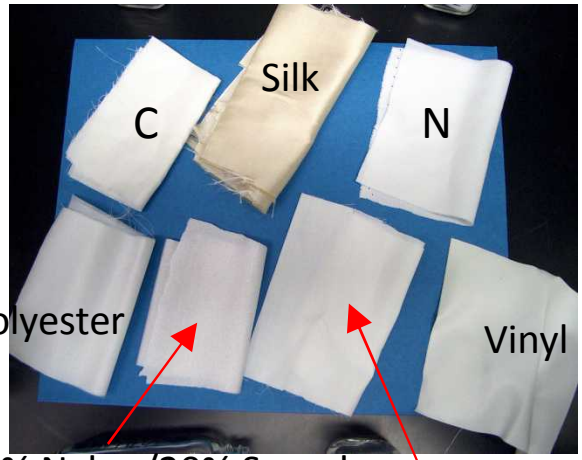
- Sample/Collect
  - liquids, solids, gases
- Separate
  - time, space, mass
- Detect
  - optical, mass, other properties



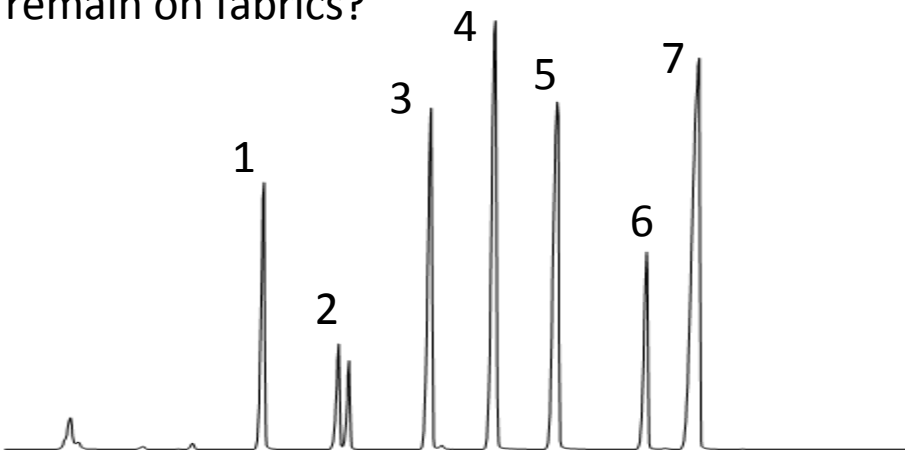
Mass spectrometry examples

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



How long do chemical weapons simulants remain on fabrics?

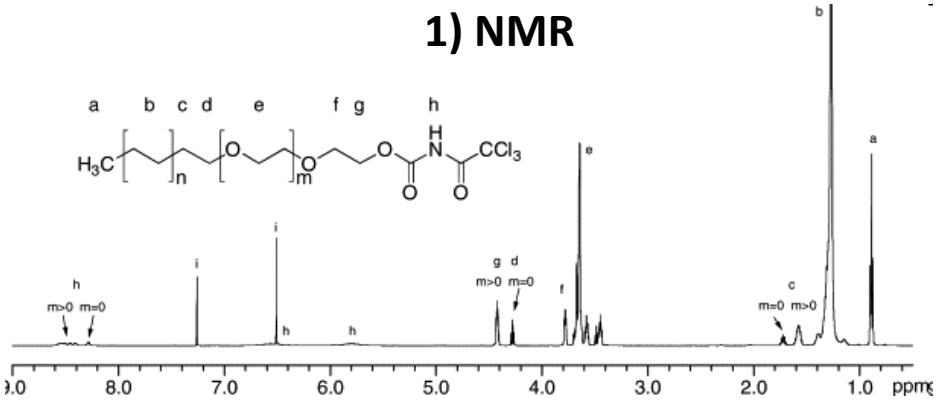


For Safety and Security, Aging and Composition of Polymers is Useful Knowledge

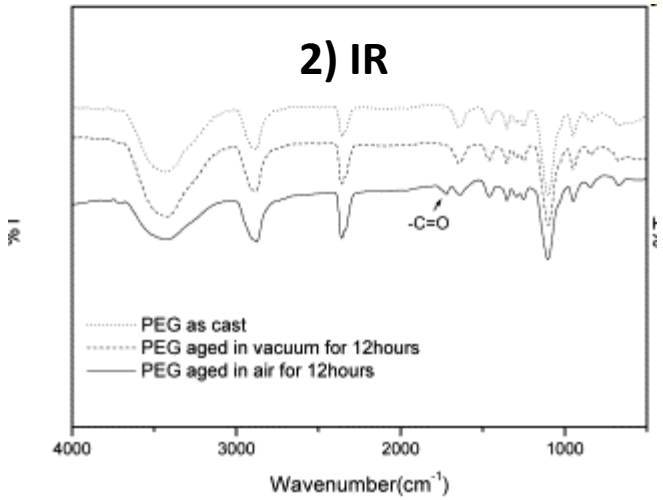
- Seals / O-rings
- Plastics
- Binders
- Wiring
- Connectors
- Circuit boards

Tried and true methods for polymer analysis provide chemical information.

