Safety Assessments of Thermally Damaged Energetic Materials

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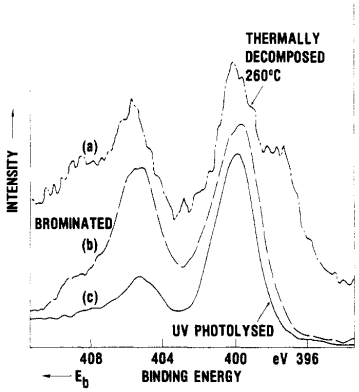
Thermal Damage of Energetic Materials

- What is thermal damage of TATB: thermal damage is defined as when TATB is heated, it becomes more sensitive to stimuli (decomposes into more sensitive compounds)
- Why do we care: because if TATB is more sensitive and can react, then we must know how to handle the material safely
  - Example: testing facilities—sensitized material can not be the same is the parent material. New protocols and protective measures must be in place
  - Example: fire!—first responders will have to be guided to handle the fire safely. When to fight and when to run
  - Example: clean-up—when the event is over, how do you handle the residue safely?
- How do we do understand thermal decomposition of TATB: determine what causes the sensitivity
  - Determine whether intermediates are more sensitive
  - Detect intermediates in damaged samples so the danger can be assessed
  - Improve decomposition models to predict time to explosion to covert the space

This presentation summarizes our research into the thermal sensitization of TATB

Previous Studies on Thermal Decomposition Products

Characterization decomposition products
Sharma et al. *circa* 1980



XPS of N1s binding energies of TATB heated to 260 °C

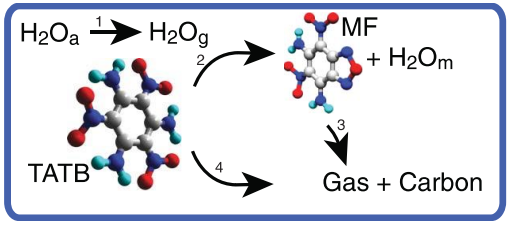
Changes in sensitivity upon heating
Hsu et al. circa 2006

Volume and density of LX-17 heated to 190 and 250 °C

Sample	Wt., g	Vol., cc	Bulk density, g/cc	%TMD*
Pristine LX-17	9.7379	5.1183	1.9024	97.86
190 °C, 4 hrs	9.7289	5.3316	1.8248	93.87
% Change	-0.090	+4.16	-4.08	
Pristine LX-17	9.7364	5.0967	1.9103	98.27
250 °C, 2 hrs	9.726	5.5272	1.7572	90.39
% Change	-0.240	+8.45	-8.01	

* TMD is theoretical maximum density

Models of decomposition
Hobbs & Kaneshigi *circa* 2014



4 step reaction mechanism

Synthesis of decomposition products
Belmas et al. *circa* 2004

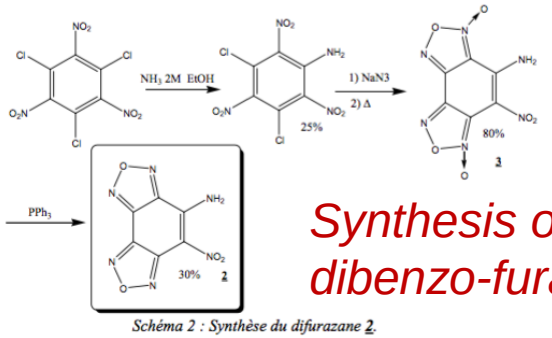


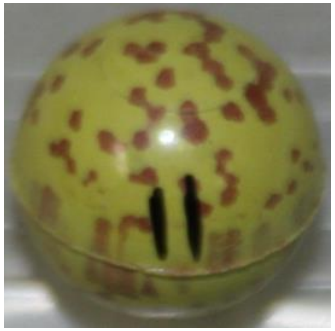
Schéma 2 : Synthèse du difurazane 2.

Synthesis of dibenzo-furazan

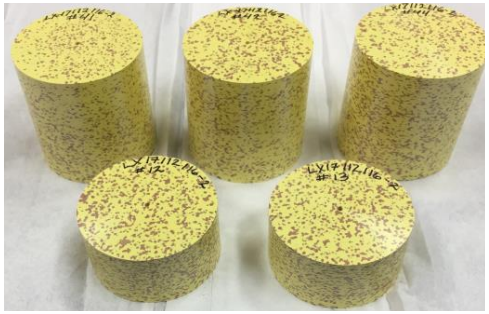
TATB thermal decomposition studies started around 1970

What happens to TATB when heated?

Mild severity PODTX



More Severity SSVCT



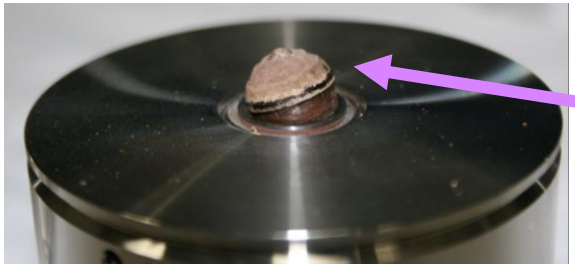
Most severe STEX

Before

After

Experimental—Sensitization Methods

PODTX (Pressure monitored One Dimensional Time to Explosion)

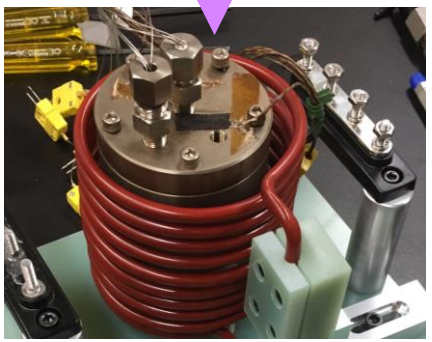


Reacted ~ 2-g sample
Sample heated 200 to 300 °C
Held for s to h
Seals did not rupture
Not taken to explosion

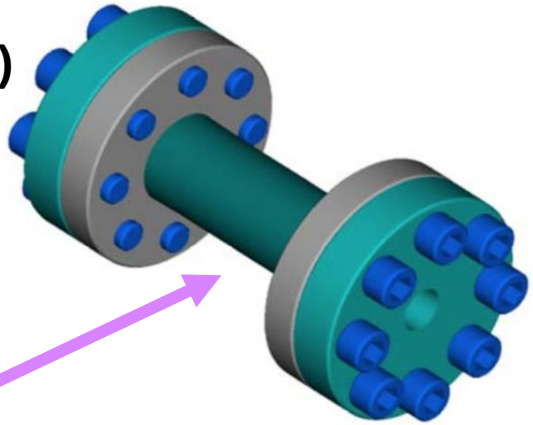
LX-17 86 & 98% TMD

Top come off

SSVCT (Small-Scale Vessel Cook-off Test)



STEX (Scaled Thermal Explosion eXperiment)



