SAND2015-1103PE

STMBMS Studies of Thermally-Cycled DNAN

Jeffrey J. Kay, Jeffrey D. Steill, Deneille Wiese-Smith, and Aaron Highley

Sandia National Laboratories, Livermore, CA

TTCP WPN Meeting

CP 4-46 Phenomenology of DNAN / Sensitivity & Growth

23 February 2015

Quebec, Canada

Sandia National Laboratories

Energetic Materials Research at SNL/CA

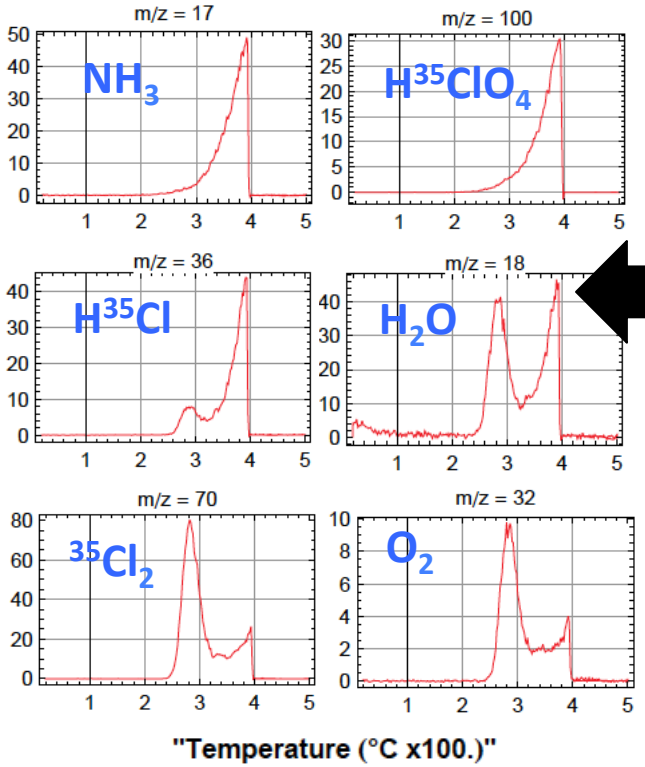
- Our work is focused on understanding the reactive chemistry that drives response of energetic materials to **shock**, **impact**, **heat**, and **time** and developing models to predict that response
- Experimental work involves extensive use of mass spectrometry
  - **Simultaneous Thermogravimetry and Modulated Beam Mass Spectrometry (STMBMS)**; analysis of evolved products from heated samples
  - **Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FTICR)**; high-resolution mass spectrometry for unique identification of molecular species
  - X-ray diffraction (XRD) also used for sample characterization
- Work is supported by US DoD/DOE Joint Munitions Program (JMP)

Energetic Materials Research at SNL/CA

STMBMS data is used to develop reaction mechanism

Example: Ammonium perchlorate thermal decomposition

STMBMS Data



Reaction Mechanism

R1: $NH_4ClO_4(or.) \longleftrightarrow NH_3(g) + HClO_4(g)$

R2: $NH_4ClO_4(or.) \longrightarrow H_2O(s*) + O_2(s*) + HCl(s*) + N_2O(s*) + NO_2(s*) + Cl_2(s*) + NH_4ClO_4(m.s.)$

R3: $NH_4ClO_4(or.) \xrightarrow{240\,^{\circ}C} NH_4ClO_4(cub.)$

$H_2O(sLRE) + O_2(s*) + HCl(s*) + N_2O(s*) + NO_2(s*) + Cl_2(s*) \longrightarrow H_2O(g) + O_2(g) + HCl(g) + N_2O(g) + NO_2(g) + Cl_2(g)$

R5: $NH_4ClO_4(cub.) \longleftrightarrow NH_3(g) + HClO_4(g)$

R6: $NH_3(ads.) + HClO_4(ads.) + NH_4ClO_4(m.s.) \longrightarrow H_2O(g) + O_2(g) + HCl(g) + N_2O(g) + NO_2(g) + Cl_2(g) + NH_4ClO_4(m.s.)$

R7: $NH_3(g) + HClO_4(g) \longrightarrow H_2O(g) + O_2(g) + HCl(g) + N_2O(g) + NO_2(g) + Cl_2(g)$

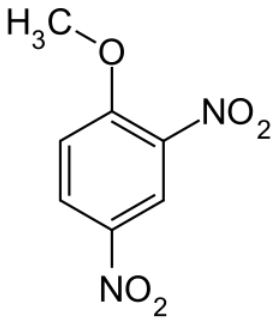
Sandia National Laboratories

Background: DNAN Growth

2,4-Dinitroanisole (DNAN) displays irreversible growth upon temperature cycling in melt-cast formulations

We have been working at the request of Philip Samuels (ARDEC) to help identify possible chemical changes in thermally-cycled DNAN

- Work presented here involves analysis of thermally-cycled DNAN powder
- Pristine and thermally-cycled DNAN are analyzed by STMBMS
- Thermally-cycled DNAN formulations will be analyzed later this FY



2,4-dinitroanisole

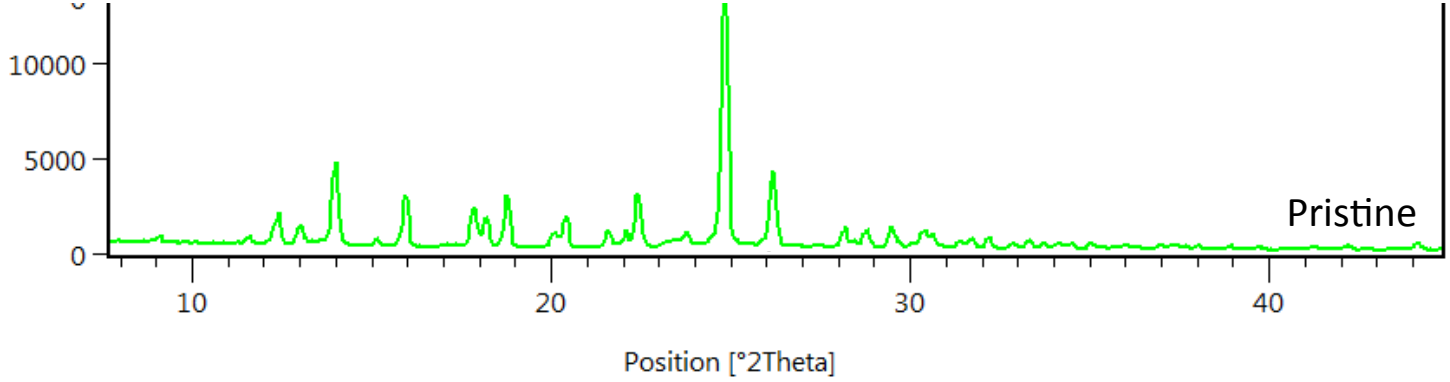
Sandia National Laboratories

DNAN Samples

DNAN powder was supplied to us by Picatinny Arsenal

- Manufactured by BAE Holston, Lot BAE 06K282-005
- Received 6/2007

XRD analysis conducted at Sandia



Sample consistent with β form[1], also called DNAN-1[2]

[1] C. Crouse, P. Samuels, S. Anderson, TTCP March 2014
[2] C. Pulham and P. Coster, TTCP March 2014

Sandia National Laboratories

DNAN Samples

Thermally-cycled sample was prepared by cycling from 25°C to 60°C 30x according to the following thermal profile:

- Heat from 25°C (77°F) to 60°C (140°F) at 0.75°C/min
- Cool to 25°C (77°F) at 0.5°C/min
- Hold at 25°C (77°F) for 2500s (42 min)
- Repeat cycle 30 times.