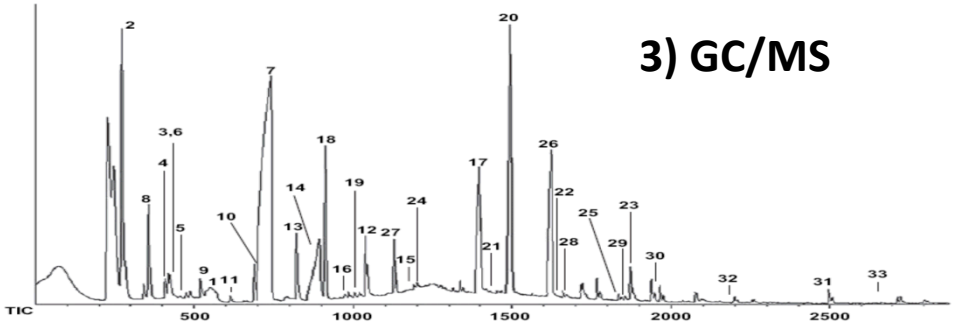
1) NMR



2) IR



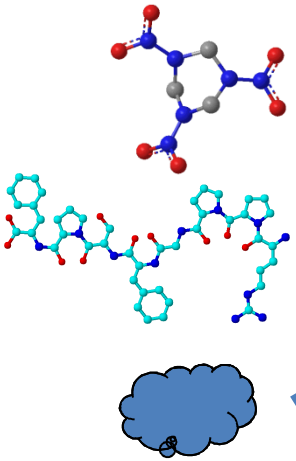
3) GC/MS



Useful
Predictable
Quick

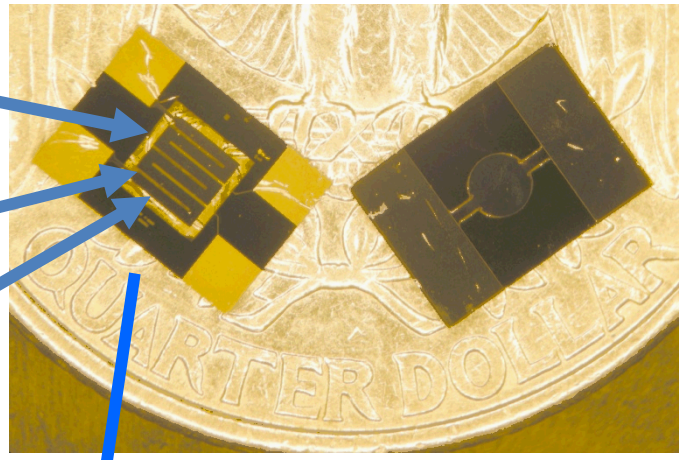
1) Postma, T.P. Davis, A.R. Donovan, G. Li, G. Moad, R. Mulder, M.S. O'shea, *Polymer*, vol. 47, pp. 1899-911, 2006.
2) W.-C. Lai, W.-B. Liau, Thermo-Oxidative Degradation of Poly(Ethylene Glycol)/Poly(-Lactic Acid) Blends, in *Polymer*, vol. 44, pp. 8103-09, 2003.
3) R. Bernstein, S.M. Thornberg, A.N.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

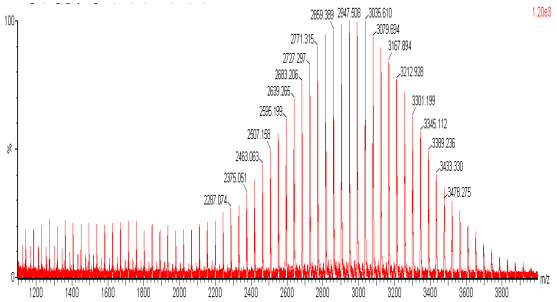
Sandia-fabricated micro-hotplates (μHP) are shown useful in new applications.