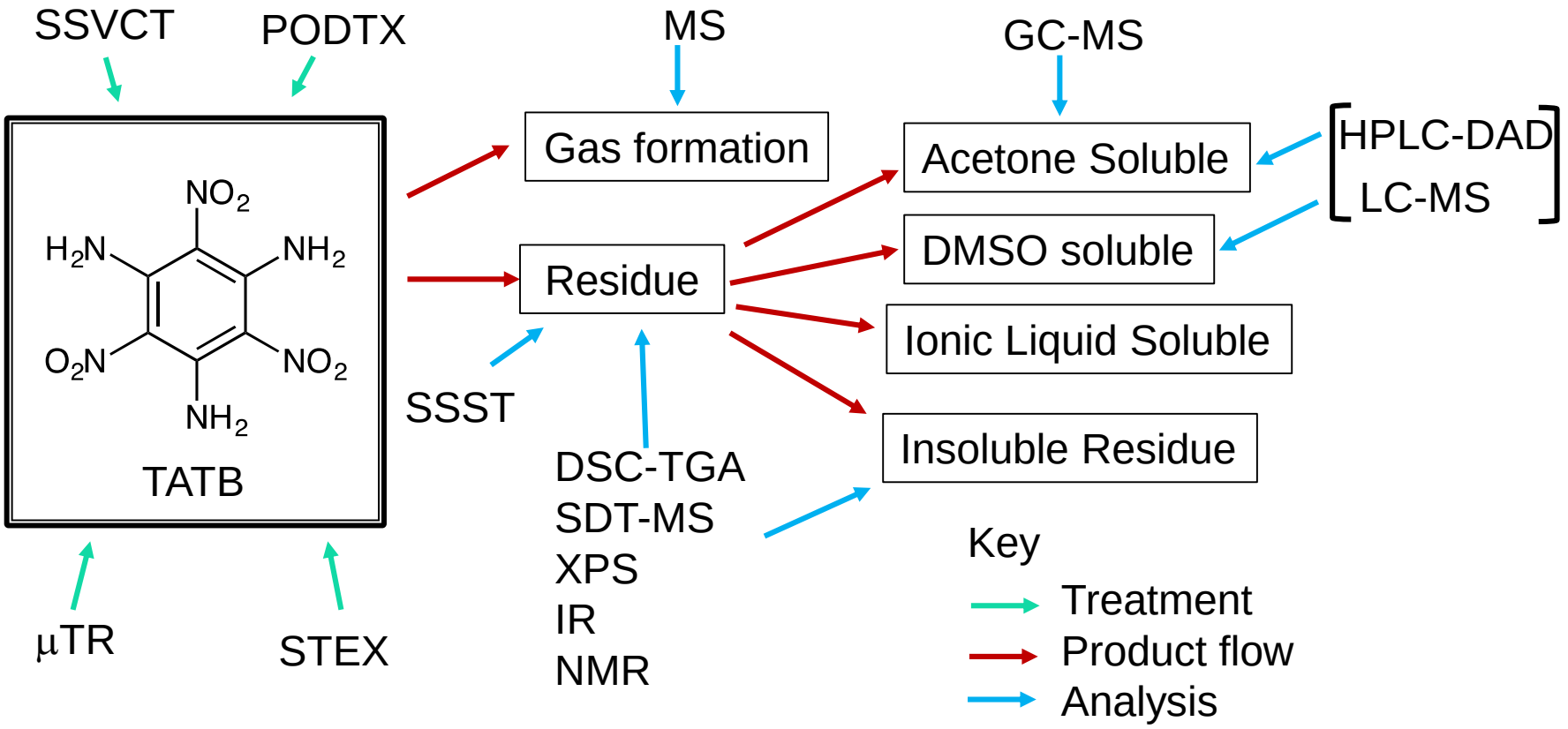
1000-g samples
Taken to explosion

Wall ruptures

100-125-g samples
Nominal 3000 psi limit
Sample taken to venting of reactor

Treatment methods chosen to widely vary thermal conditions

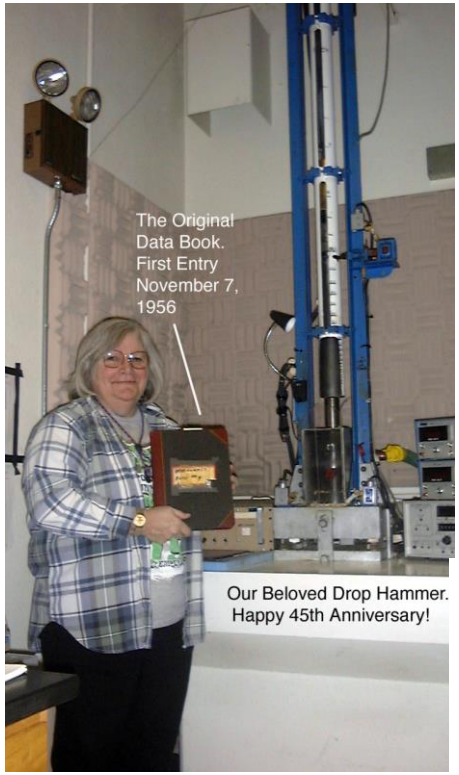
Thermal Sensitization and Analysis



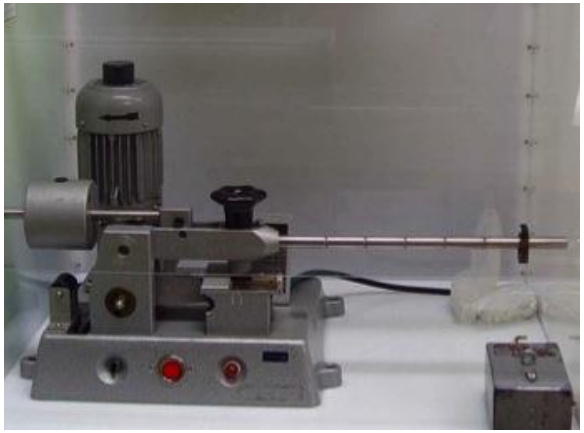
Four thermal treatments; SSST and molecular characterization