Pristine powder

Cycled powder

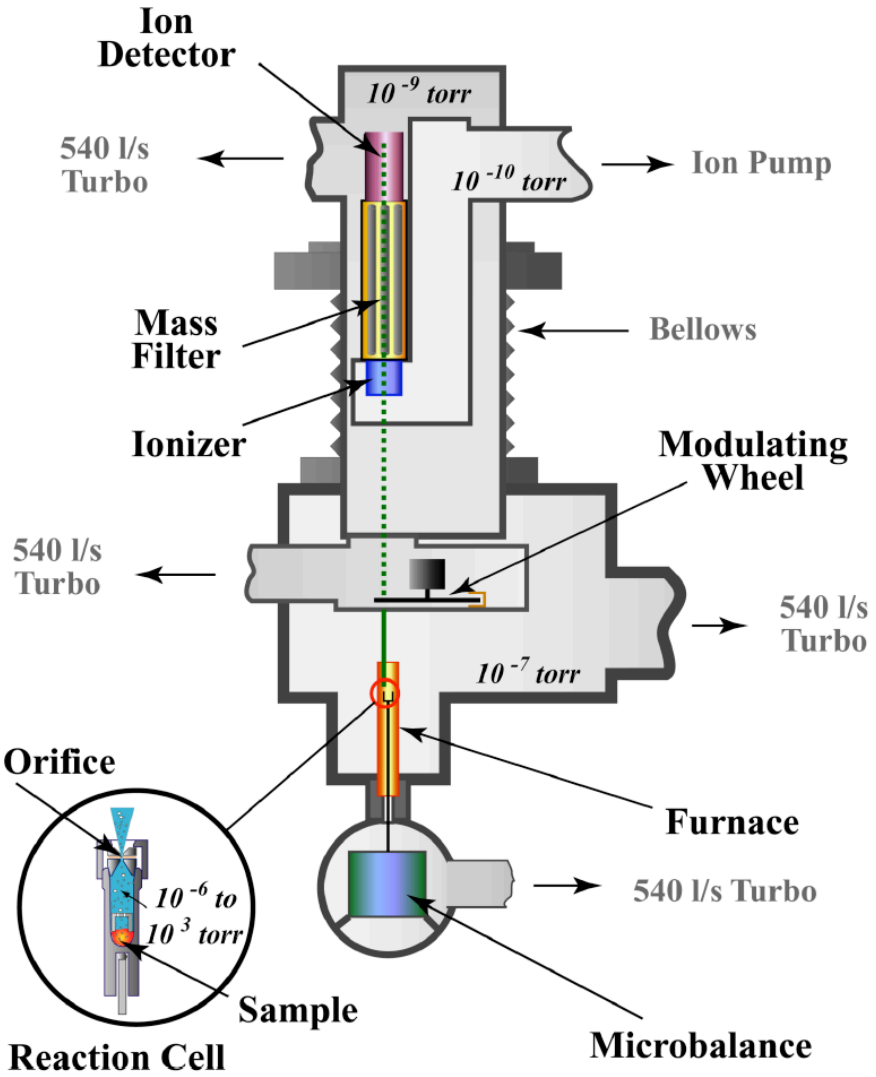
Sandia National Laboratories

**Images for qualitative comparison only: lighting conditions may not be identical; images adjusted for brightness and contrast.

Simultaneous Thermogravimetry and Modulated Beam Mass Spectrometry: Mass Spectrometry at Elevated Temperatures

Simultaneous Detection of Evolved Products

- **STMBMS experiments**
  - Samples placed in alumina reaction cell with 500 µm orifice (low confinement) or 10 µm orifice (high confinement)
  - 5-10 mg sample size
  - Samples heated from 25°C up to 350°C at 1°C/min
  - Quadrupole mass spectrometer captures mass spectrum of evolved species (electron ionization detection)
  - Microbalance simultaneously records mass loss (2 µg mass accuracy)
  - Total experiment time ~6 hours



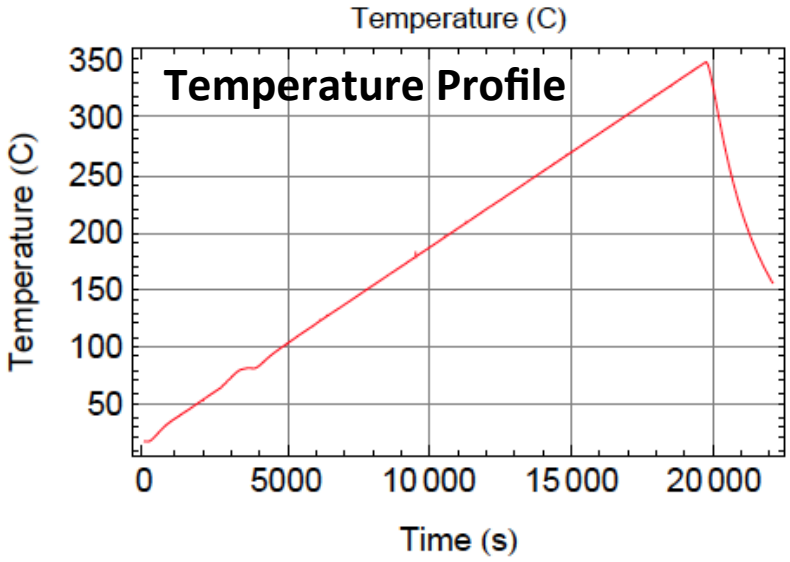
Sandia National Laboratories

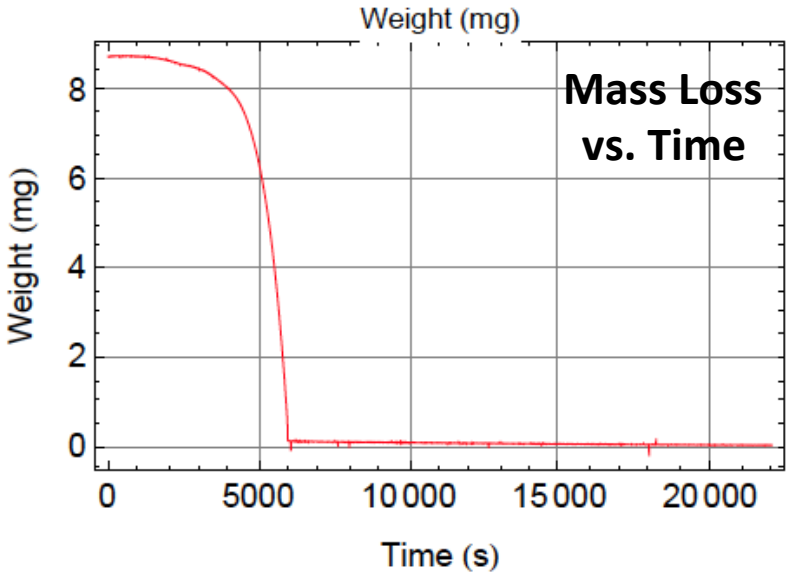
Simultaneous Thermogravimetry and Modulated Beam Mass Spectrometry (STMBMS)

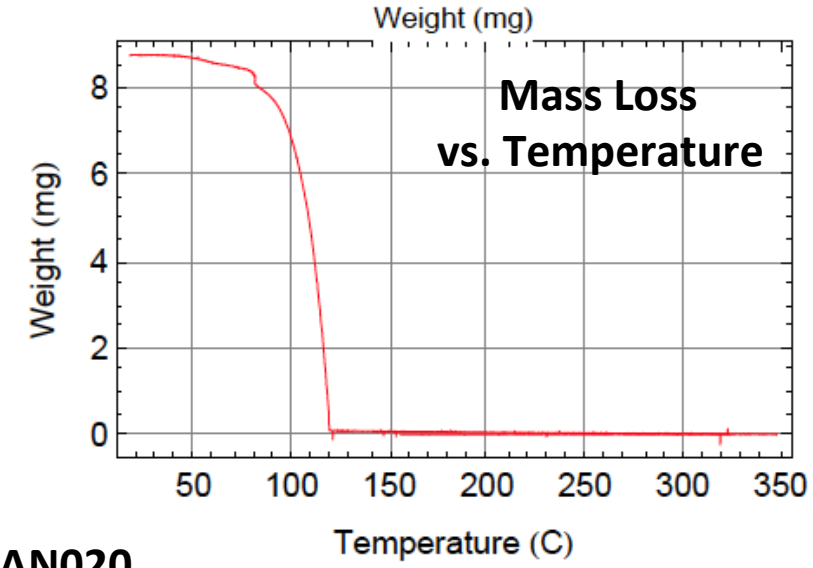
Simultaneous Thermogravimetric Modulated Beam Mass Spectrometry (STMBMS)