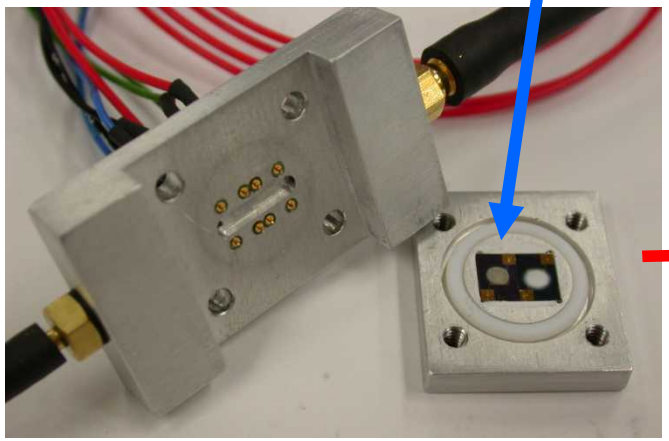
or

or

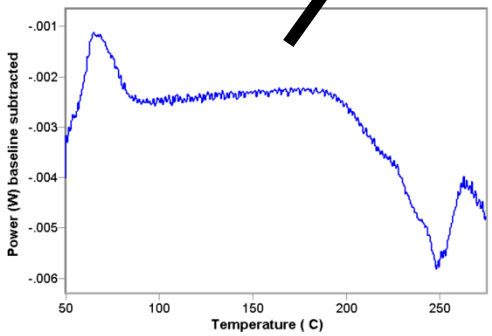




measure



heat



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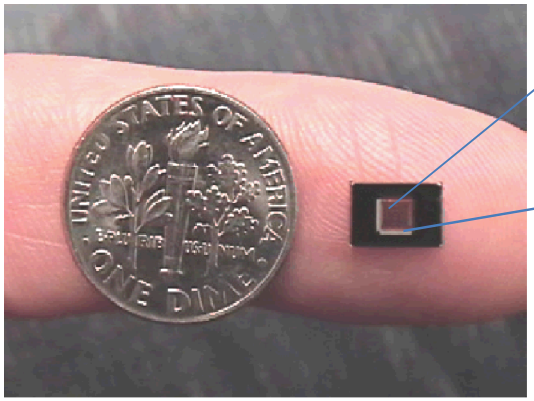
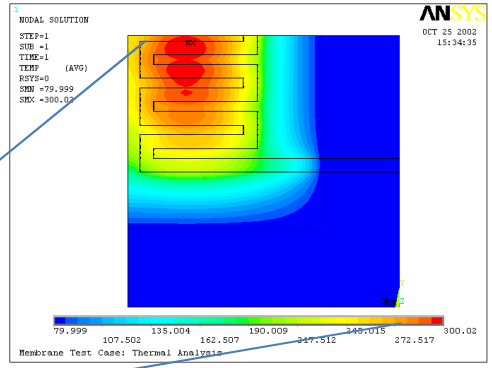
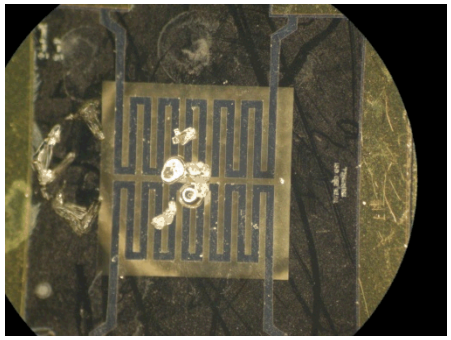
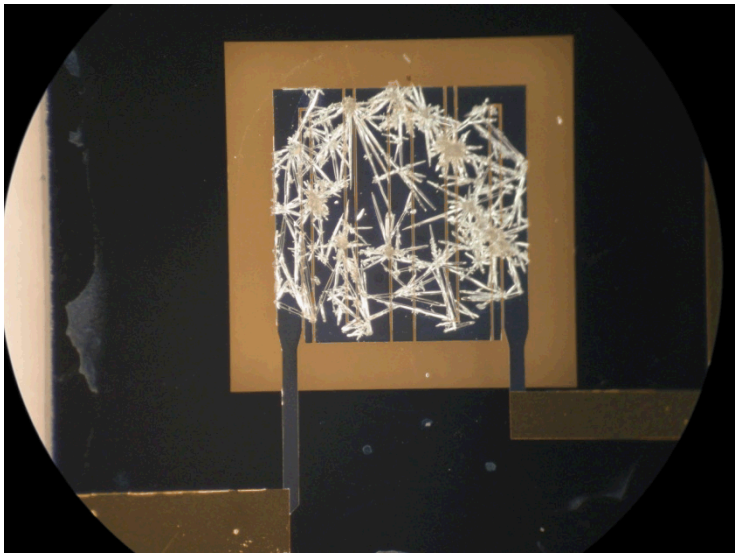
Micro-hotplates allow precise control of environment and thermal profile









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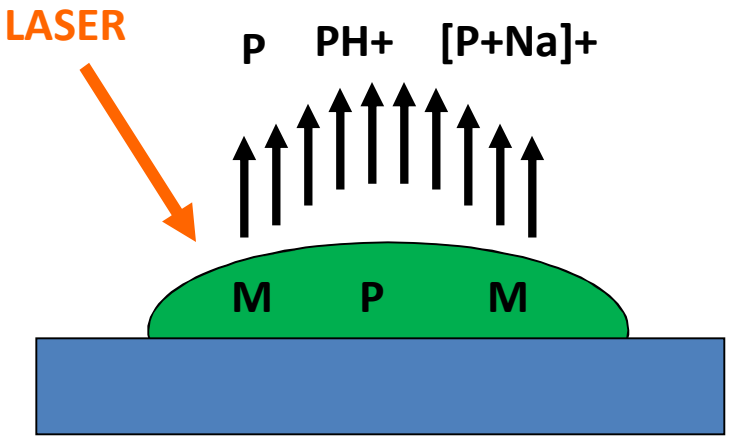
MALDI-MS is used for post heating measurements: shared 2002 Chemistry Nobel for good reasons.