Small-Scale Safety and Thermal Testing

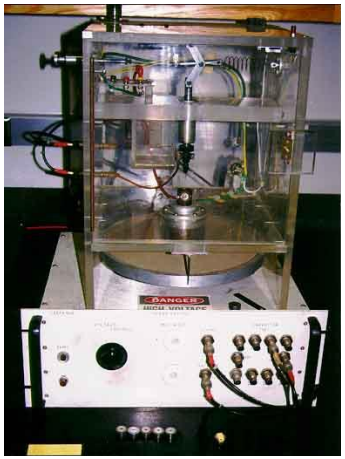
ERL Impact



ABL Friction

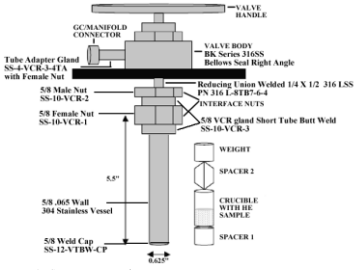


Custom ESD



DSC

CRT



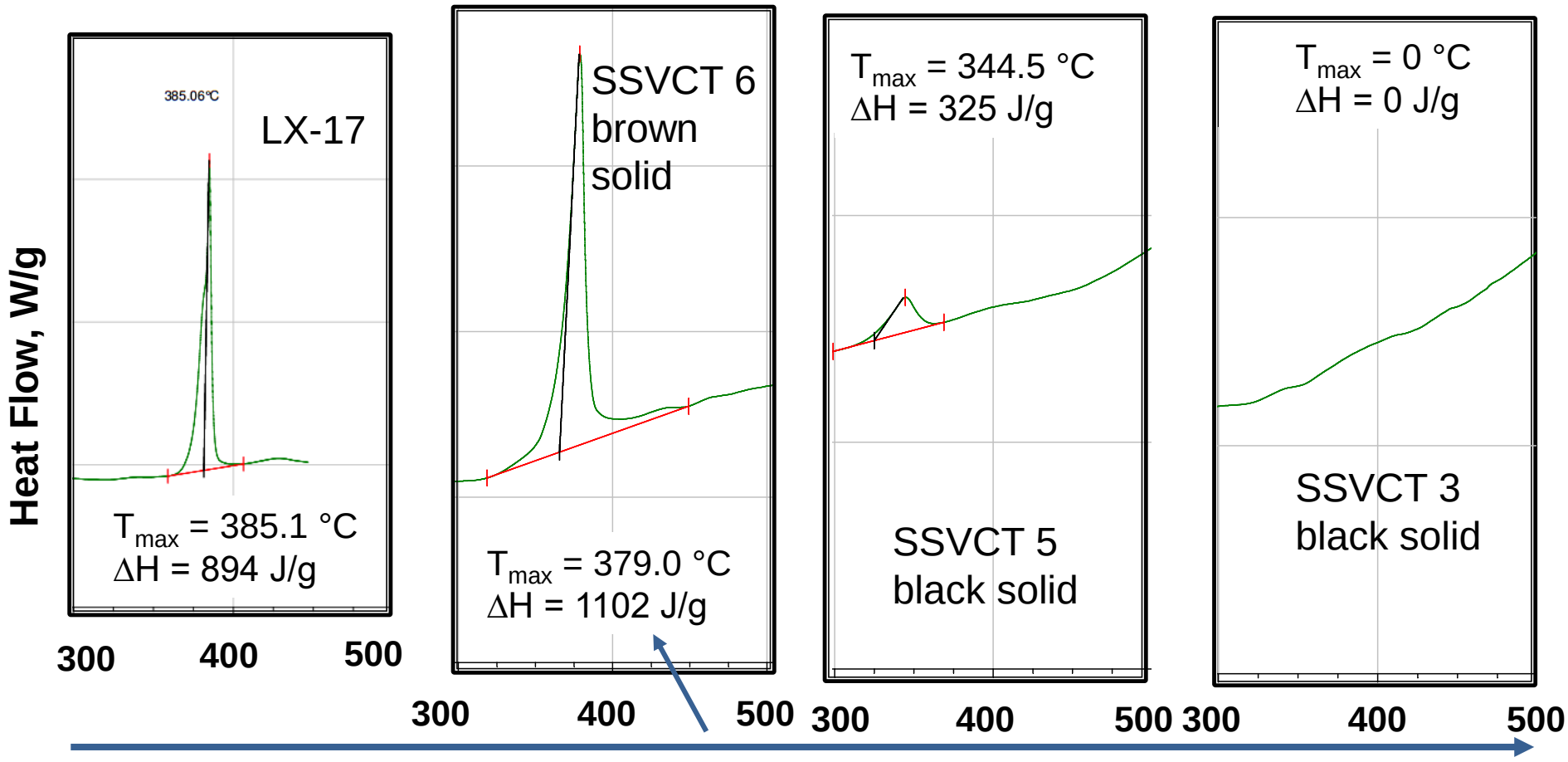
ABL ESD

SSST—Impact, Friction, Spark Sensitivity

Sample	DH_{50}, cm[1]	Friction TIL, kg[2]	ESD TIL, J[3,4]
LX-17	> 177	0/10 @ 36.0	0/10 @ 1 (510 Ω); 0/10 @ 0.31 (0 Ω)
PETN	15	1/10 @ 6.4	0/10 @ 1 (510 Ω); 0/10 @ 0.031 (0 Ω)
190 °C/4 h (u)	> 177	0/10 @ 36.0	0/10 @ 1 (510 Ω)
250 °C/2 h (u)	> 177	0/10 @ 36.0	0/10 @ 1 (510 Ω)
STEX 68 y	> 177	0/10 @ 36.0	0/10 @ 1 (510 Ω); 0/10 @ 0.075 (0 Ω)
STEX 68 b	> 177	0/10 @ 36.0	0/10 @ 1 (510 Ω); 0/10 @ 0.88 (0 Ω)
STEX 69 b	> 177	0/10 @ 36.0	
STEX 69 y	> 177	0/10 @ 36.0	0/10 @ 1 (510 Ω); 0/10 @ 0.88 (0 Ω)
STEX 70 y	> 177	0/10 @ 36.0	0/10 @ 1 (510 Ω); 0/10 @ 0.13 (0 Ω)
STEX 71 y	> 177	0/10 @ 36.0	0/10 @ 1 (510 Ω); 0/10 @ 0.25 (0 Ω)
SSVCT 1	> 177	0/10 @ 36.0	0/10 @ 1 (510 Ω); 0/10 @ 0.88 (0 Ω)
SSVCT 3	> 177	0/10 @ 36.0	0/10 @ 1 (510 Ω); 0/10 @ 0.88 (0 Ω)
SSVCT 5	> 177	0/10 @ 36.0	0/10 @ 1 (510 Ω); 0/10 @ 0.88 (0 Ω)
SSVCT 6	> 177	0/10 @ 36.0	0/10 @ 1 (510 Ω); 0/10 @ 0.88 (0 Ω)
1 (200 °C)	> 177	0/10 @ 36.0	0/10 @ 1 (510 Ω); 0/10 @ 0.38 (0 Ω)
2 (310 °C)	> 177	0/10 @ 36.0	0/10 @ 1 (510 Ω); 0/10 @ 0.075 (0 Ω)
PODTX 17054	> 177	0/10 @ 36.0	
PODTX 17053	> 177	0/10 @ 36.0	

Products do not show sensitivity by Drop Hammer and BAM Friction, Minor changes in ABL ESD testing, closer to HMX than PETN

SSST—Standard Scanning Calorimetry (DSC)



Most samples look like this one

DSC (from SSVCT) shows wide range of profile parameters

SSST—Thermal Stability Test (CRT)