Sandia National Laboratories

STMBMS: Pristine DNAN (Low Confinement)







In this experiment (low confinement), DNAN sublimes without apparent decomposition

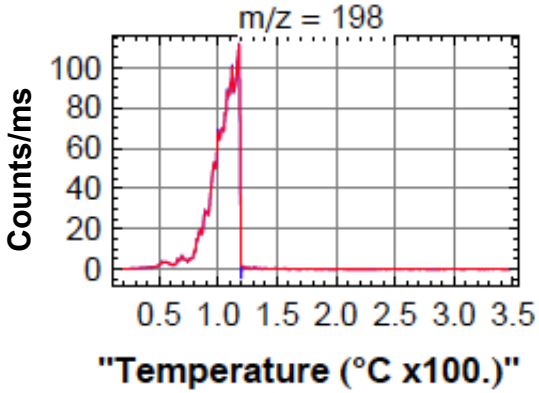
Sandia National Laboratories

DNAN020

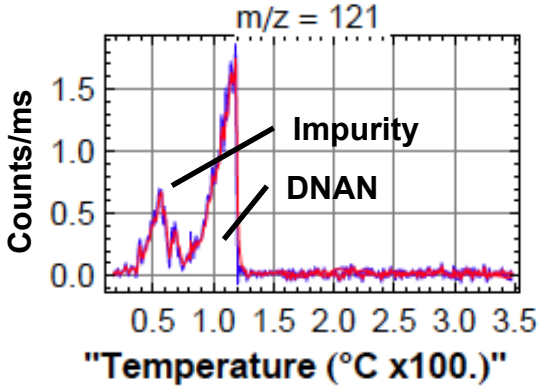
STMBMS: Pristine DNAN (Low Confinement)

Sublimation of DNAN is observed, along with impurity (DNCB)

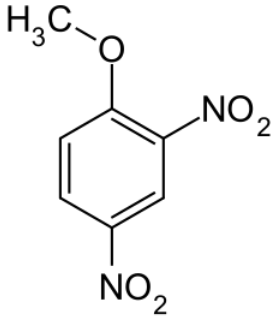
Parent mass peak



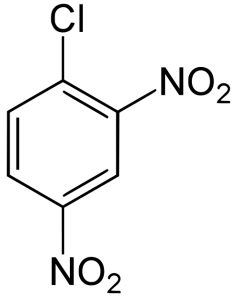
DNAN peak + Impurity



Impurity evolves ~40-60°C with mass peaks m/z = 121, 98, 91, others



2,4-dinitroanisole
m.w. 198 g/mol

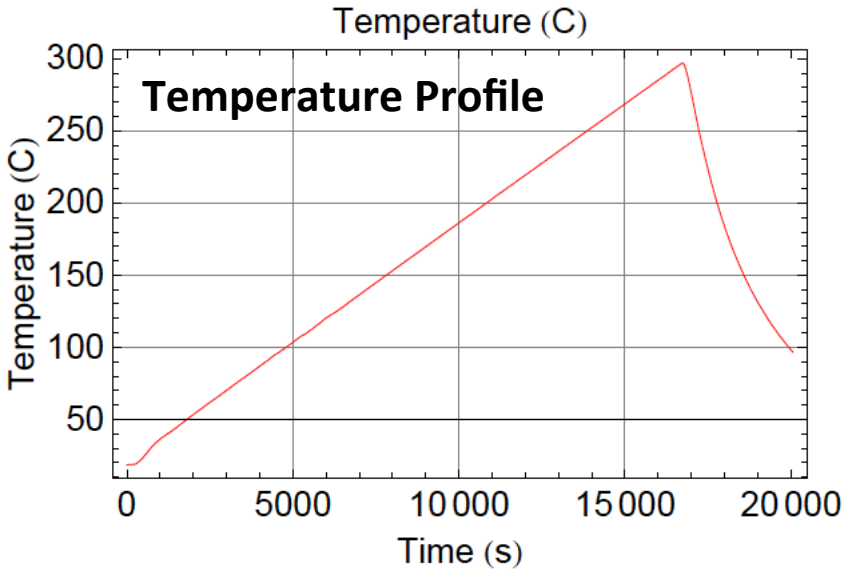


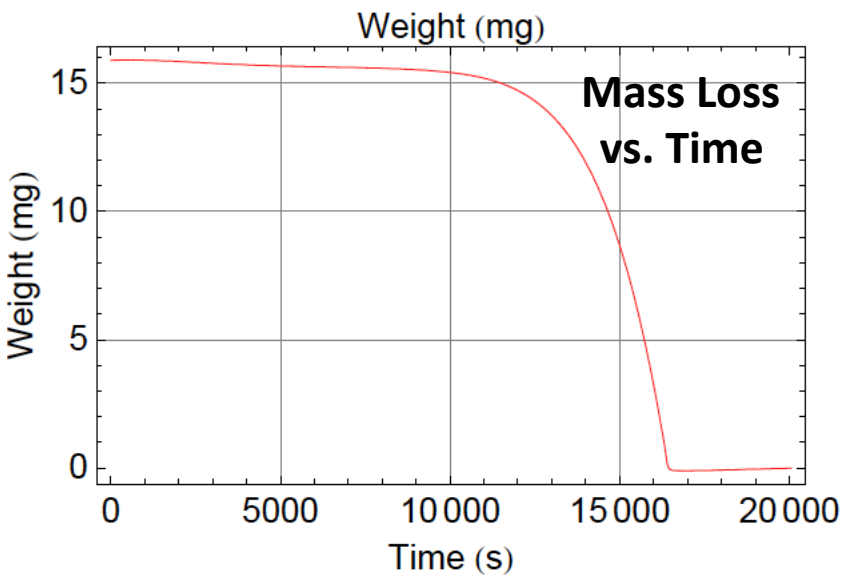
2,4-dinitrochlorobenzene
m.w. 202 g/mol (^{35}Cl), 204 g/mol (^{37}Cl)
m.p. 54°C

Sandia National Laboratories

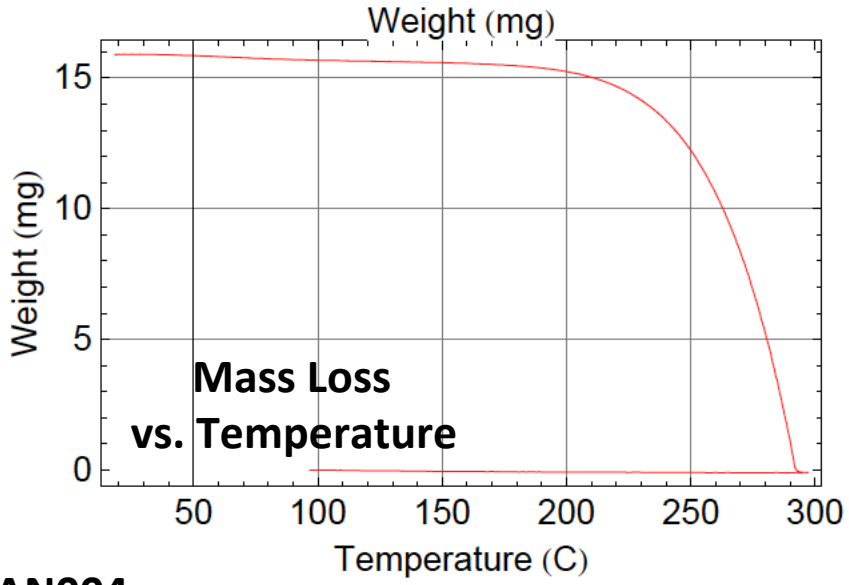
DNAN020

STMBMS: Pristine DNAN (High Confinement)





