SAND2007-2906C

Jeol MStation Mass Spectroscopy Capability at Sandia Applied to Polymer Degradation and Low MW Compounds

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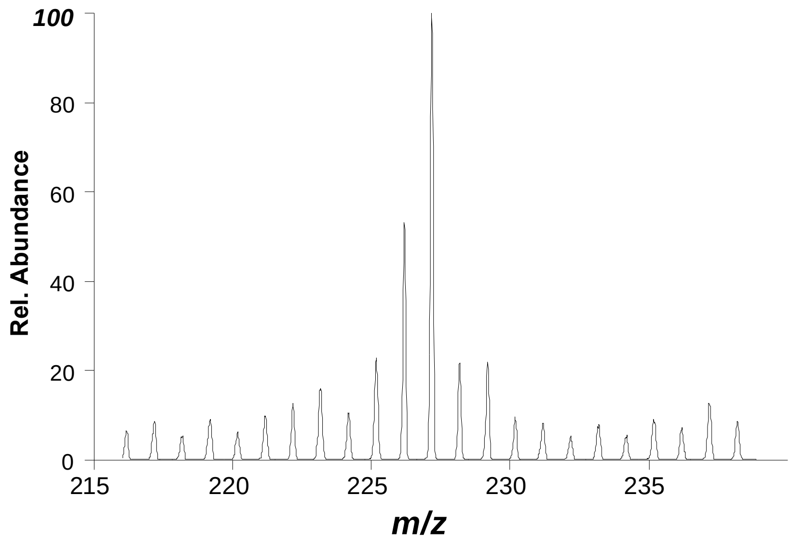
Overview

Question:

- **How does the new Jeol MStation compare with the Jeol GCMate II?**

Comparisons:

- **Specification**
- **Polymer degradation**
- **Low MW gases**



Direct probe, chemical ionization - nylon

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Jeol GCMate II

- Although it is described as a “bench top” instrument, the best configuration requires the manufacturer’s table and use of the floor space under that table.

- We added the Gerstel autosampler. It has worked flawlessly.

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Jeol MStation

- **The integrated GC, autosampler, and the many other options for sample input and ionization makes the MStation very flexible.**
- **It fit in approximately the same space as the Finnigan MAT-271 (sent to SRNL).**

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Specifications (1 of 2)

	GCMate II	MStation
Sample input	Good, most require source changes	Very good, fewer source changes required
Scan	Magnetic sector, HV	Magnetic sector, HV
Mass range	0-1000 (2.5 kV) Up to 3000 dalton	0-2400 (10kV) >8000 dalton
Resolution ($m/\Delta m$)	500, 1000, 3000, 5000 (fixed slits)	500-60,000 Continuously variable

Specifications (2 of 2)

	GCMate II	MStation
Peak tuning	Very automated	Automated, but more involved (i.e., flexibility)
Size (floor footprint)	3 feet x 6 feet	12 feet x 14 feet
Utilities	230V 1P, chiller, helium, house N2	230V 3P, chilled water, chiller, helium, house N2
Software platform	Windows	Unix

Polymer studies: Experimental

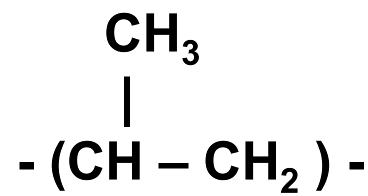
Infer chemical mechanisms for polymer degradation through the study of volatiles evolved during the breakdown of the polymer molecular structure.

Steps:

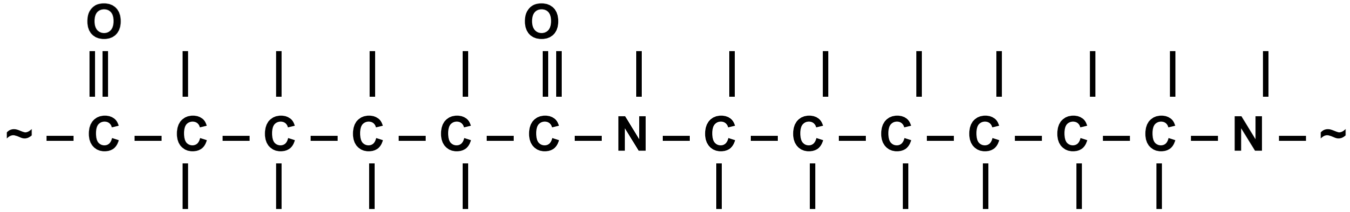
1. Use 3 polymers: polypropylene, polyurethane, nylon
2. Preconcentrate trace volatile organics
   – Cryofocusing preconcentration
   – Solid phase microextraction (SPME)
3. Analyze volatiles
   – Gas chromatography (trace organic separation)
   – Mass spectroscopy
      • MStation
      • GCMate II

Three polymers studied

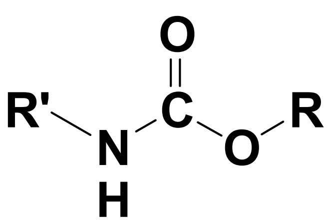
Polypropylene
Monomer mass: 42 dalton



Nylon
Monomer mass: 226 dalton



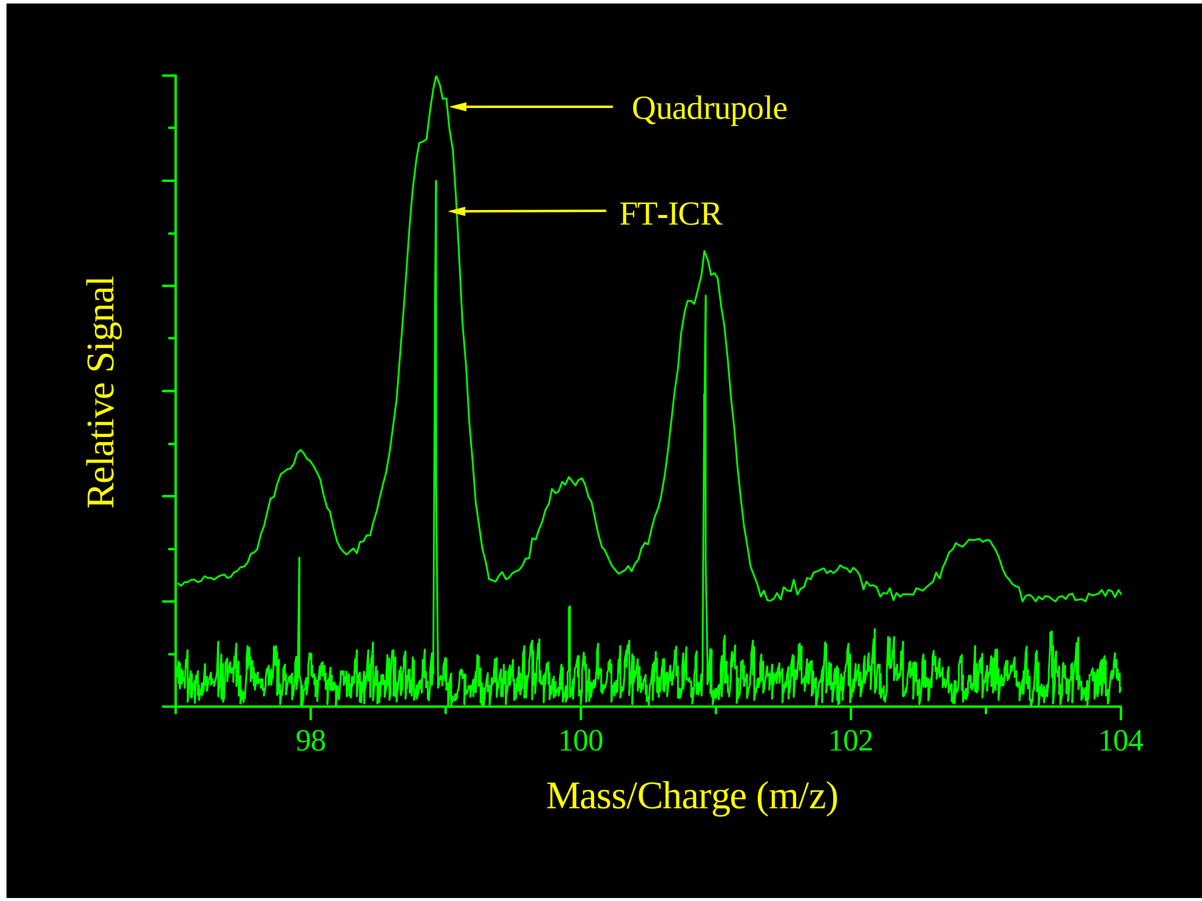
Polyurethane
Monomer mass: depends on R and R'