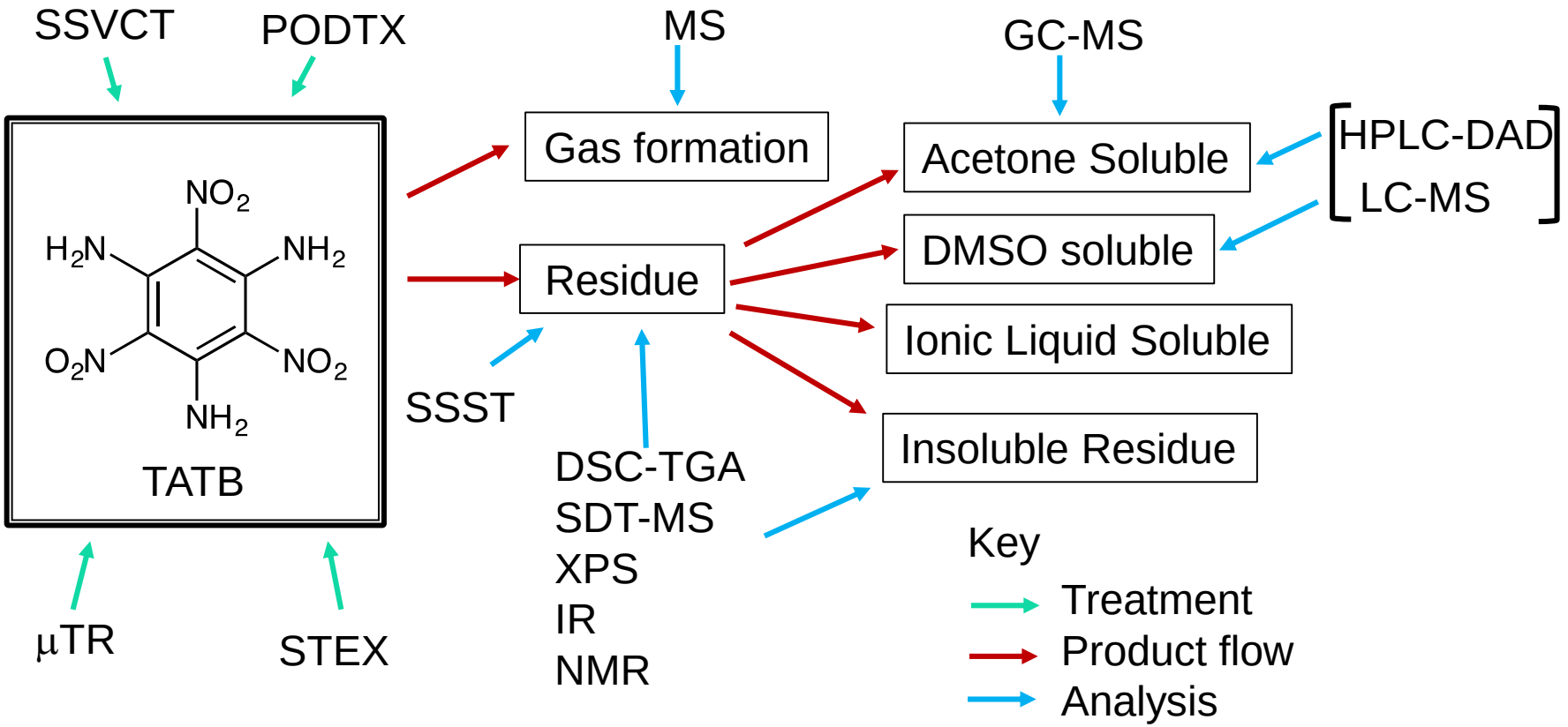
Samples heated @ 120 °C for 24 hours
Gas species detected by gas meter
Sample size 0.125 to 0.251 g

Gas values are in cc
Y = stable; N = unstable
B = black residue; y = yellow residue

sample	N_2	O_2	CO	NO	CO_2	N_2O	$\sum$	cc/g	
STEX 68b	0.0124	0	0.0052	0	0.1001	0.0031	0.1208	0.96	Y
STEX 68y	0.0029	0	0.0011	0.0063	0.0301	0.0035	0.0439	0.17	Y
STEX 69b	0.7940	0	0.0372	0	0.8152	0.0054	1.6518	6.56	N
STEX 70y	0	0	0	0	0.0258	0.0016	0.0273	0.11	Y
STEX 71y	0.0050	0	0.0013	0.0104	0.0259	0.0020	0.0445	0.18	Y
SSVCT 1b	0	0	0.0165	0	0.1721	0.0012	0.1897	1.50	Y
SSVCT 3b	0	0	0.0136	0	0.1317	0.0005	0.1458	1.16	Y
LX-17	0	0	0	0	0.0127	0.0008	0.0135	0.05	Y
PODTX 17054	0.0276	0	0.0110	0.0046	0.1196	0.0028	0.1656	0.66	Y
PODTX 17053	0.0009	0	0.0014	0.0015	0.0413	0.0020	0.0471	0.19	Y

All thermally treated samples produce more gas than LX-17

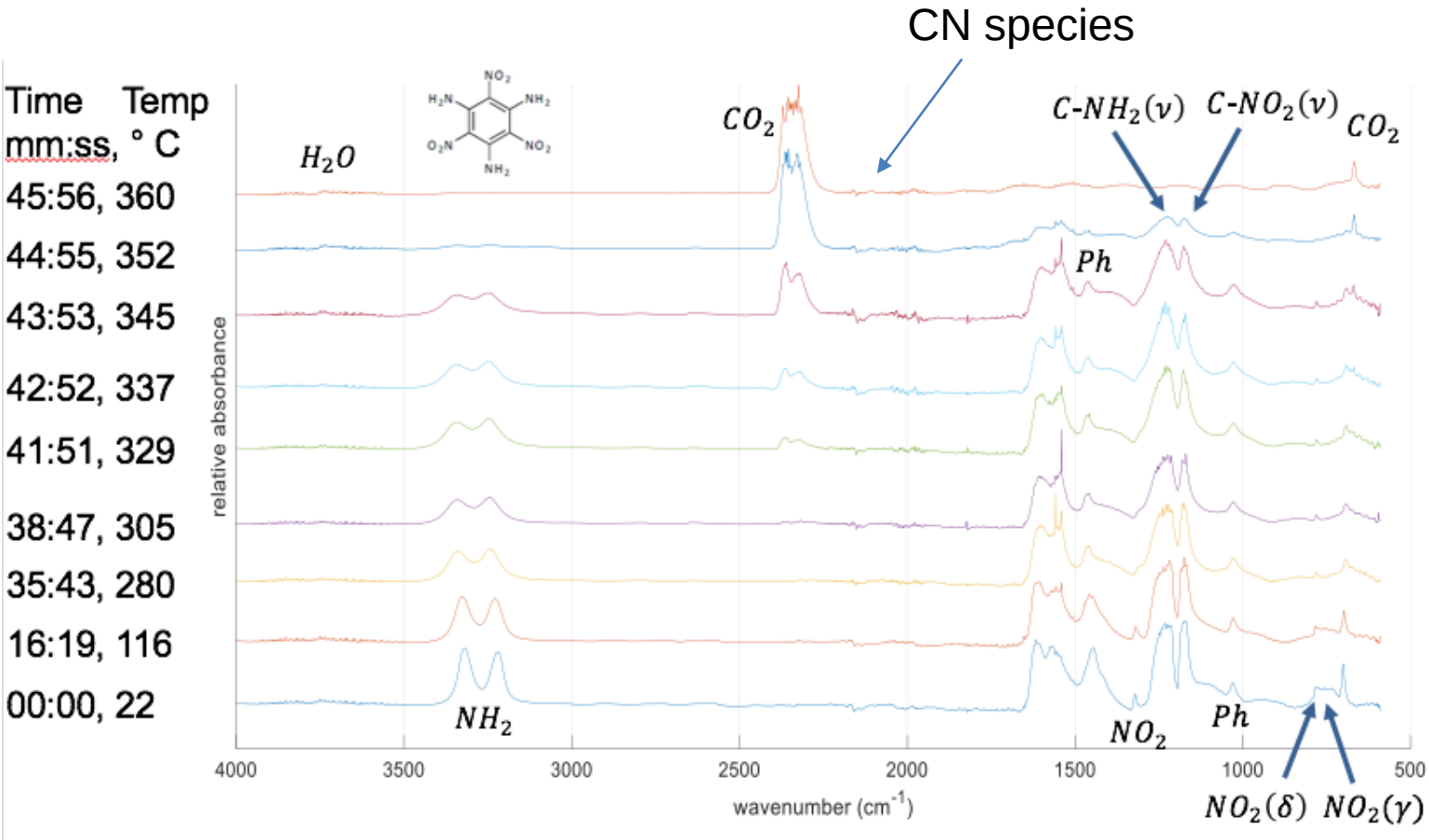
Thermal Sensitization and Analysis



Four thermal treatments; SSST and molecular characterization

Reaction of LX-17 in Micro Thermal Reactor (μTR)