In this experiment (low confinement), DNAN sublimes in tandem with decomposition

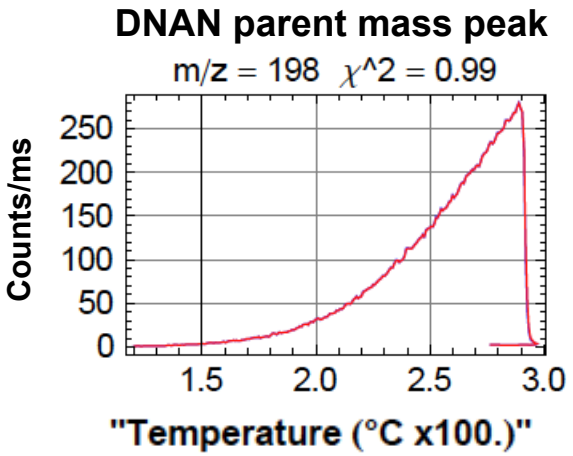


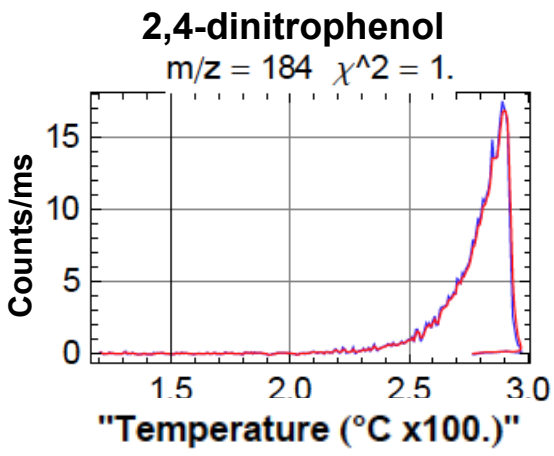
DNAN004

Sandia National Laboratories

STMBMS: Pristine DNAN (High Confinement)

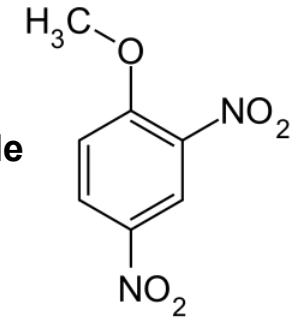
Sublimation of DNAN is observed along with partial decomposition to produce 2,4-dinitrophenol



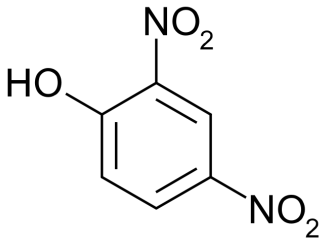


2,4-dinitrophenol evolves above ~225°C

2,4-dinitroanisole
m.w. 198 g/mol



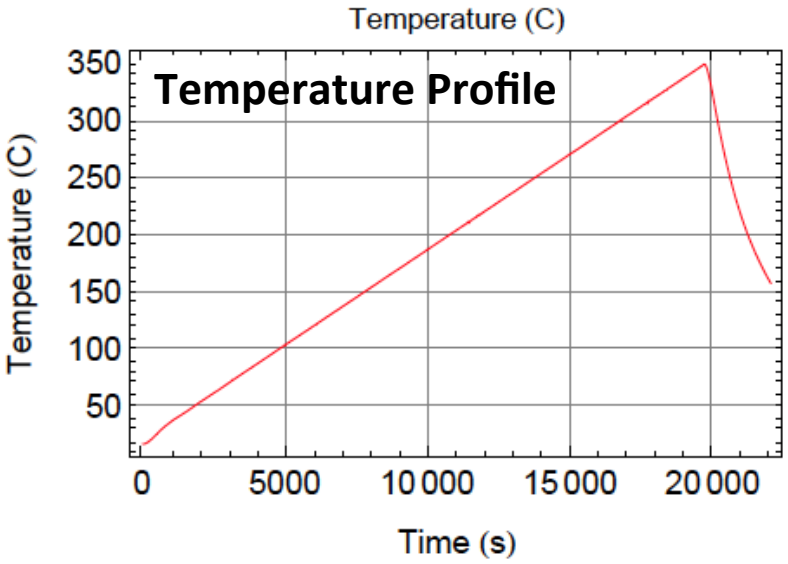
2,4-dinitrophenol
m.w. 184 g/mol

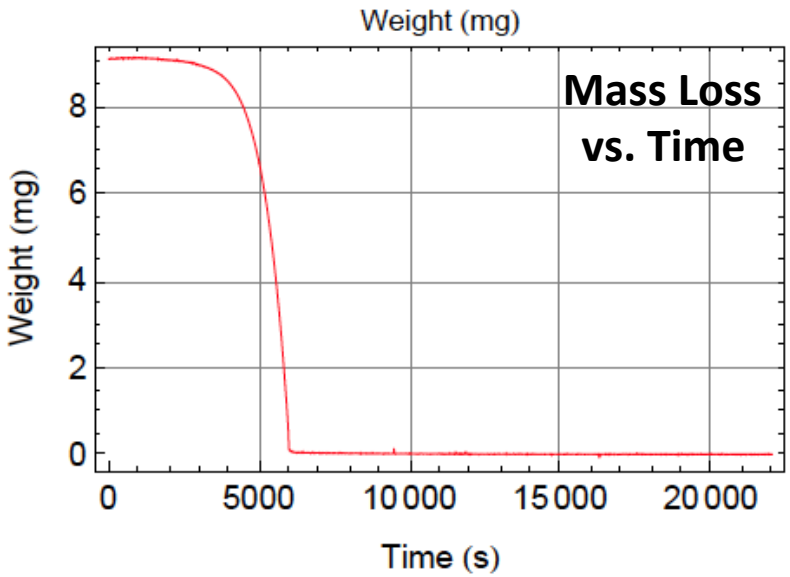


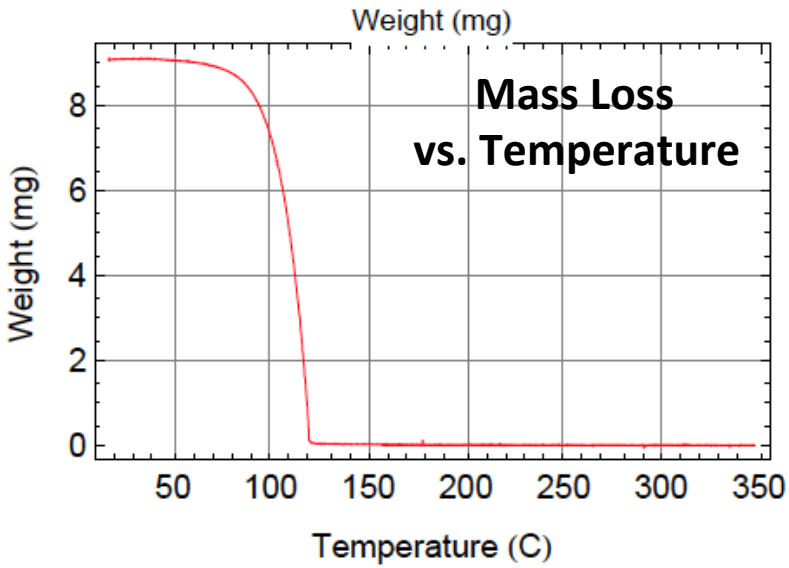
Sandia National Laboratories

DNAN020

STMBMS: Cycled DNAN (Low Confinement)







Sublimation of the cycled DNAN is observed; similar mass loss profile as pristine material