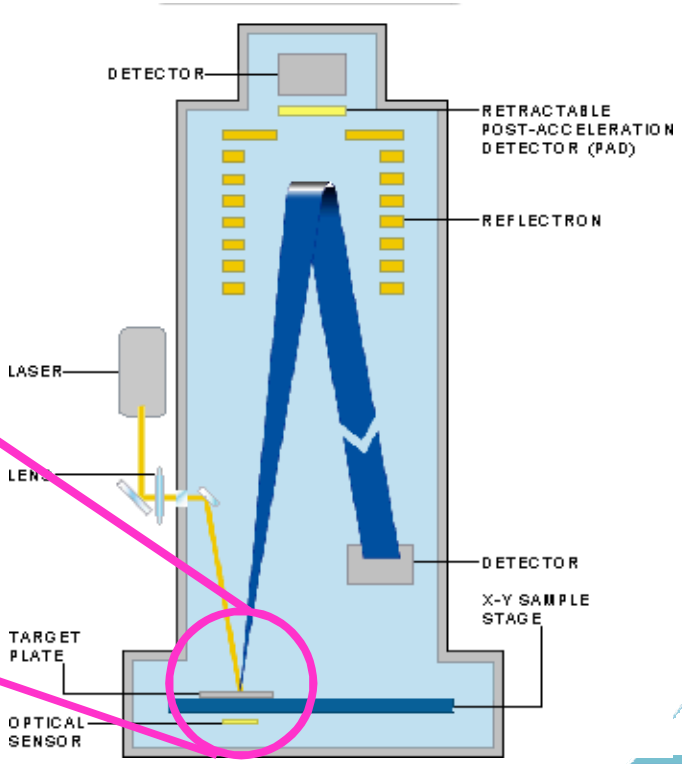
1. Generate ions



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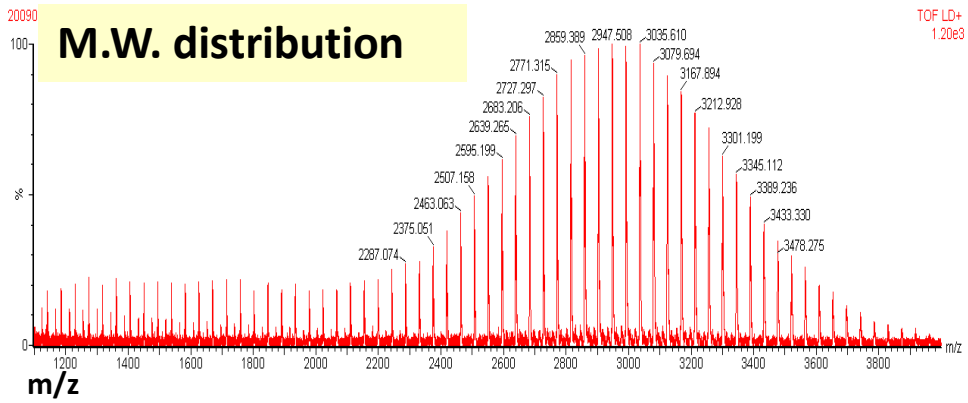
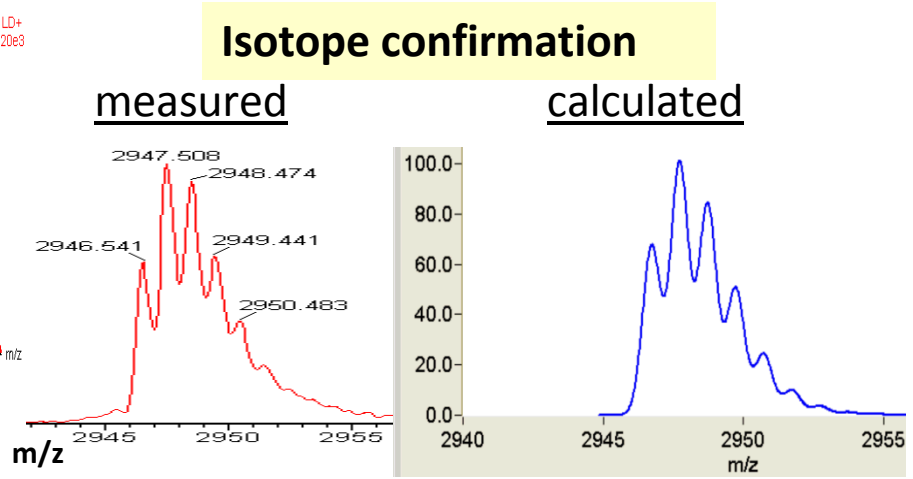
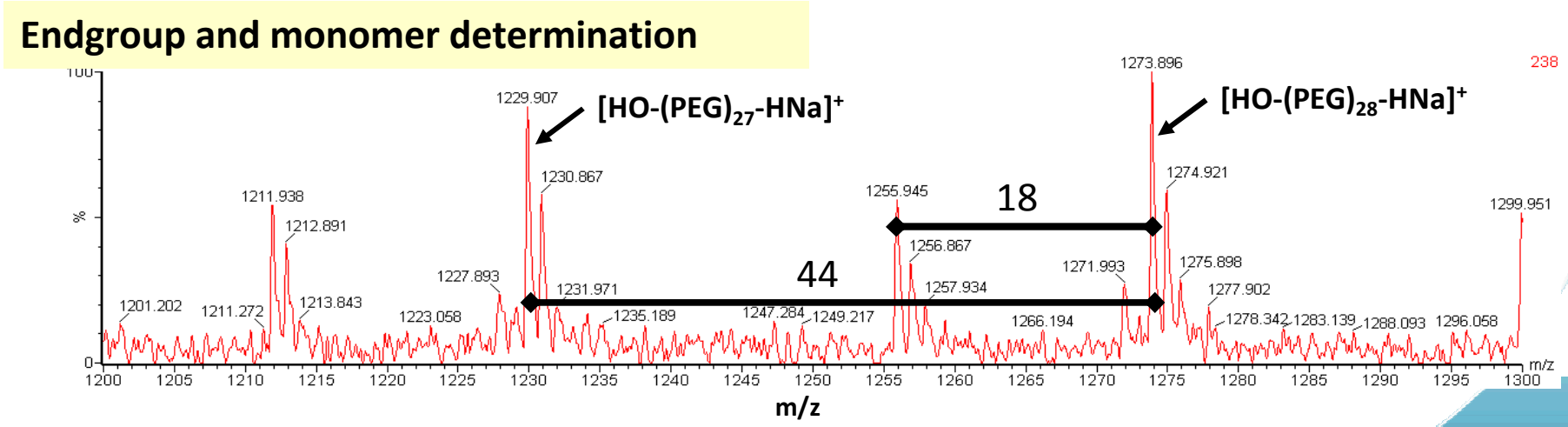
MALDI-MS provides rich information because polymers are measured fully intact.