High-resolution vs. typical residual gas analyzer (RGA) results

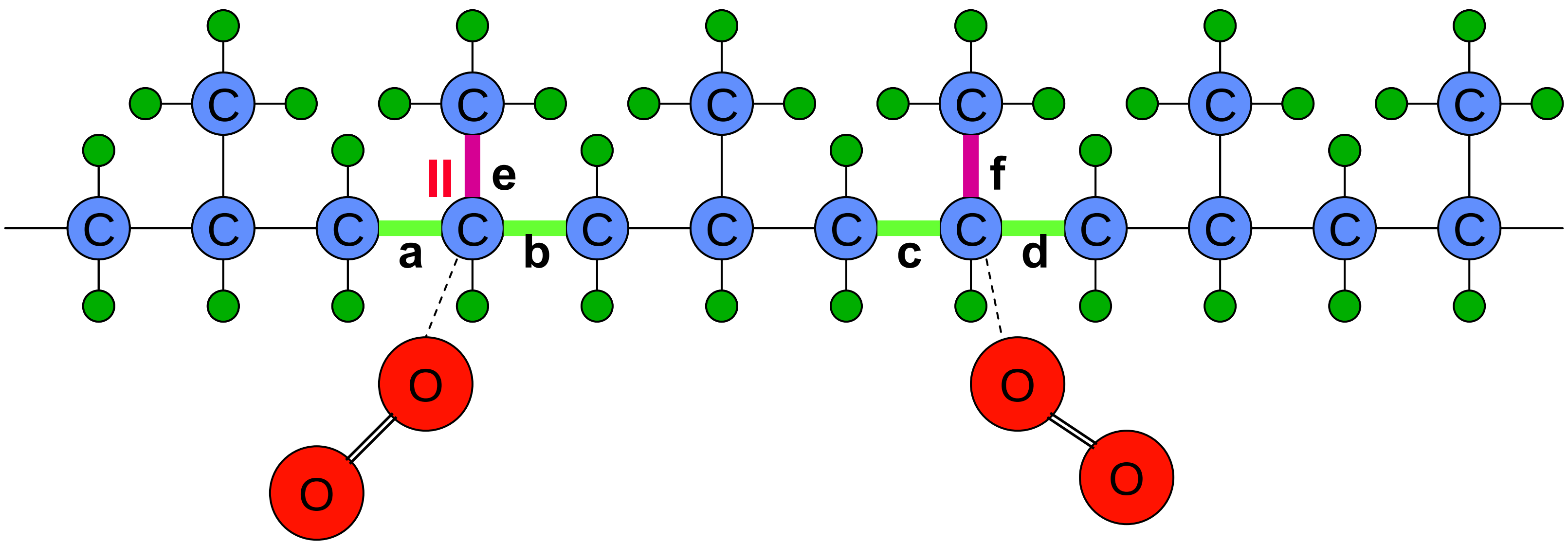
High-resolution mass spectroscopy provides much more information than typical RGA results (unit mass resolution)

Exact mass determination greatly reduces the number of possibilities for the empirical formula of a molecule.



An oxygen molecule attacks, then liberates fragments of the polypropylene chain

- The mass spectra is consistent with a mechanism where two bonds on the backbone chain are cleaved to release the molecule detected.
- The bond to the CH_3 group can be cleaved to produce other variations.



- The dominant series observed arises from a-c or b-d bonds being cleaved (symmetric).

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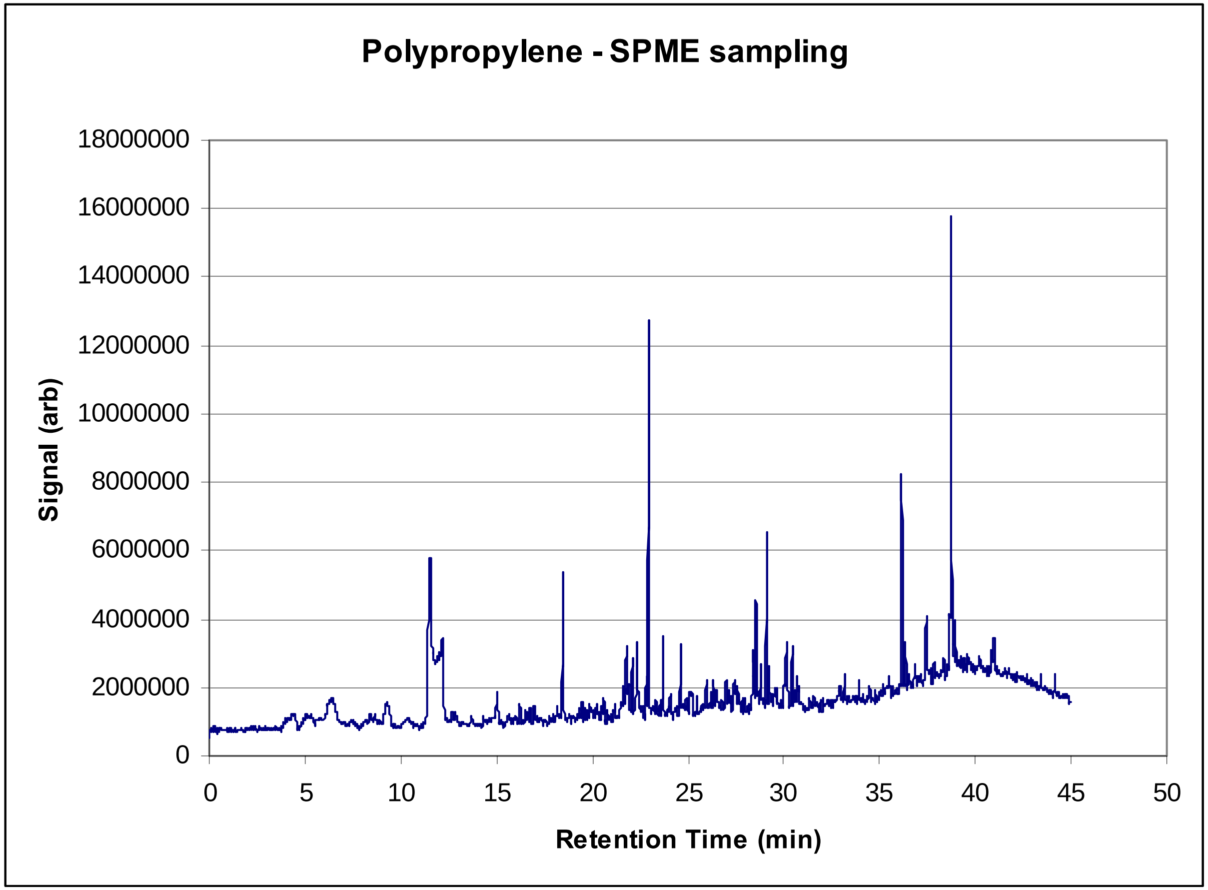
Many compounds evolve from Polypropylene

The chromatogram shows many compounds are detected from thermal degradation (100C) of polypropylene.