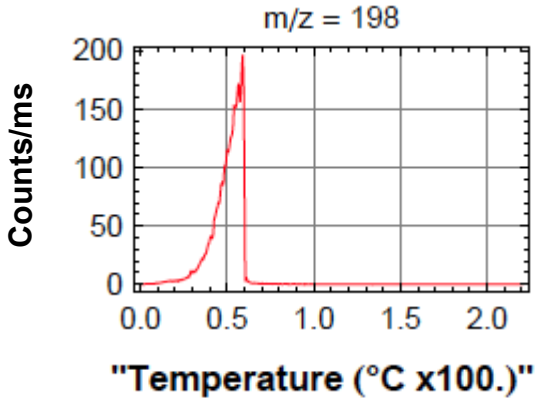
Sandia National Laboratories

DNAN021

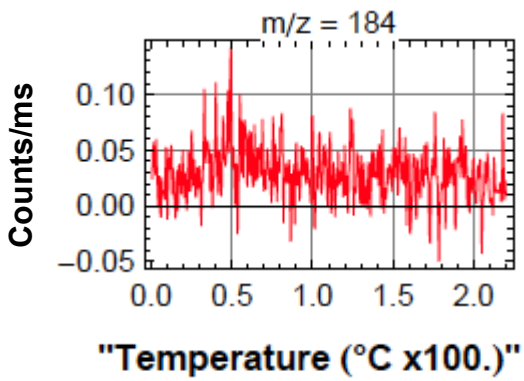
STMBMS: Cycled DNAN (Low Confinement)