In-situ thermal with spectroscopic characterization by Infrared
LX-17 powder; 7 °C/min heating rate; μTR under pressure



TATB goes away and thermal products form

Characterization—Detection of Molecular Intermediates

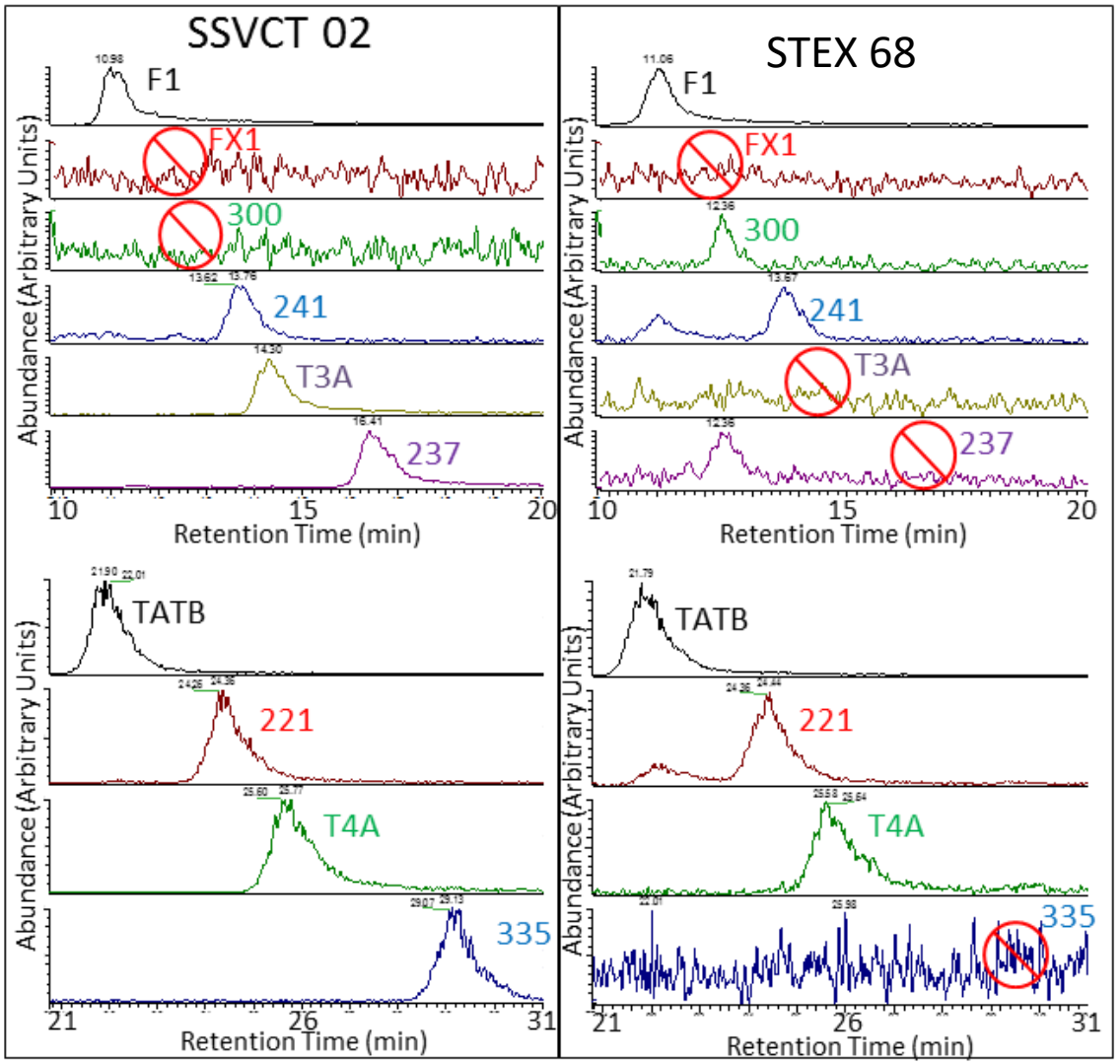
HPLC separation of **DMSO extract** of residues

APCI-MS mass verification at specific retention times

⃠ indicates no intensity at a specific retention time

TATB, F_{x1}, F_2, F_{x2}, F_3, F_{x3}, T3A, T4A verified by standards

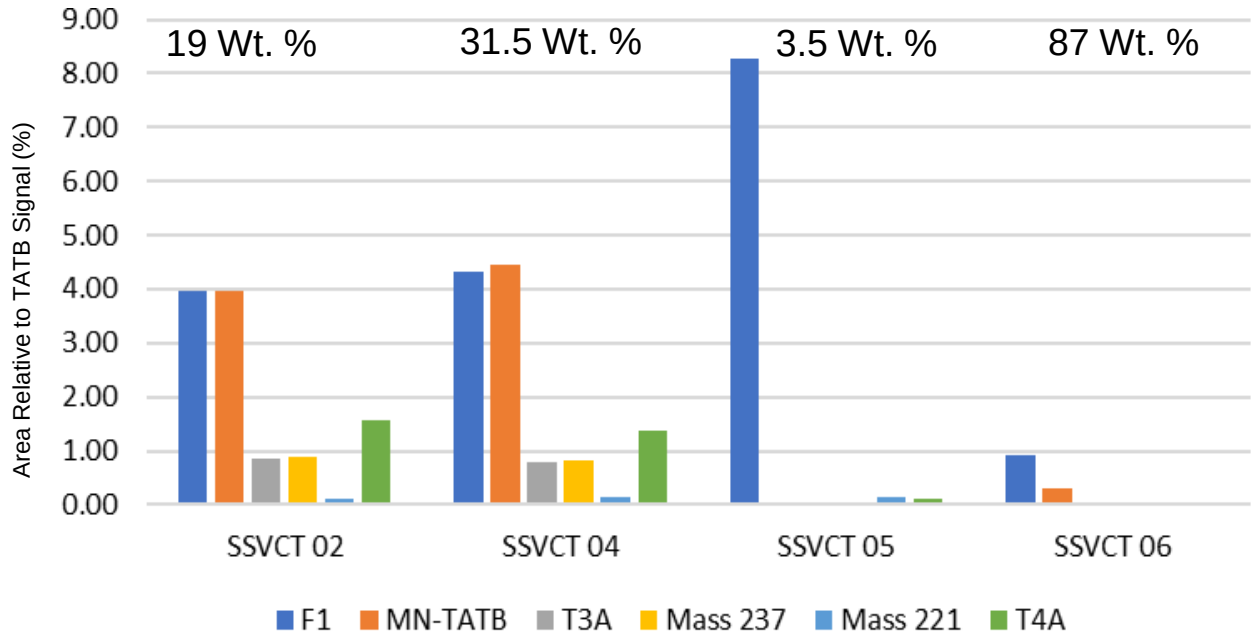
m/z 241, 300, 237, 221, 335 yet to be unequivocally identified (M-H)



Column separation of DMSO extracts shows several high molecular weight intermediates by APCI-MS detection

Characterization—Intermediates Distribution

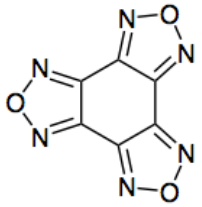
SSVCT Products; DMSO Extract; relative concentrations to TATB concentration