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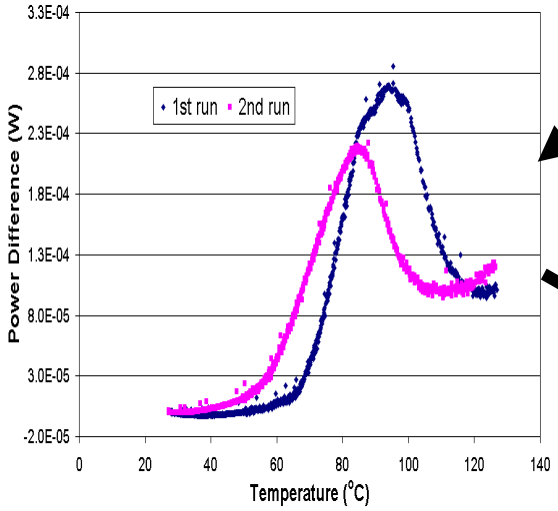
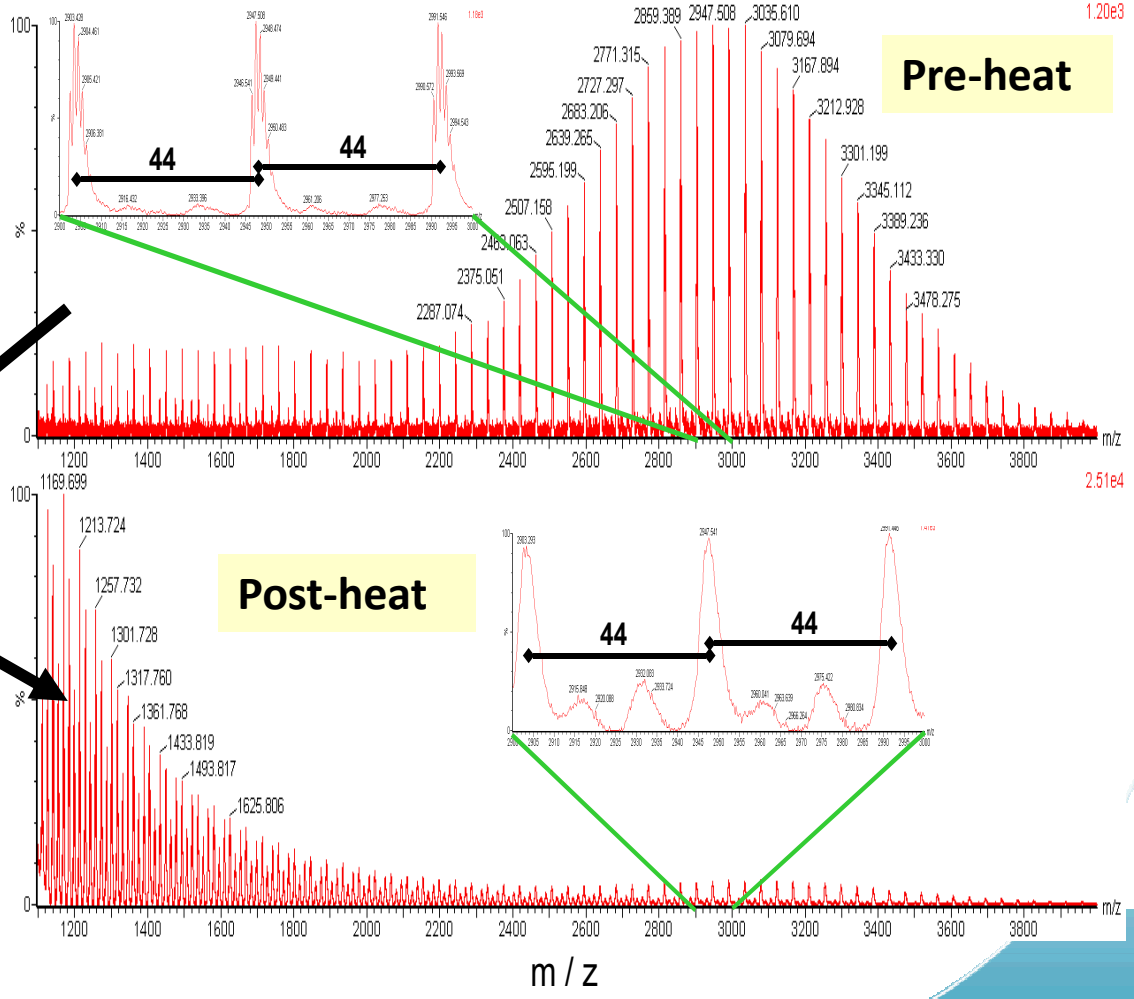
µHP allows precise temperature ramping and MALDI-MS directly from surface.