(MStation data)



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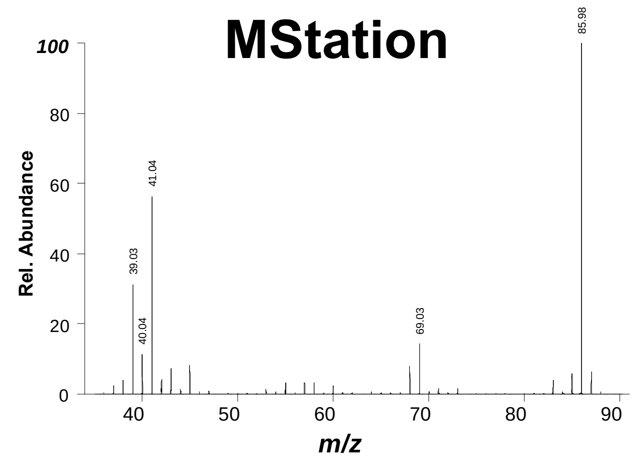
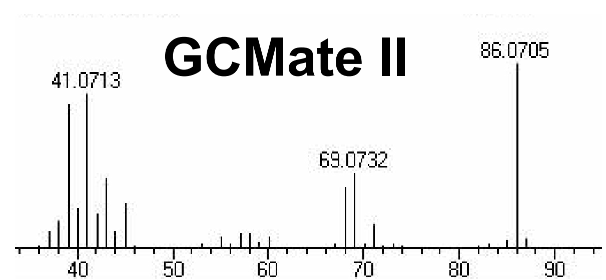
Polypropylene degradation product

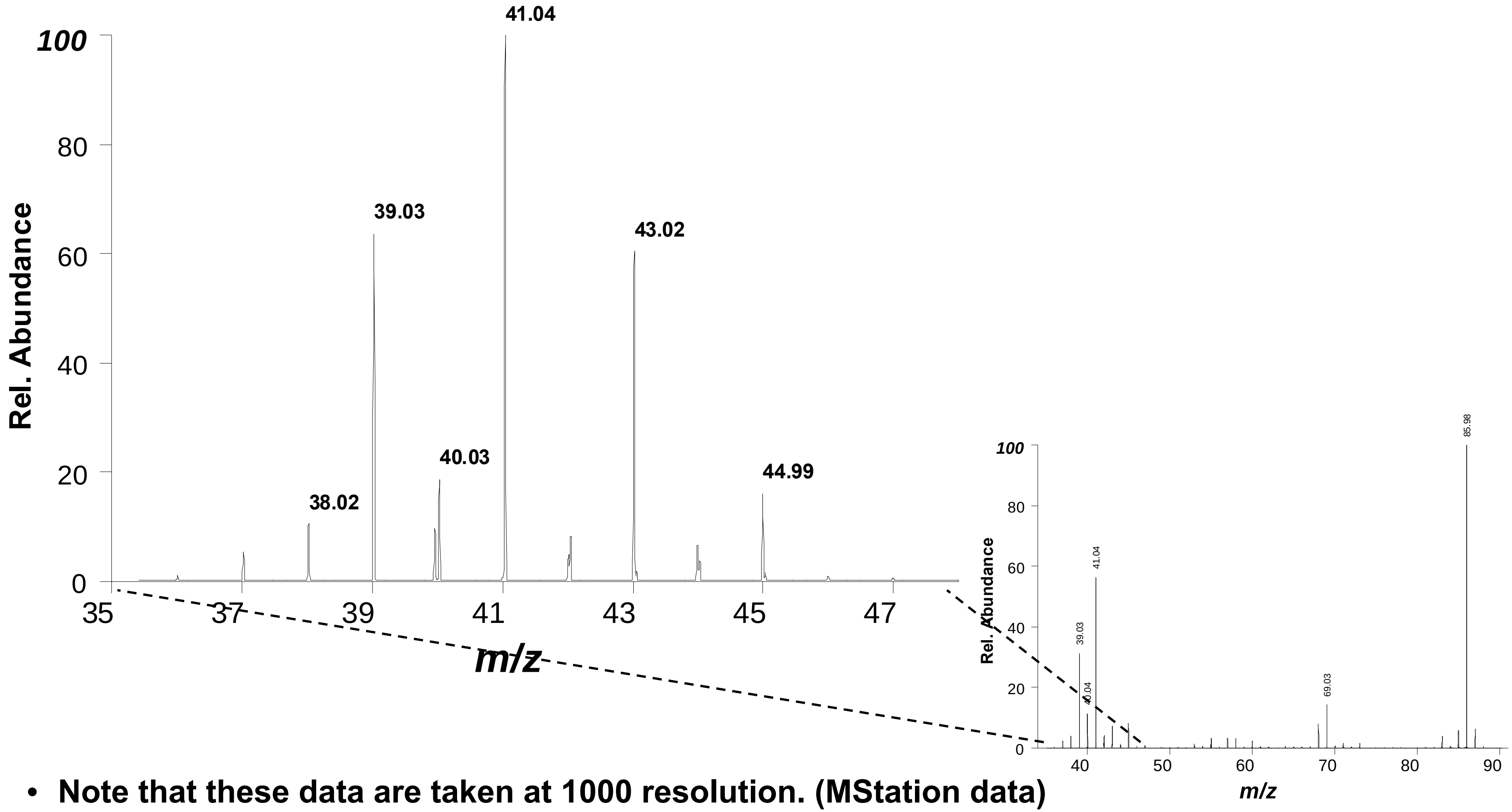
- These figures show the comparison of a degradation product for polypropylene obtained with the MStation and the GCMate II.