Sublimation of DNAN is observed; decomposition products not observed

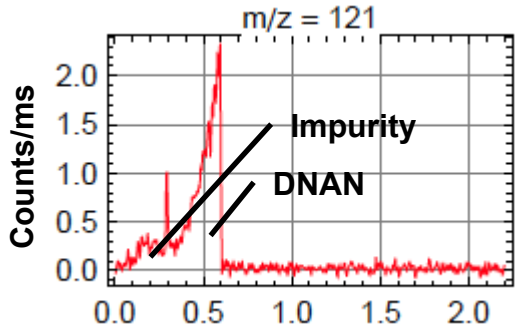
DNAN parent mass peak



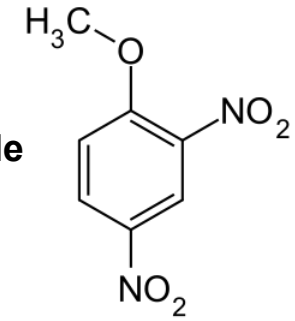
m/z = 184



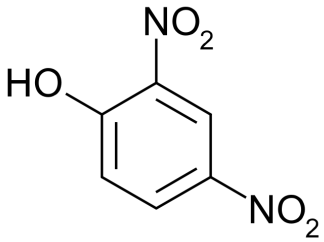
DNAN peak + impurity



2,4-dinitroanisole
m.w. 198 g/mol



2,4-dinitrophenol
m.w. 184 g/mol

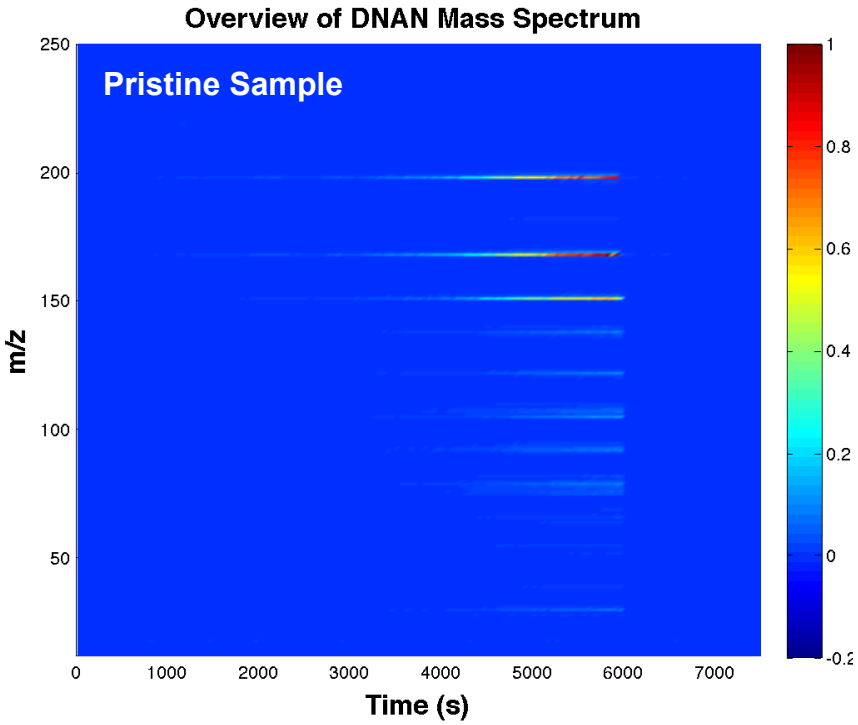


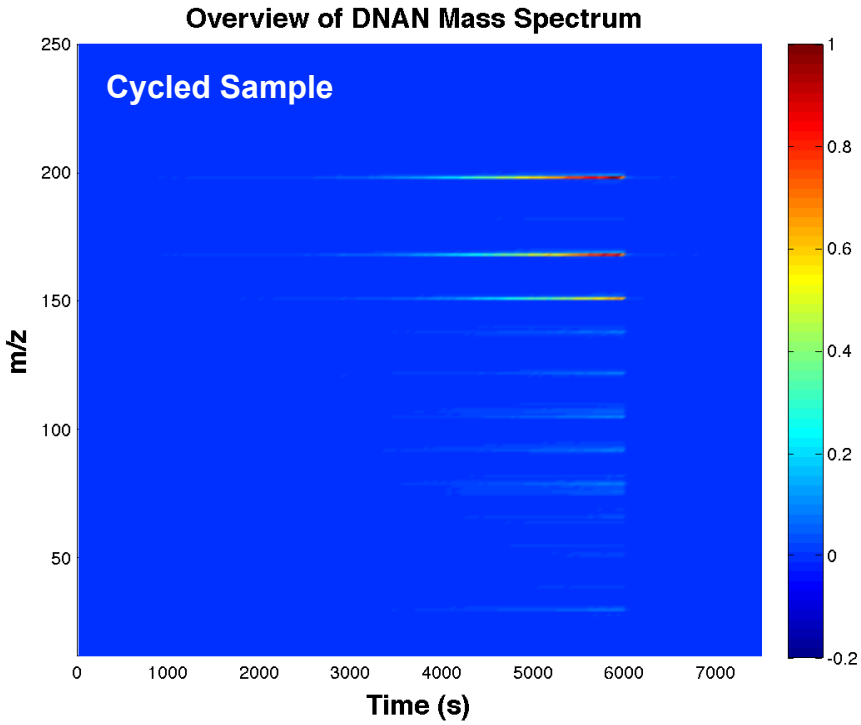
Sandia National Laboratories

DNAN021

Comparison of Pristine and Cycled Samples

Generation of new chemical compounds is not evident in our experiments



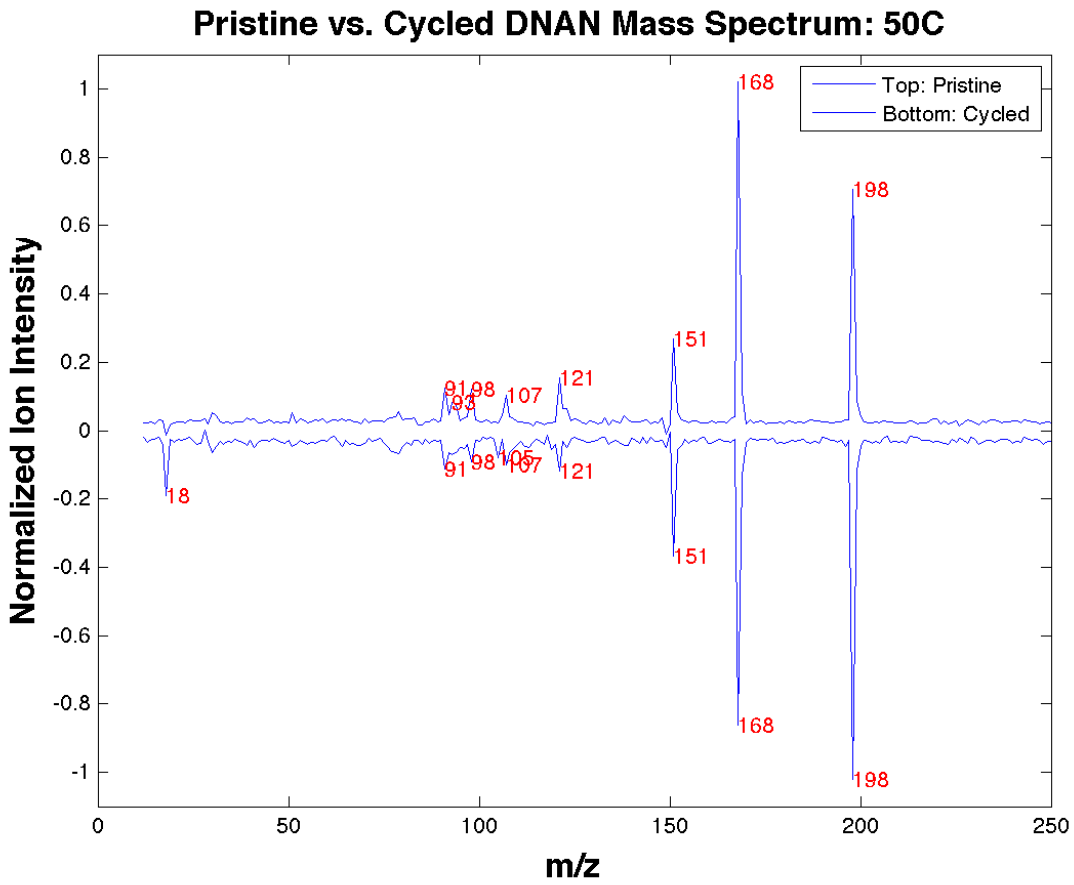


Sandia National Laboratories

DNAN020, DNAN021

Comparison of Pristine and Cycled Samples

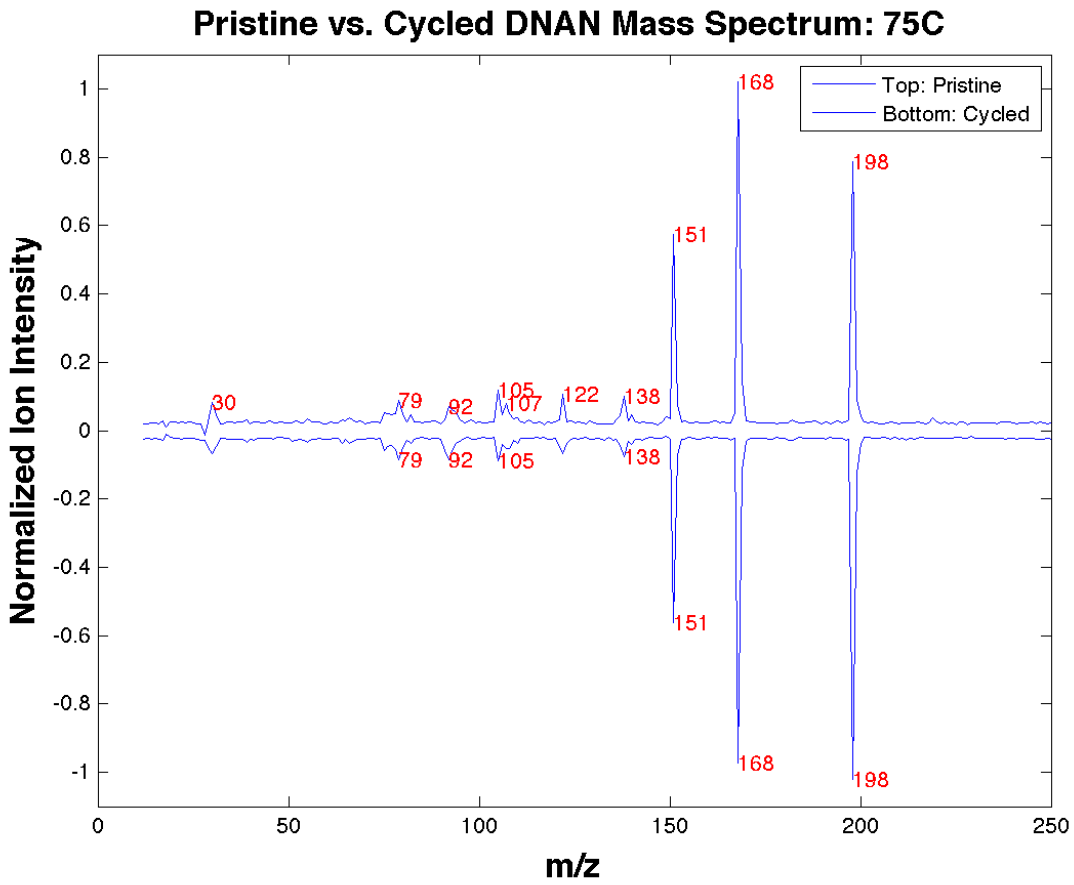
Generation of new chemical compounds is not evident in our experiments