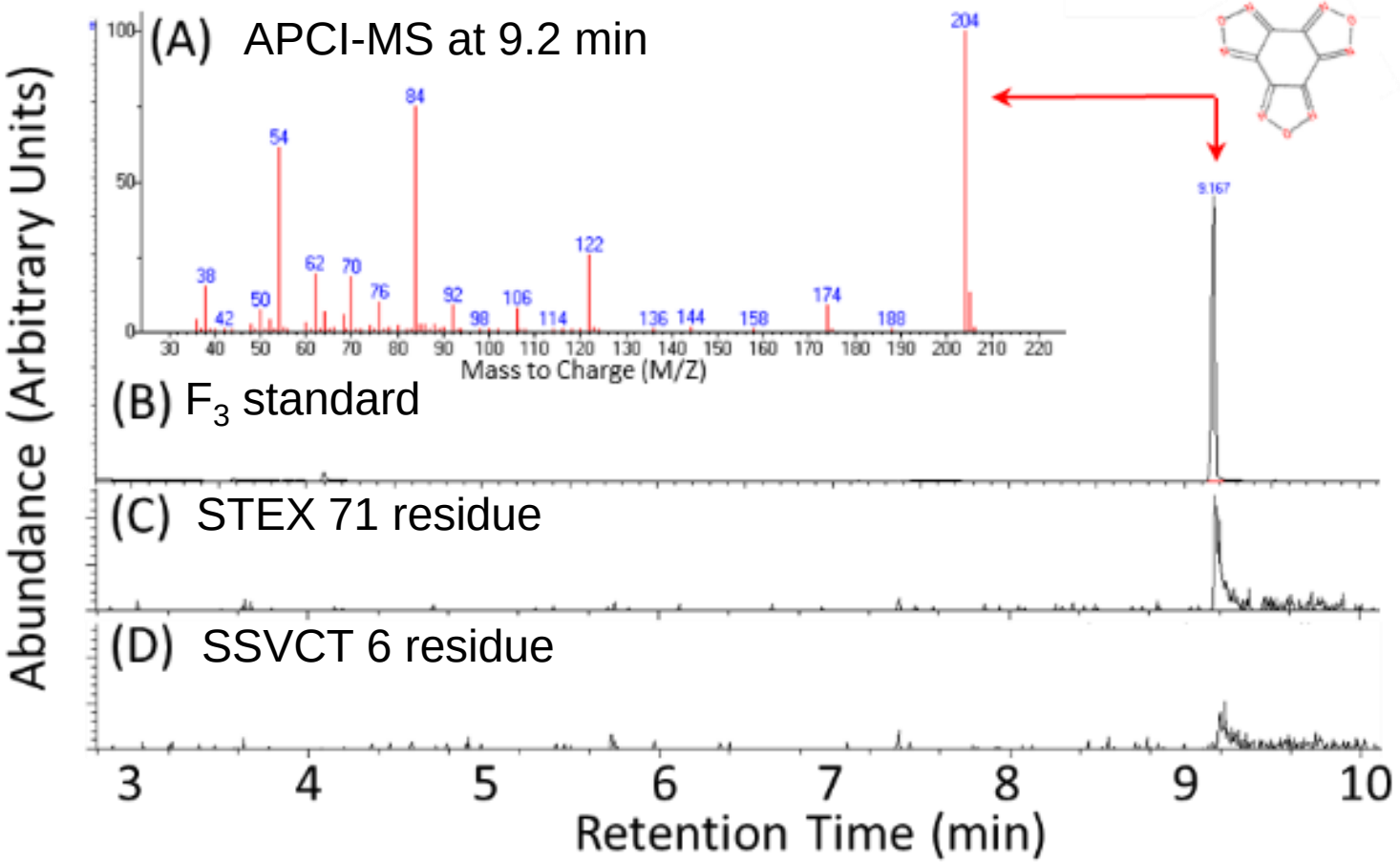
F_1 is the most abundant TATB-like decomposition product
Concentrations follow inverse of TATB concentration in sample
Similar behavior appears in the STEX and PODTX samples

Characterization—Detection of Molecular Intermediates

GC separation of acetone extract of residue
APCI MS verification at specific retention times



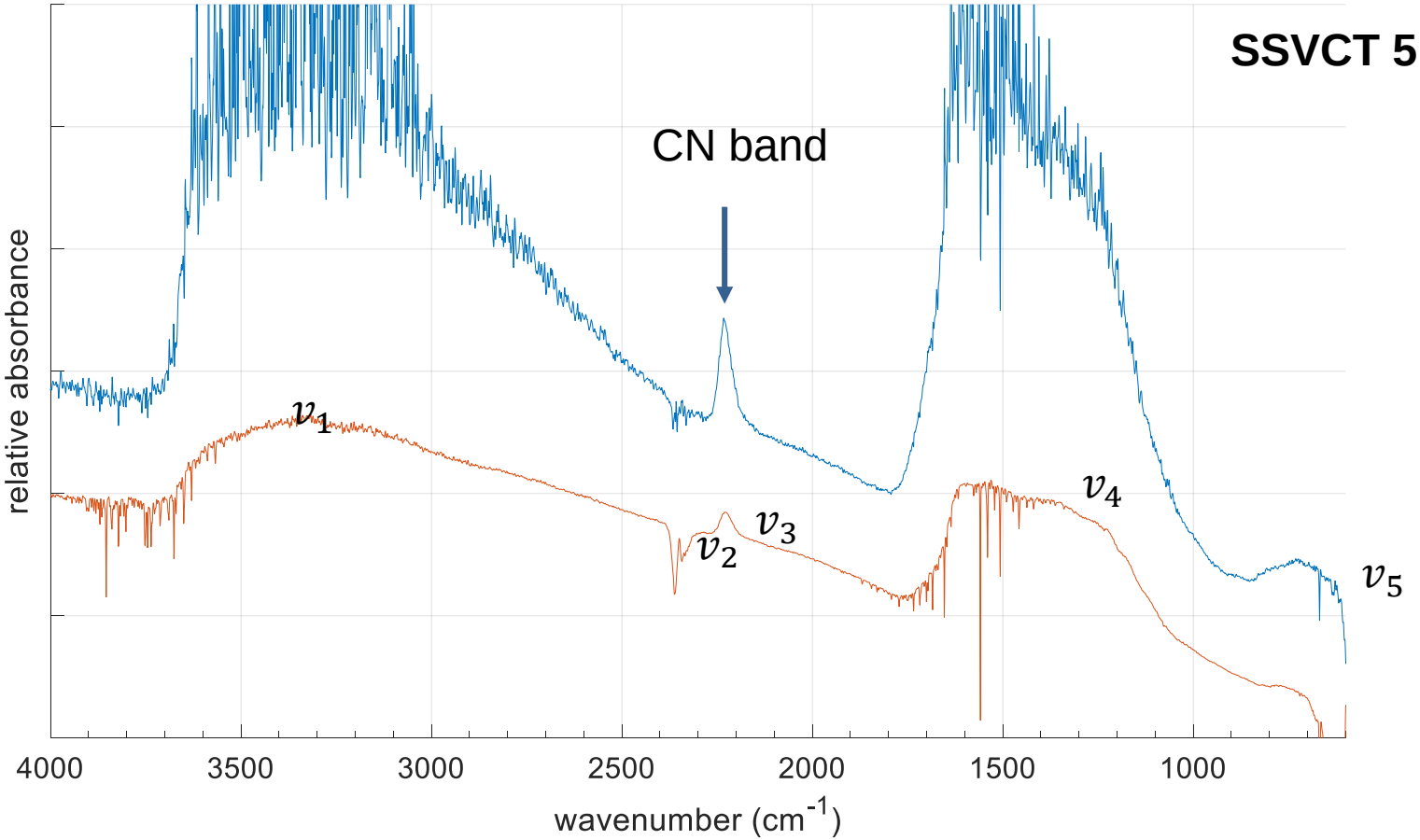
TATB-F_3



Acetone extract shows significant amount of F_3 in most residues

Characterization—FTIR of Solid Residue

FTIR shows functional groups; residue spectra taken in diamond anvil cell; Two concentration of the same sample