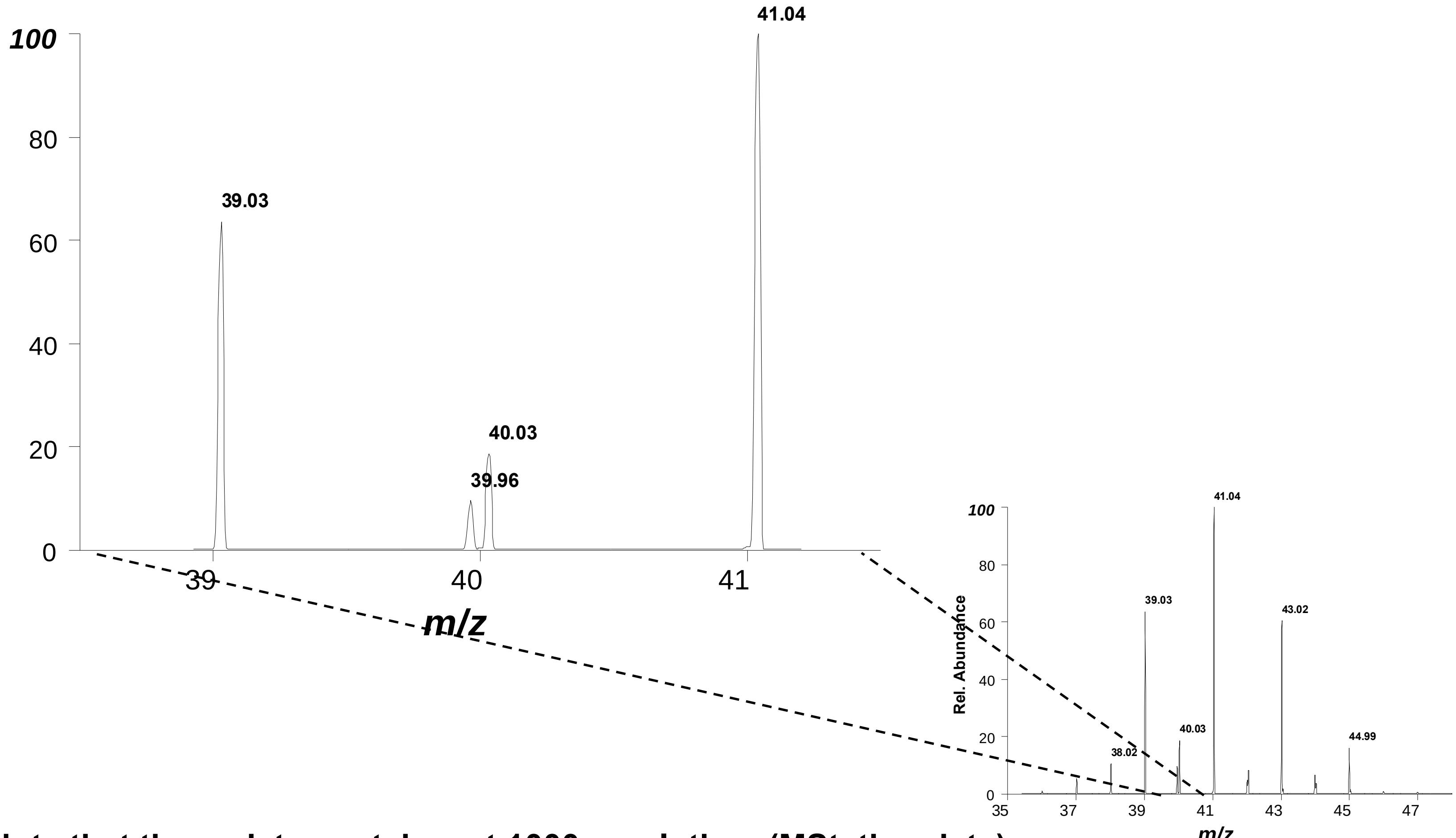
Isochrotonic acid

Expansion of 35-48 dalton range



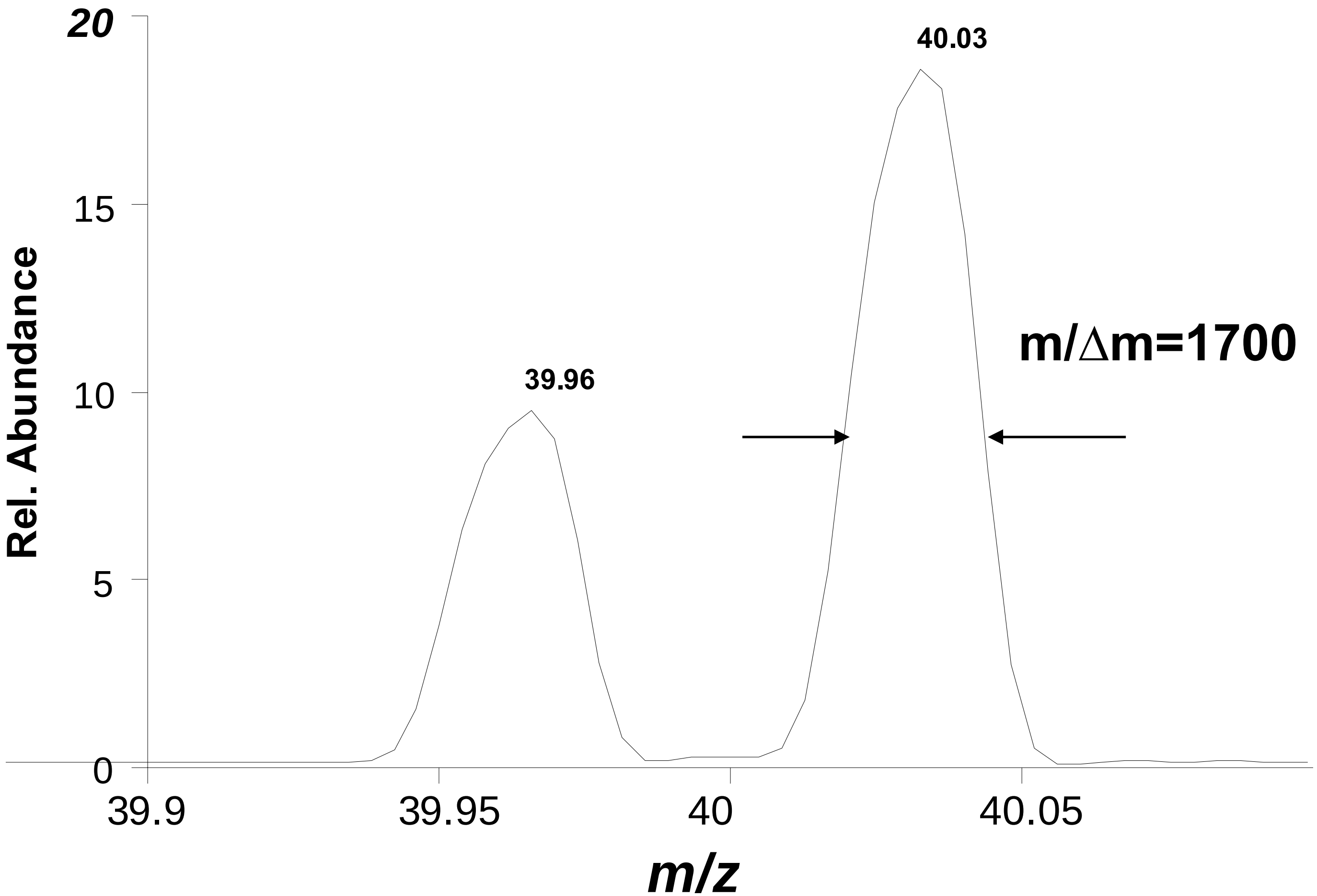
- **Note that these data are taken at 1000 resolution. (MStation data)**

Expansion of 38.5-41.5 dalton range



- **Note that these data are taken at 1000 resolution. (MStation data)**

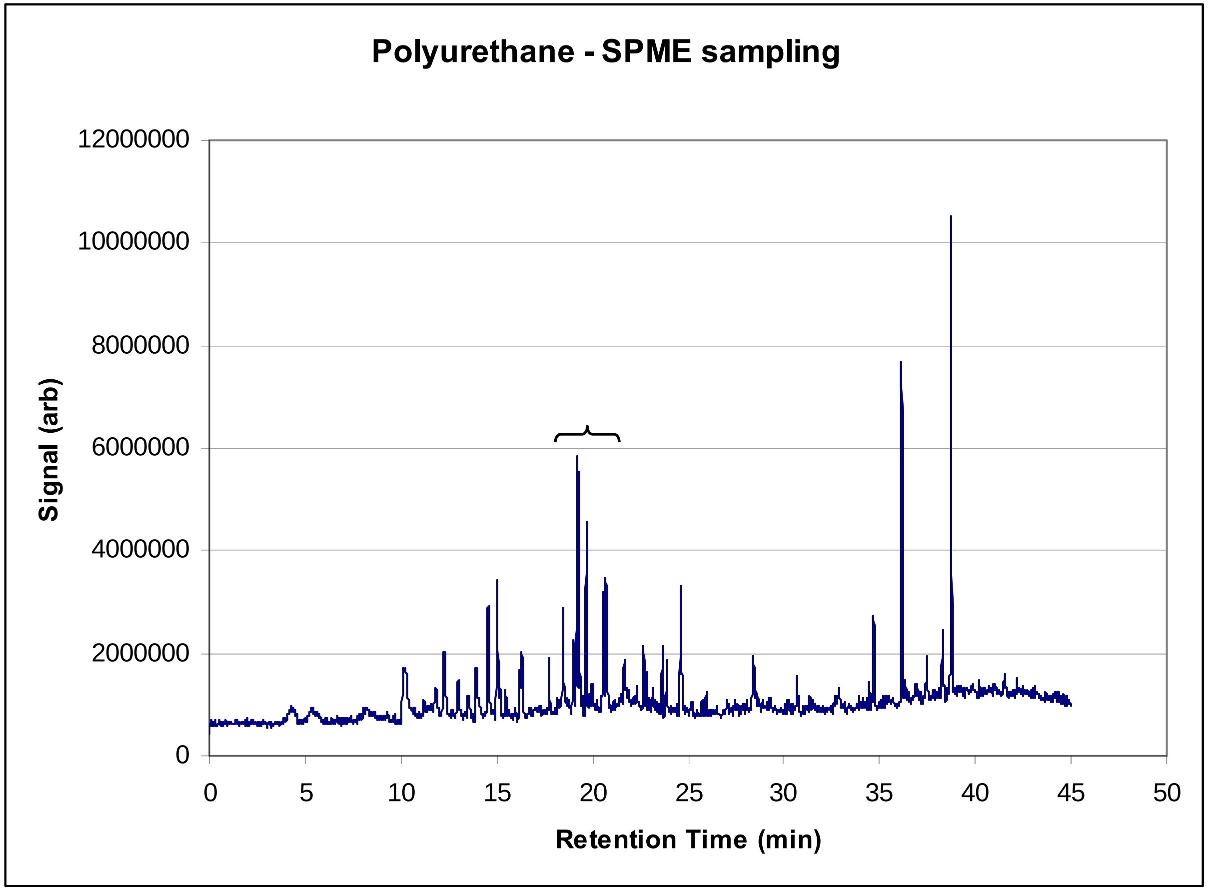
Effective Resolution (at 1000 res)