DNAN020, DNAN021

Comparison of Pristine and Cycled Samples

Generation of new chemical compounds is not evident in our experiments

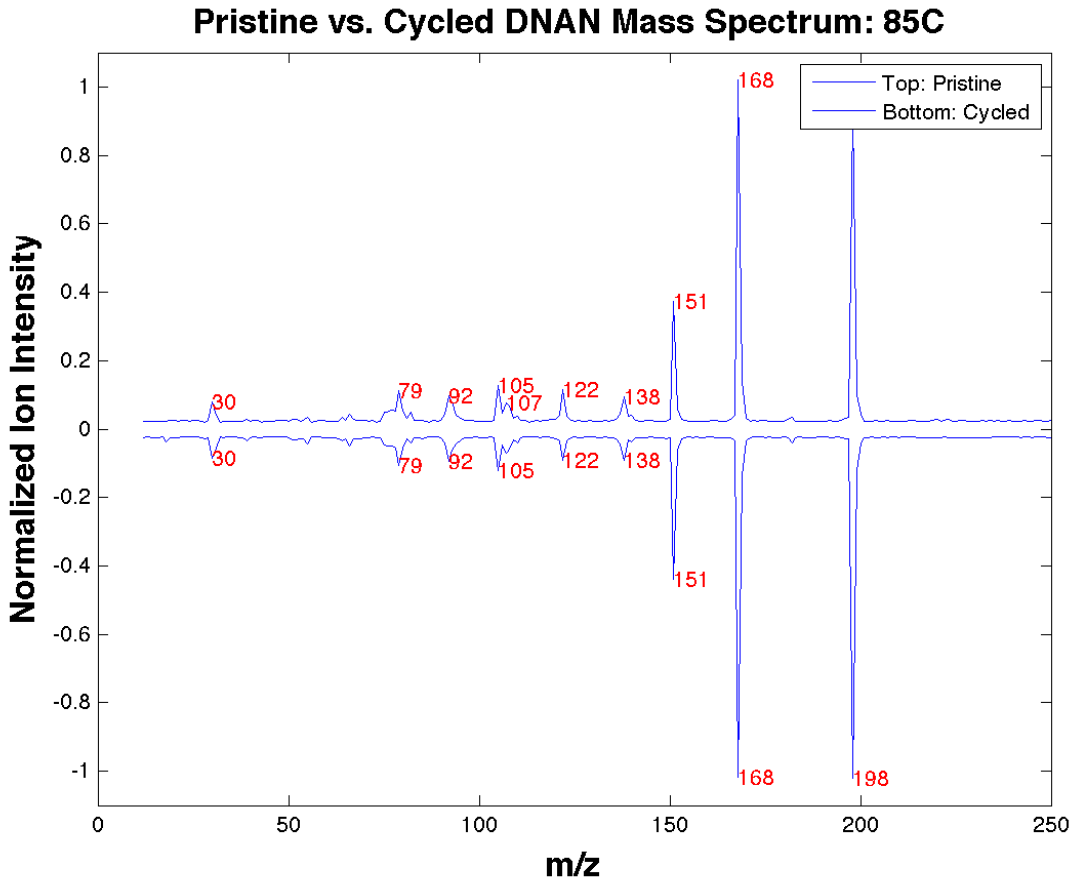


DNAN020, DNAN021

Sandia National Laboratories

Comparison of Pristine and Cycled Samples

Generation of new chemical compounds is not evident in our experiments

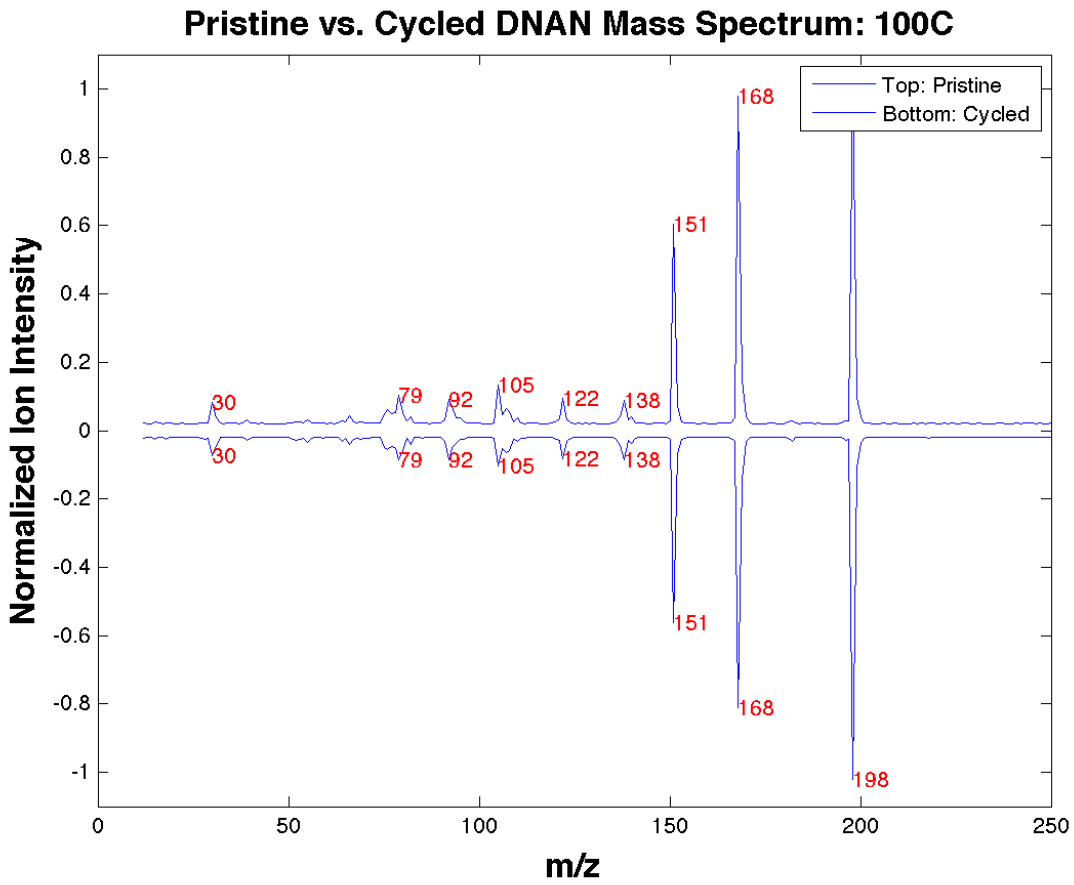


DNAN020, DNAN021

Sandia National Laboratories

Comparison of Pristine and Cycled Samples

Generation of new chemical compounds is not evident in our experiments

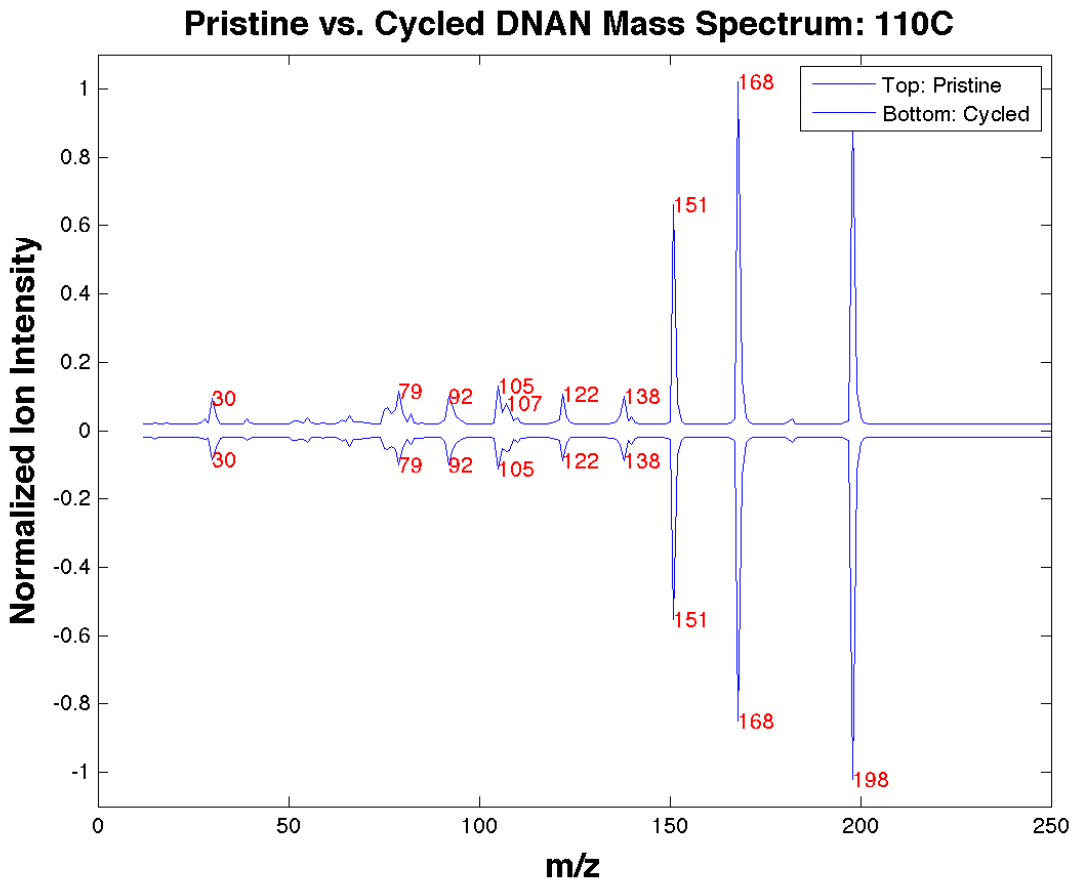


DNAN020, DNAN021

Sandia National Laboratories

Comparison of Pristine and Cycled Samples

Generation of new chemical compounds is not evident in our experiments

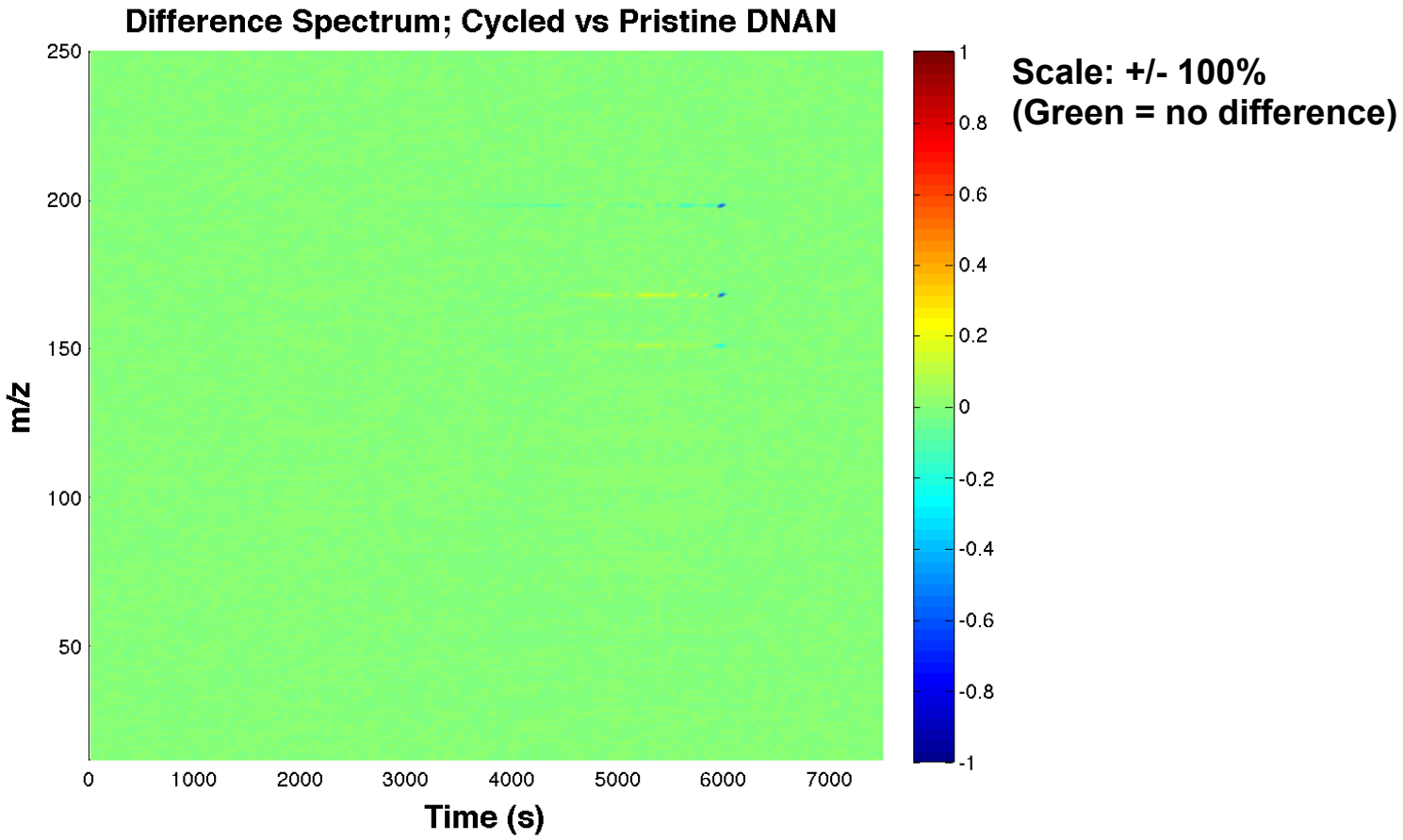


DNAN020, DNAN021

Sandia National Laboratories

Comparison of Pristine and Cycled Samples