Consecutive heating ramps





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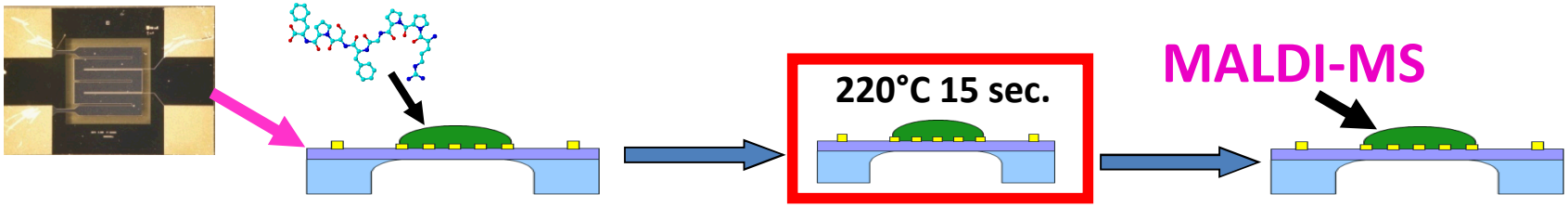
µHP allows precise heating profile and MALDI-MS directly from surface.



Pre-heat

RPPGFSPF

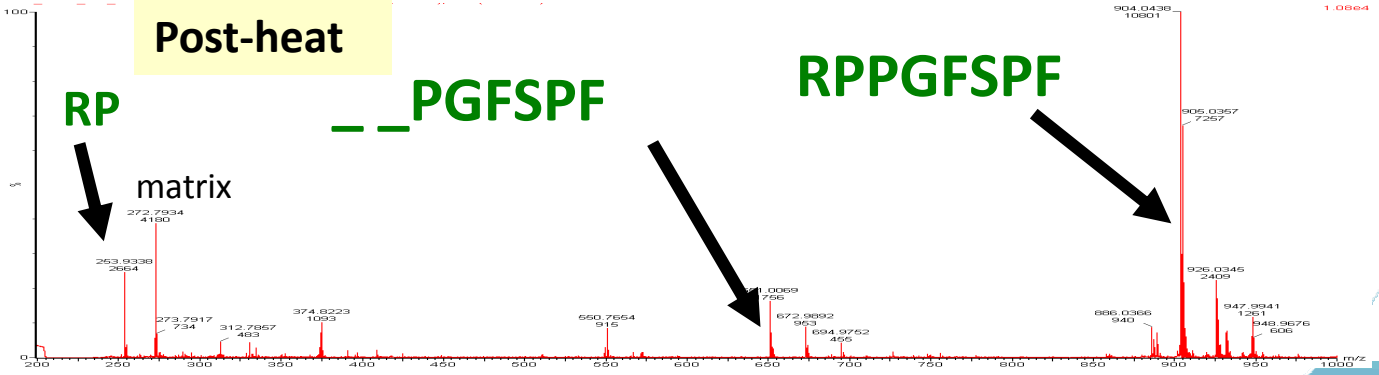
MALDI-MS detects intact and thermally degraded fragments.

Post-heat

RP

_ _PGFSPF

RPPGFSPF



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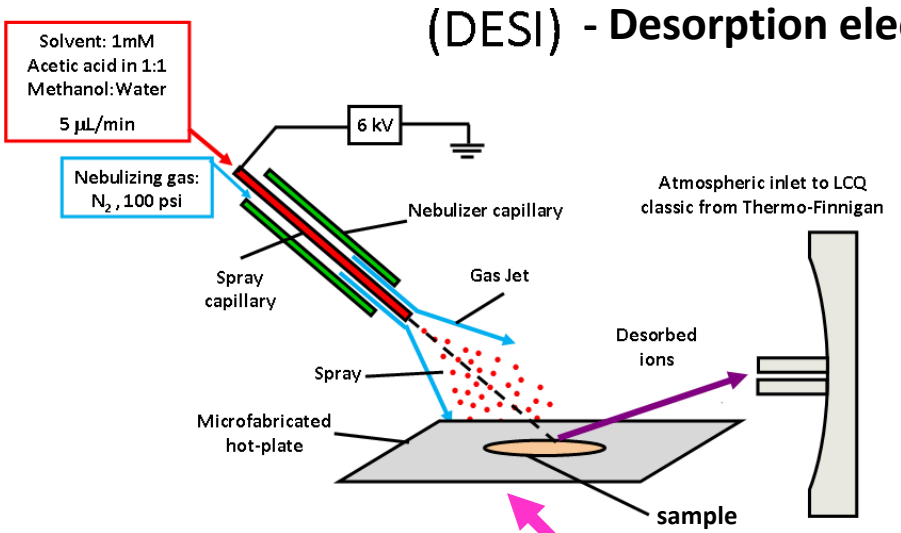
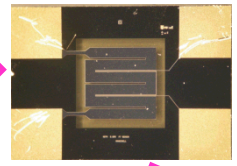
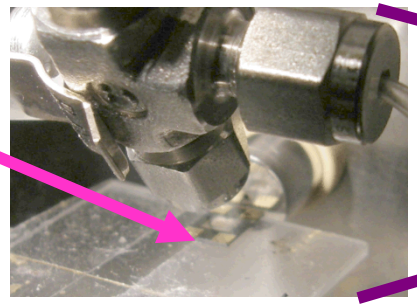
DESI-MS measures mass of molecules INTACT and without sample prep.