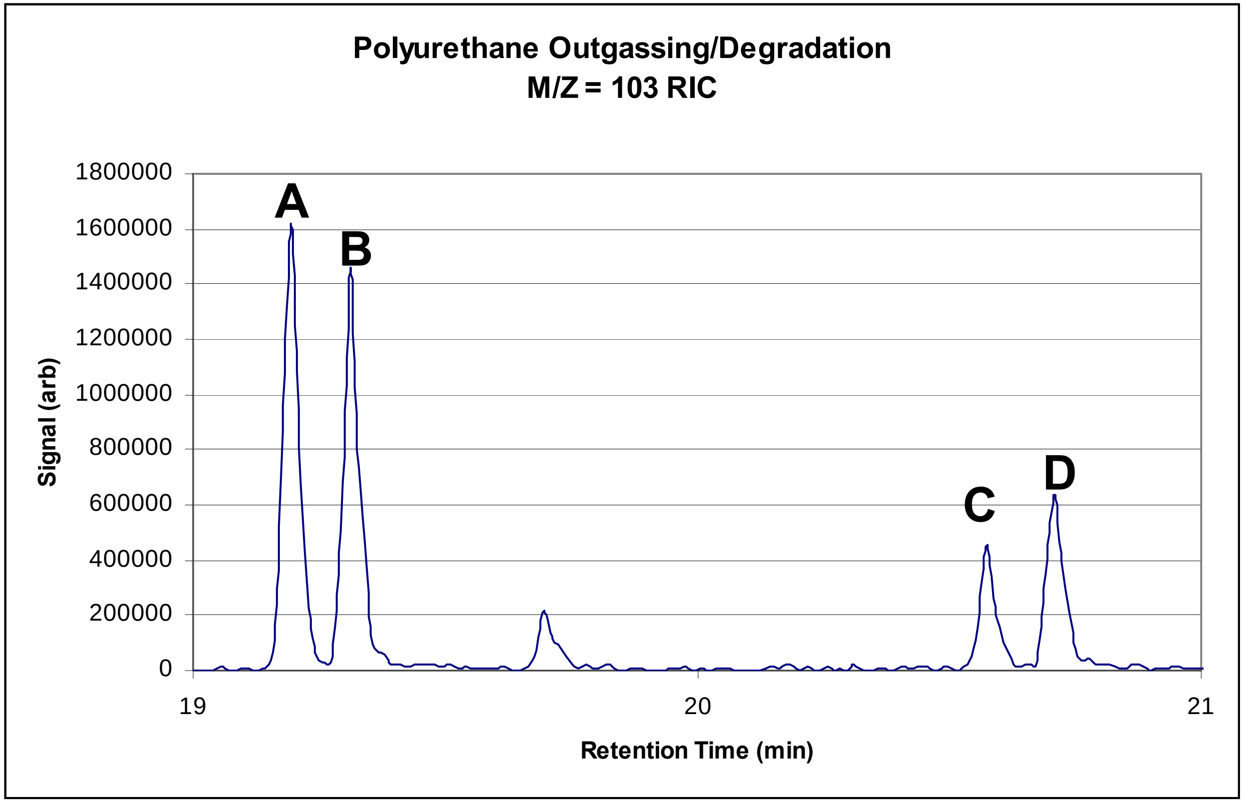
Many compounds evolve from Polyurethane

The chromatogram shows many compounds are detected from thermal degradation (100C) of polyurethane.

(Mstation data)

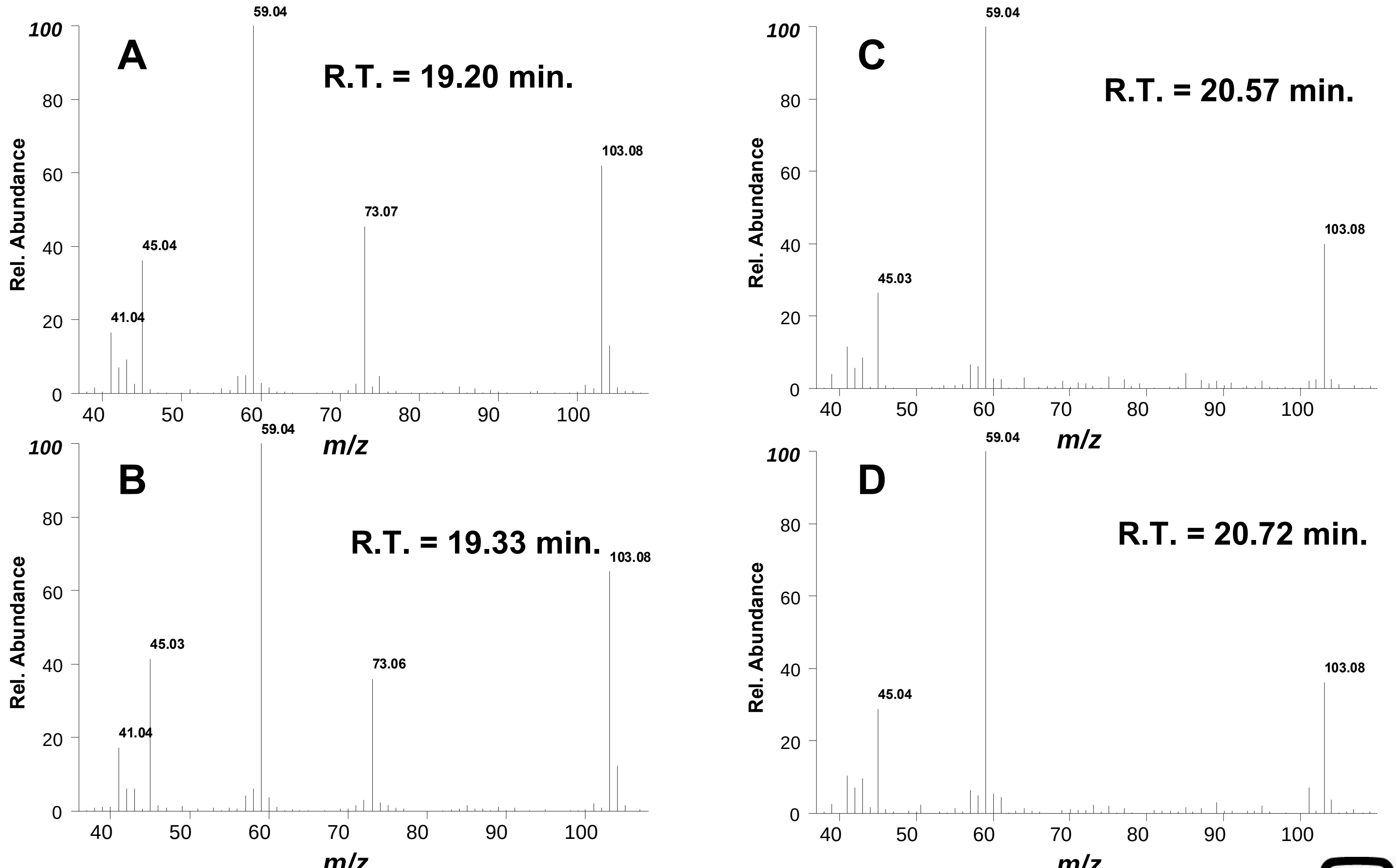


Polyurethane Degradation/Outgassing – Structural isomers?