Generation of new chemical compounds is not evident in our experiments

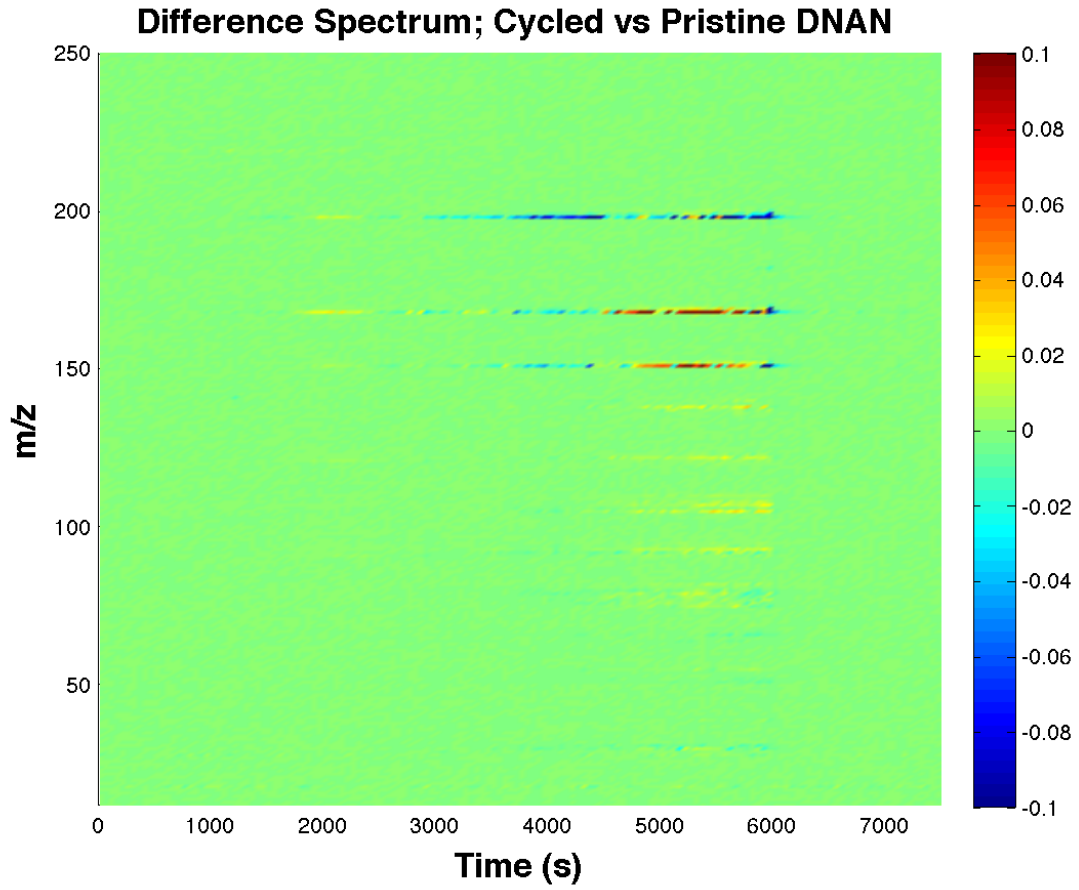


DNAN020, DNAN021

Sandia National Laboratories

Comparison of Pristine and Cycled Samples

Generation of new chemical compounds is not evident in our experiments



Scale: +/- 10%
(Green = no difference)

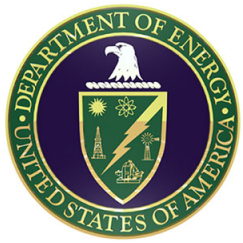
DNAN020, DNAN021

Sandia National Laboratories

Conclusions and Future Directions

- We have conducted STMBMS experiments on DNAN powder and thermally-cycled DNAN powder
- Thermal cycling was conducted between 25^{o}C to 60^{o}C, 30x
- Generation of new chemical compounds upon thermal cycling is not evident in our experiments
- Work later this FY will investigate a second, more aggressively thermally-cycled powder (25^{o}C to 70^{o}C, 40x) and thermally-cycled formulations from Picatinny Arsenal

Questions?



Thank you to:

Philip Samuels, ARDEC
US DoD/DOE Joint Munitions Program