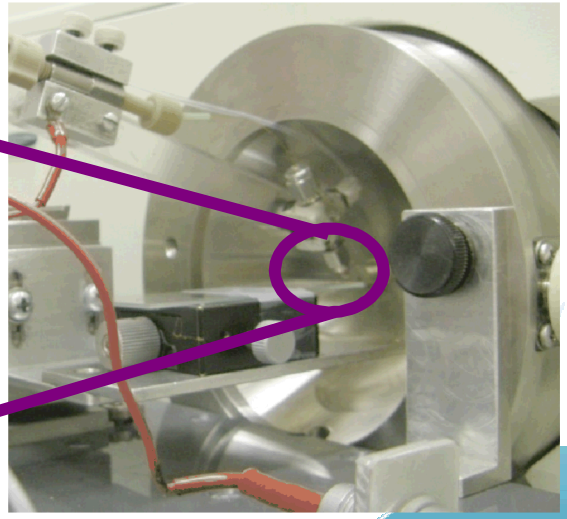


No sample preparation
in situ analysis
m.w. upper limit?

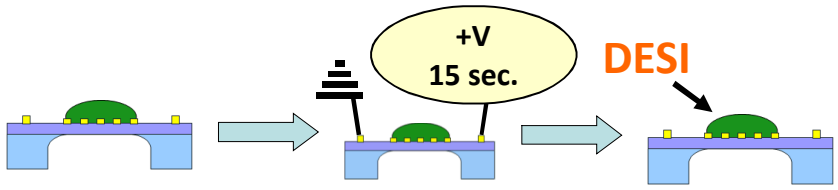
Examples:
Explosives
Drugs
Polymers
Oils



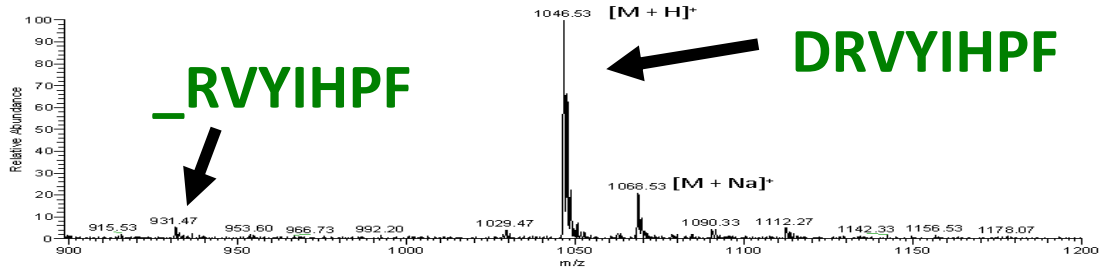




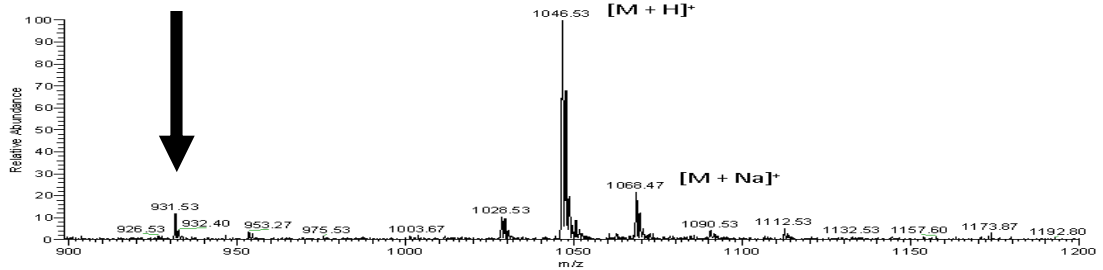
DESI-MS shows thermal degradation of polypeptide on surface of µHP after heating.