- **This is a portion of the chromatogram generated from the extracted ion plot of m/z=103 daltons. (MStation data)**

Structural isomers are evident in the data



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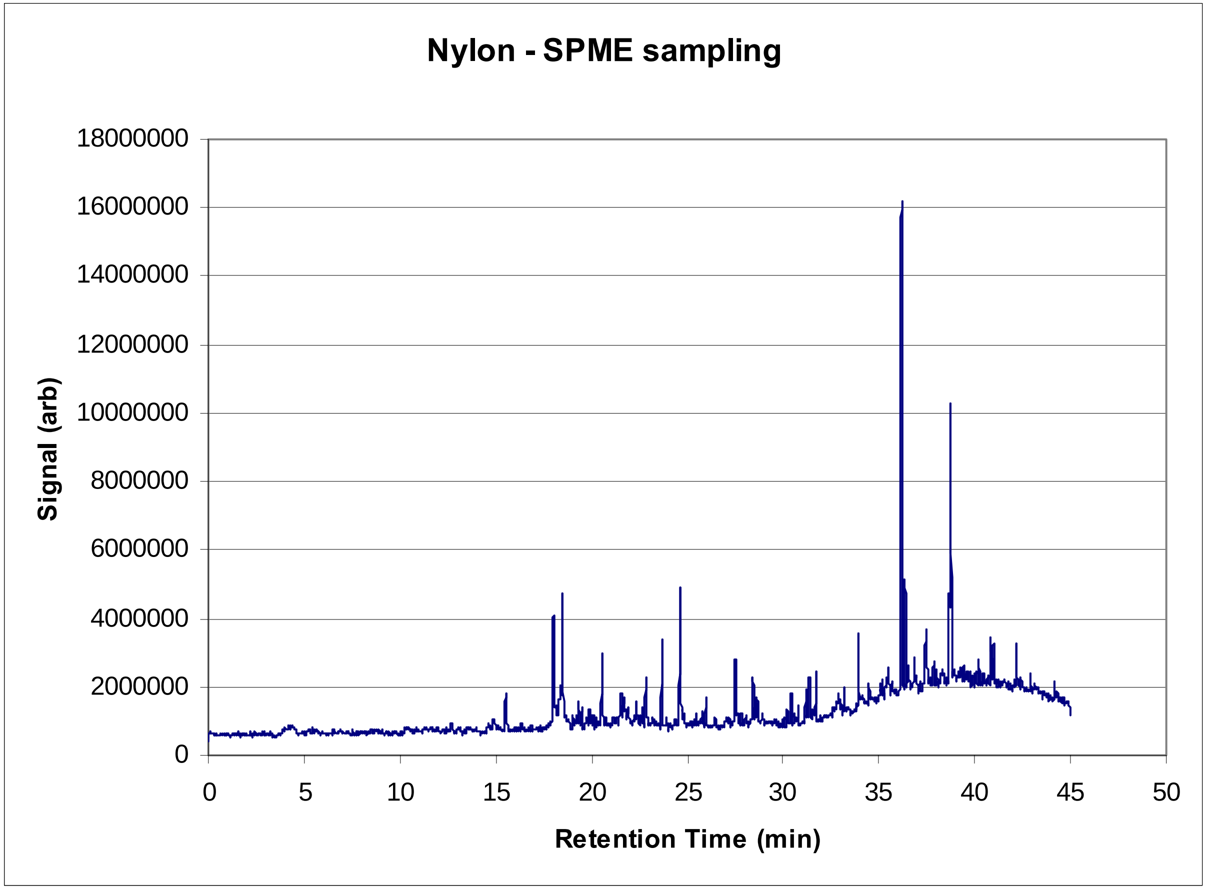
Many compounds evolve from nylon

The chromatogram shows many compounds are detected from thermal degradation (100C) of nylon.

(MStation data)



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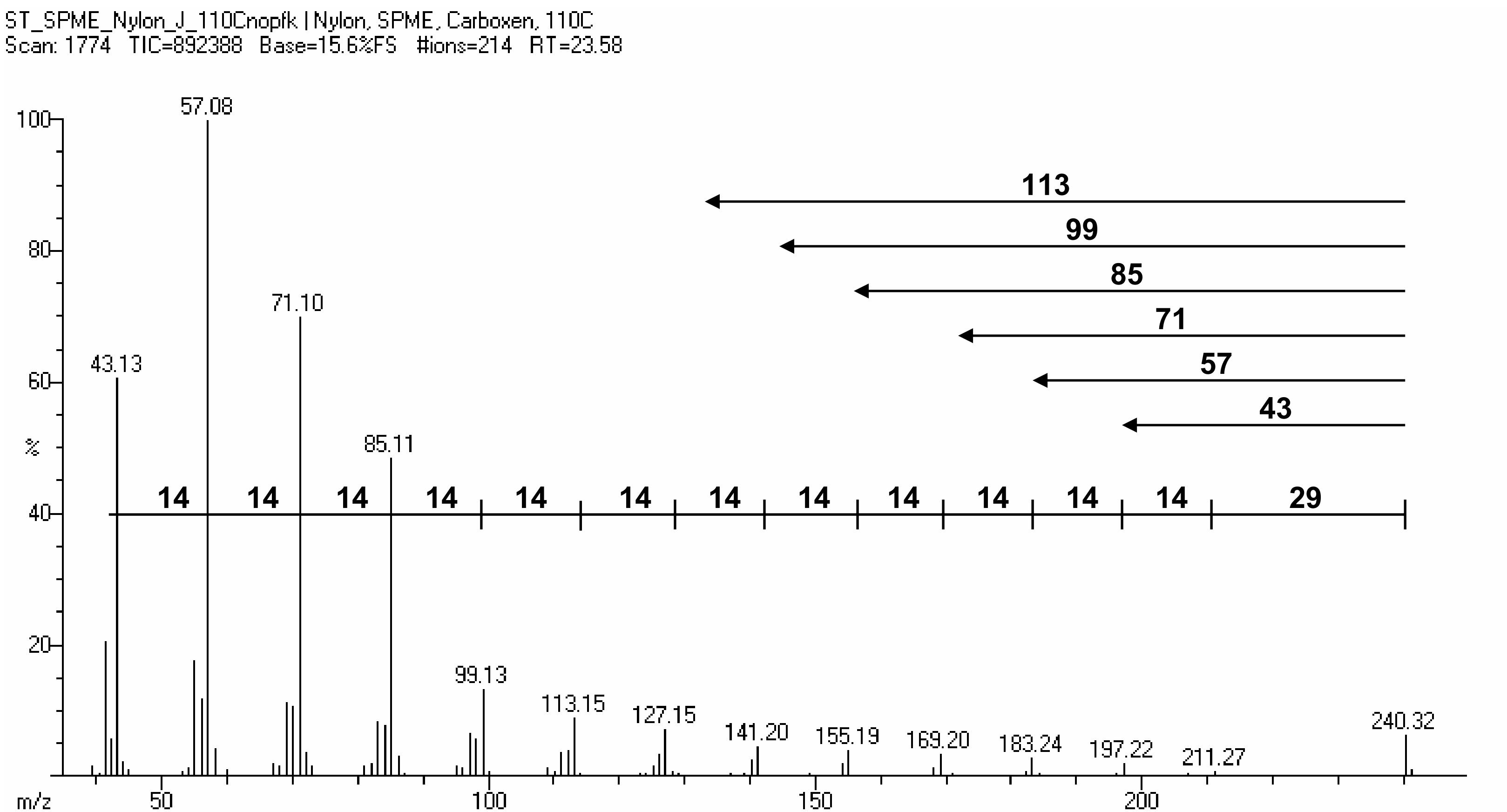
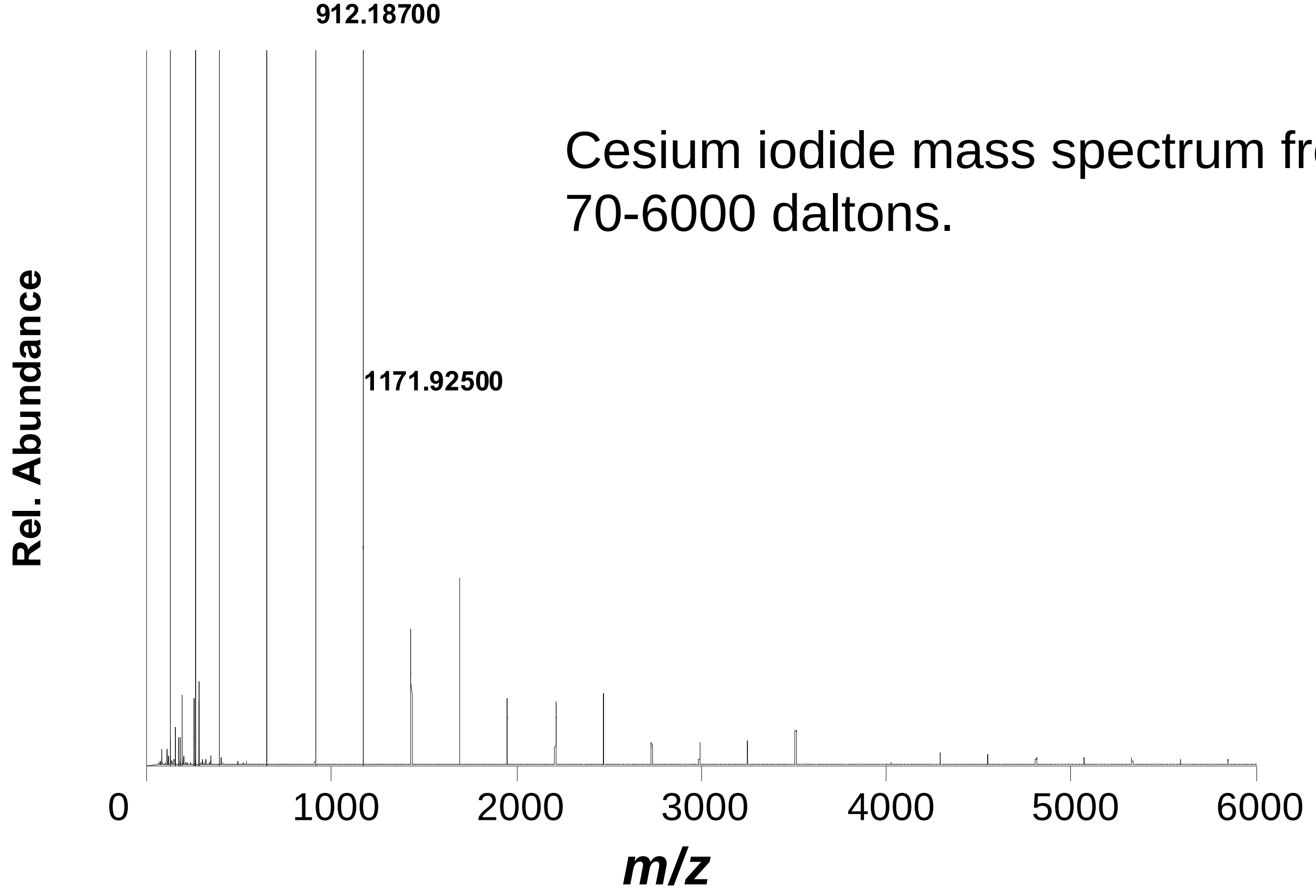
Nylon mass spectra contains structural information