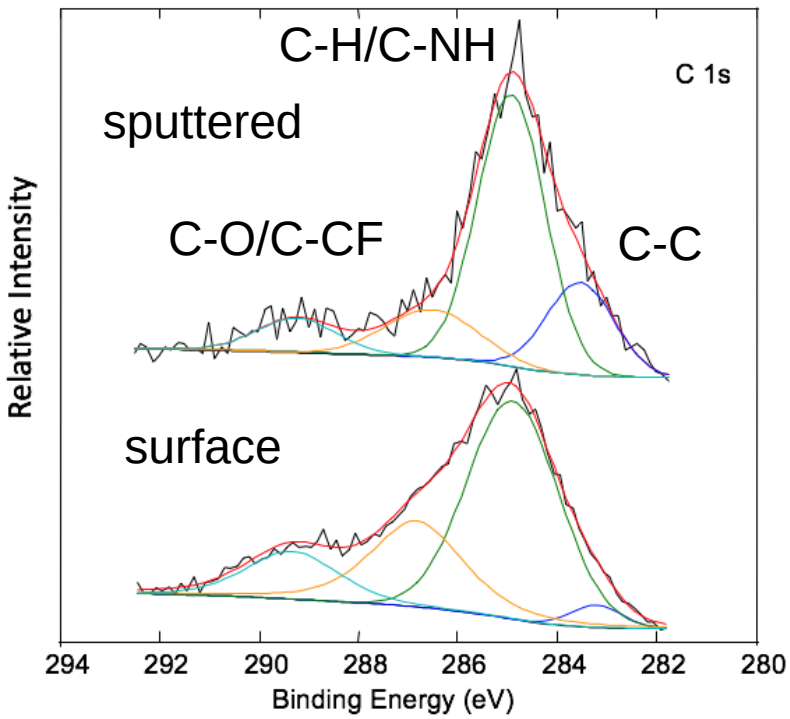
v_1, v_3, v_4, v_4 are indicative of C-N bonding, v_2 is background subtraction CO_2

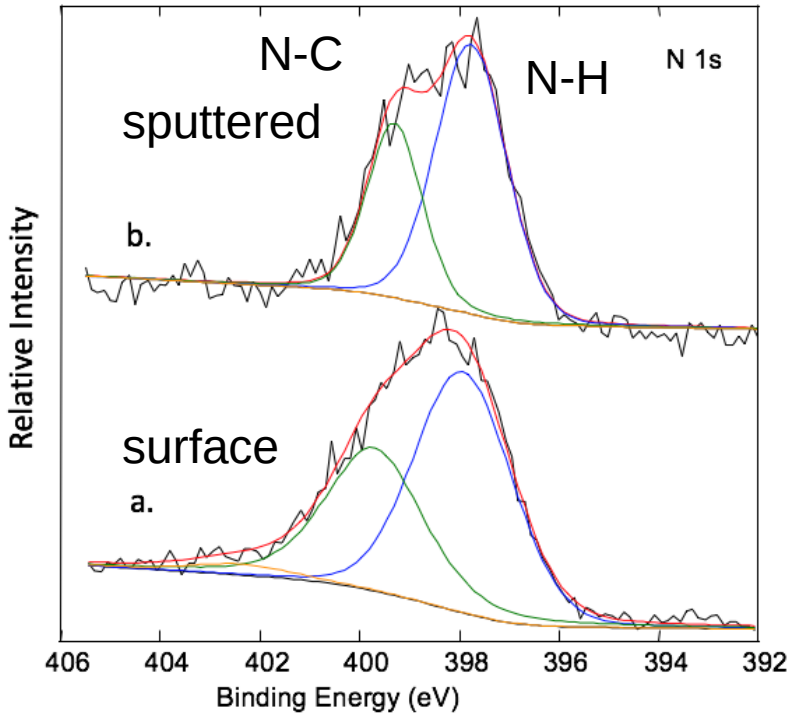
FTIR shows carbon-nitride bonding network, similar to para-*iso*-cyanogen

Characterization—XPS of Solid Residue

X-ray photoelectron spectroscopy shows functional groups
Sputtered is using atom sputtering to clean surface