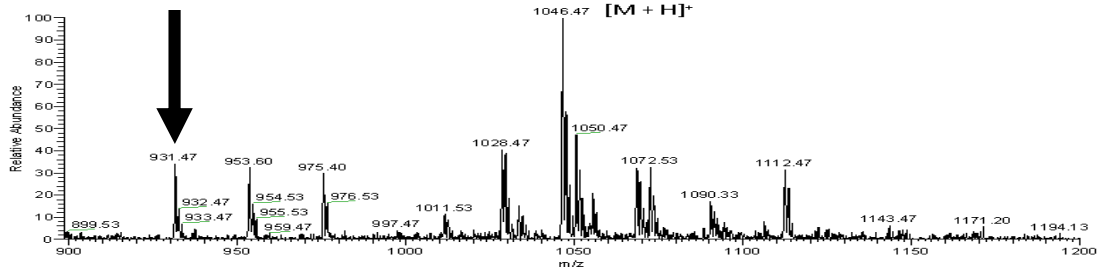
218°C



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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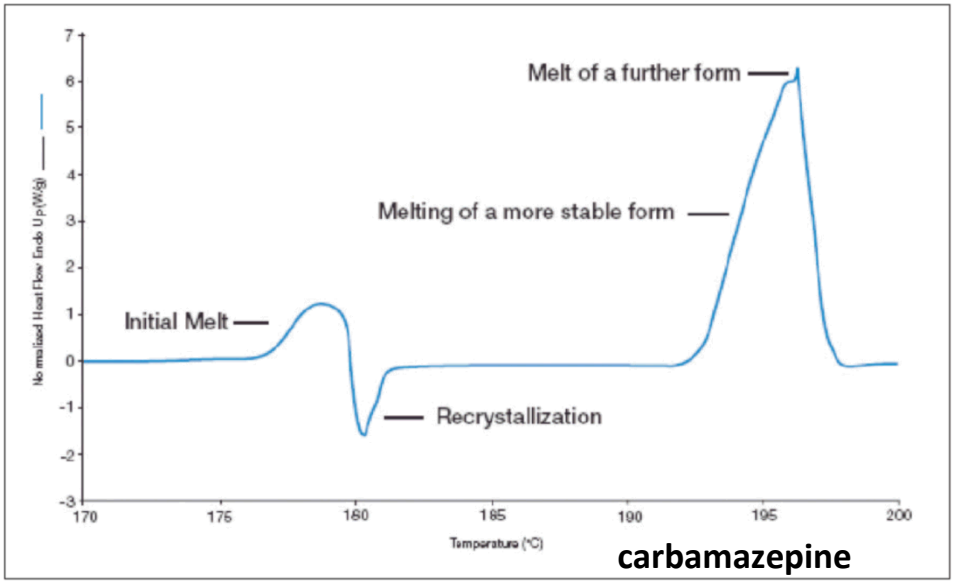
Typical calorimetry provides insight into chemical processes.

Perkin Elmer DSC 8500
scanning rates to 750ºC/min



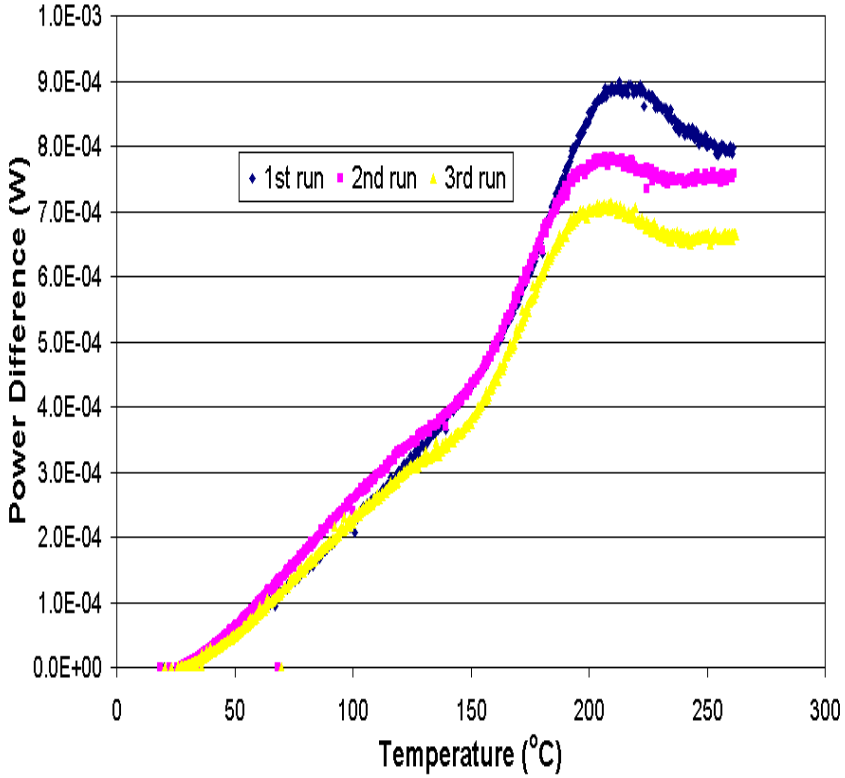
Measurements: shape/width of curve, onset temp, variation w/ ramp rate, energy flow

Applications: heat capacity, purity, energetics, crystal phase

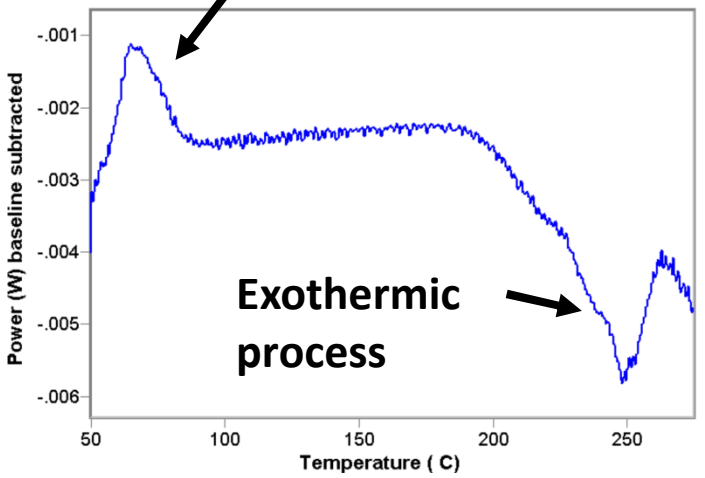
Perkin Elmer sales literature data shown.

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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A new polymer characterization tool with unique calorimetric and mass spectrometric functionality has been demonstrated.

Sandia micro-hotplates (µHPs) are

- fabricated in-house and in multiple form factors,
- low heat capacity and capable of high temperature,
- inert to many chemicals, and
- robust for heating and mass spectrometry sample introduction.

We have demonstrated that

- calorimetry of polymers using µHPs is viable,
- polymers can be analyzed with mass spectrometry methods after heat treatment, and
- this combination of heating and chemical analysis can be useful with respect to polymer characterization.

Future work includes

- Improvements in procedures / devices
- Better sample deposition
- Application to additional aging problems / polymers