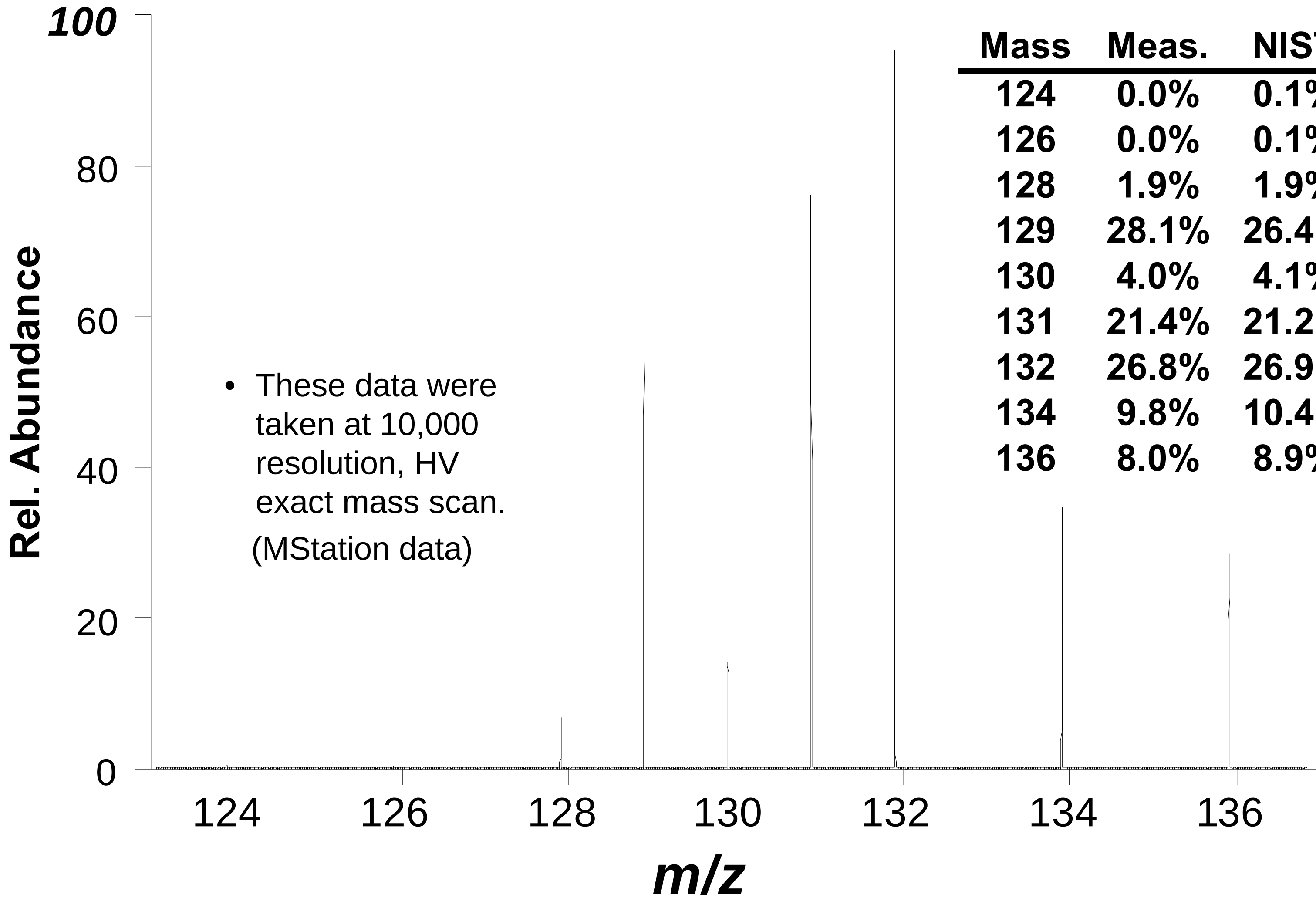
(GCMate II data.)

MStation has a Wide Mass Range



Cesium iodide mass spectrum from 70-6000 daltons.