SSVCT 5

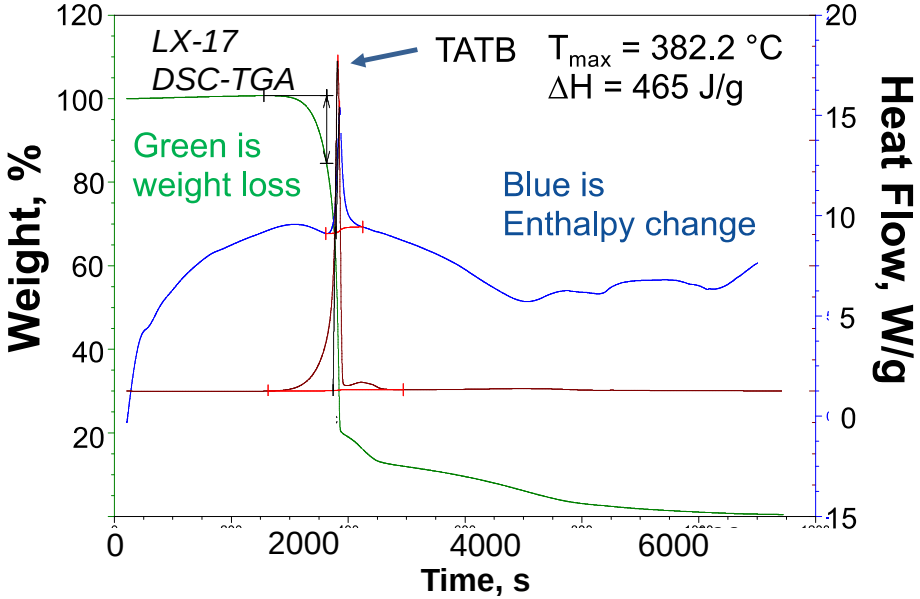


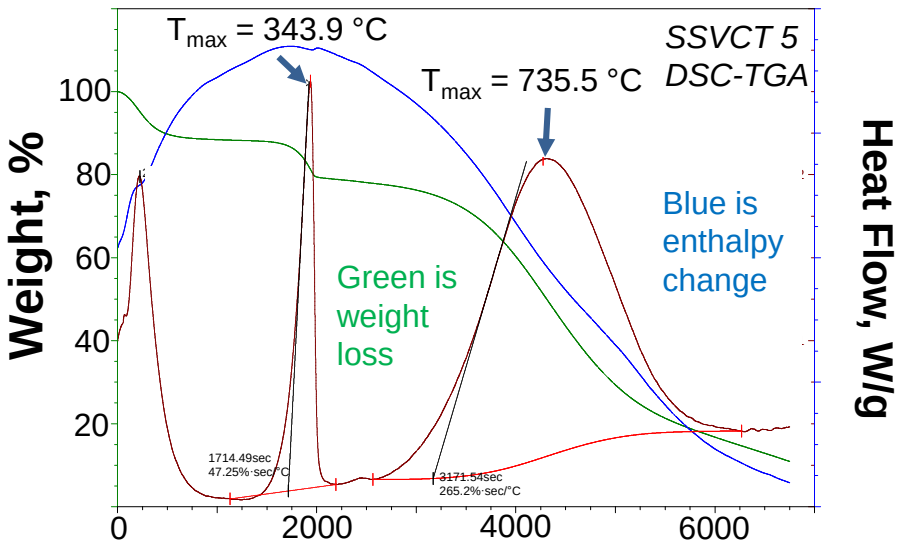


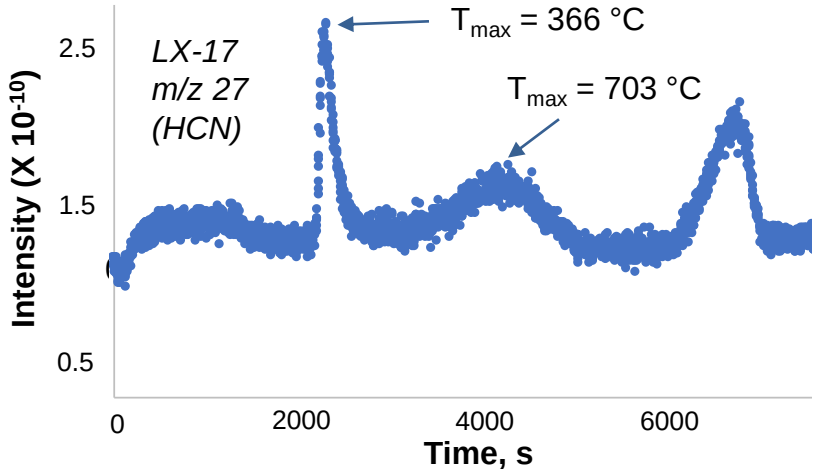
^{13}C-NMR corroborates complex C-N structures

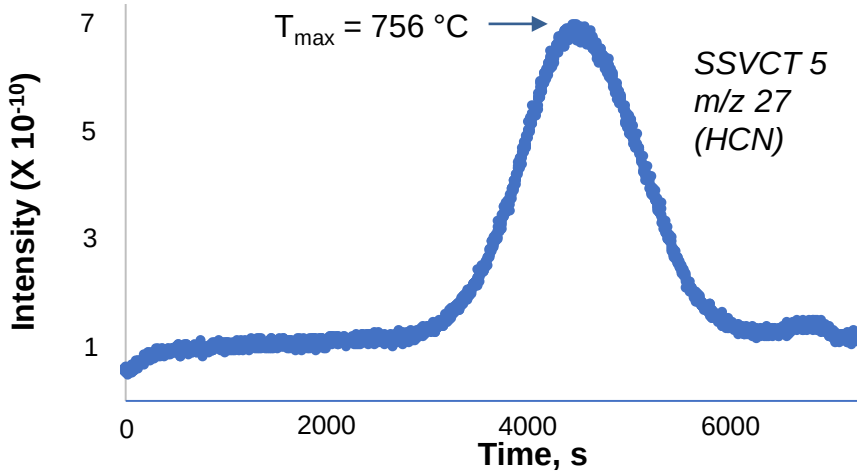
C 1s and N 1s XPS analyses indicate amorphous carbon-nitride in amorphous carbon; no indication of nitro groups

Characterization—Light Gas Analysis by SDT-MS



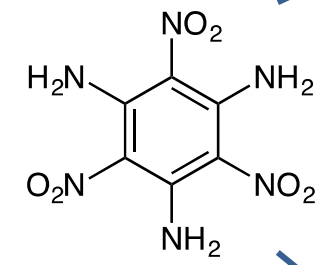




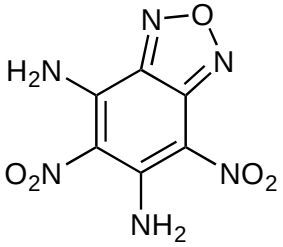


Light gas evolution follows overall enthalpy release and weight loss

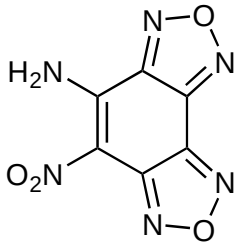
Current Visualized Decomposition Mechanisms



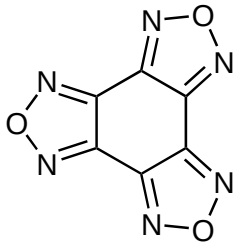
TATB $C_6N_6O_6H_6$



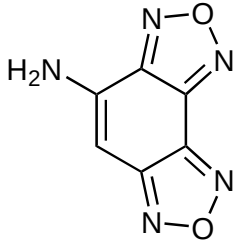
TATB-F_1 $C_6N_6O_5H_4$



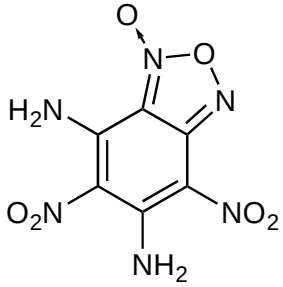
TATB-F_2 $C_6N_6O_4H_2$



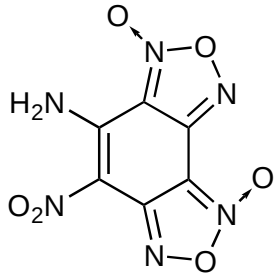
TATB-F_3 $C_6N_6O_3$



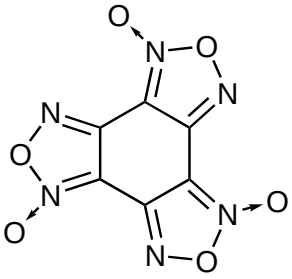
TATB-F_{2A} $C_6N_6O_2H_3$



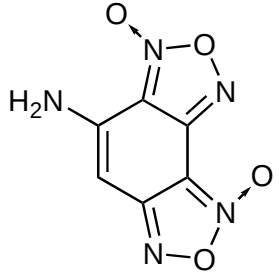
TATB-F_{x1} $C_6N_6O_6H_4$



TATB-F_{x2} $C_6N_6O_6H_2$



TATB-F_{x3} $C_6N_6O_6$



TATB-F_{x2A} $C_6N_6O_4H_3$

TATB $\xrightarrow[-H_2O]{}$ Mono-furazan $\xrightarrow[-H_2O]{}$ Di-furazan $\xrightarrow[-H_2O]{}$ Tri-furazan $\longrightarrow$ $CHNO_x$ + Amorphous C + C-N

Conclusions

- Bulk Properties do not show much change—impact (n), friction (n); spark (y), DSC (y), CRT (y);
- Molecular characterization show pathway—TATB to benzofurazans (benzofuroxans?) to C-N in amorphous C-residue
- Thermal analysis show gas evolution—light gases, for example HCN, are a product of TATB and TATB residue decomposition
- Parameters that have not been varied but need to be considered
  - Effects of different polymers in formulations
  - Particle size distributions
  - Water contents
  - Synthesis
- What does this indicate about design
- What does this indicate about response?