Xenon isotopic distribution (single scan)

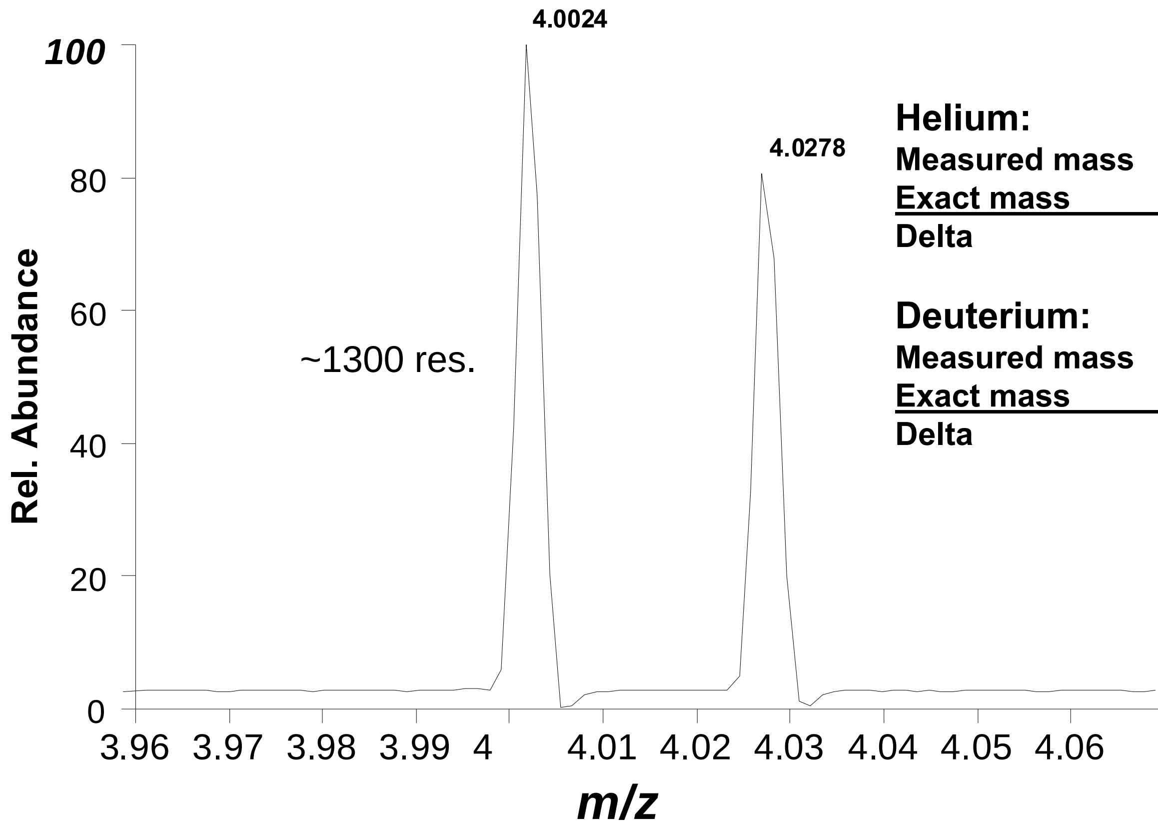


- These data were taken at 10,000 resolution, HV exact mass scan.

(MStation data)

Mass	Meas.	NIST
124	0.0%	0.1%
126	0.0%	0.1%
128	1.9%	1.9%
129	28.1%	26.4%
130	4.0%	4.1%
131	21.4%	21.2%
132	26.8%	26.9%
134	9.8%	10.4%
136	8.0%	8.9%

Deuterium and helium scan using the MStation



Helium:

Measured mass	**4.0024 daltons**
Exact mass	**4.0026 daltons**
Delta	**0.0002 daltons**

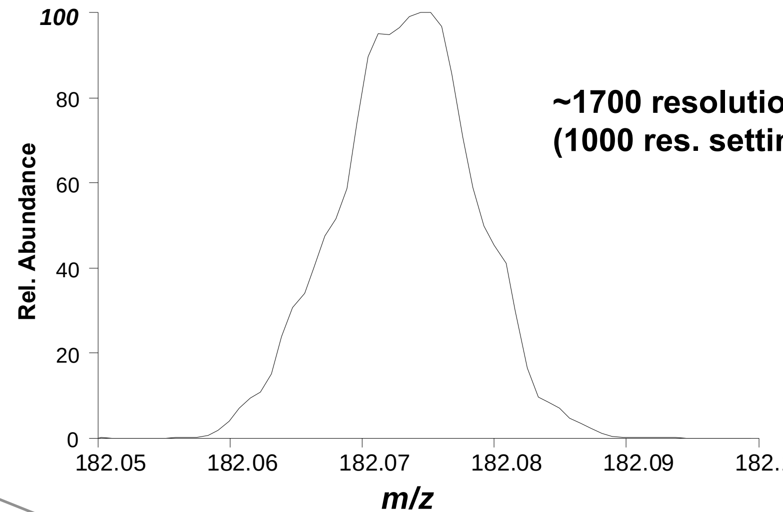
Deuterium:

Measured mass	**4.0278 daltons**
Exact mass	**4.0282 daltons**
Delta	**0.0004 daltons**

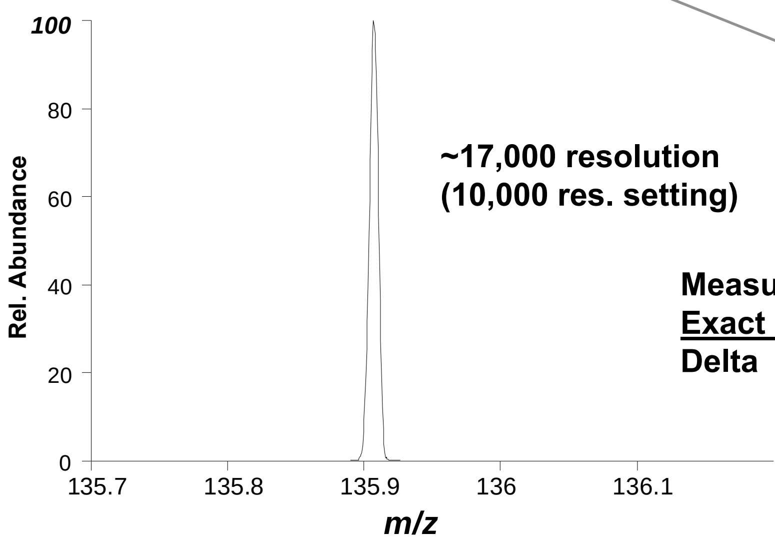
- These data were taken at 1000 resolution, magnet scan (not HV exact mass scan).

Accurate Mass Scans – HV

Measured mass	182.07330 daltons
Exact mass	182.07316 daltons
Delta	0.00014 daltons
	0.7 ppm



~1700 resolution
(1000 res. setting)



~17,000 resolution
(10,000 res. setting)

Measured mass	135.90710 daltons
Exact mass	135.90722 daltons
Delta	0.00012 daltons
	0.9 ppm

(MStation data)

Pros/Cons of MStation and GCMate II

Low masses (<10 dalton)	Easier with MStation than GCMate II
Mass range	Both instruments cover a good range; MStation has a wider range
Sensitivity	Both good
Software	Unix system of MStation is awkward, limited support
Mass "fingerprint" of organics	Both excellent

Pros/Cons of MStation and GCMate II

Resolution	Both meet specs. easily. MStation is excellent.
Size	MStation is large; GCMate II is a “bench top” instrument
Mass stability	Both good, MStation is even better
Peak height stability	Both good, MStation is even better
Mass tuning	Both good; both can be challenging

Pros/Cons of MStation and GCMate II

Probe work	MStation is much easier and superior
Data reduction	GCMate II is easier; MStation requires special software
Exact mass calculation integrated into software	MStation is superior and much more automated
Data acquisition software	GCMate is more intuitive than "hopping around" between MStation windows
Mass accuracy	"Quick-and-dirty" runs on MStation give equivalent to finely tuned GCMate runs

Conclusion

- **MStation performs extremely well, and so does the GCMate II (but with lesser capabilities).**
- ***The added capabilities of the MStation are worth the additional size, utilities, software/data reduction challenges.***
- **Methods developed provide an unprecedented level of understanding of the source of volatile products in polymer degradation**

Acknowledgments

SNL/NM Mass Spectroscopy Lab Team:

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