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Process Improvement Studies for Scale-Up of HNS at Holston Army Ammunition Plant

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BAE SYSTEMS OSI, Holston Army Ammunition Plant

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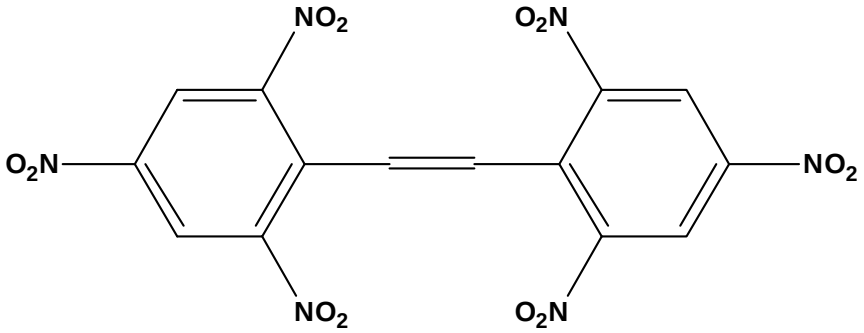
Background

- Thermally stable energetic material
- Moderate sensitivity
- Military, aviation, space applications
- TNT nucleant
- Gas and oil applications



2,2’,4,4’,6,6’-hexanitrostilbene

m.p. = 316 °C

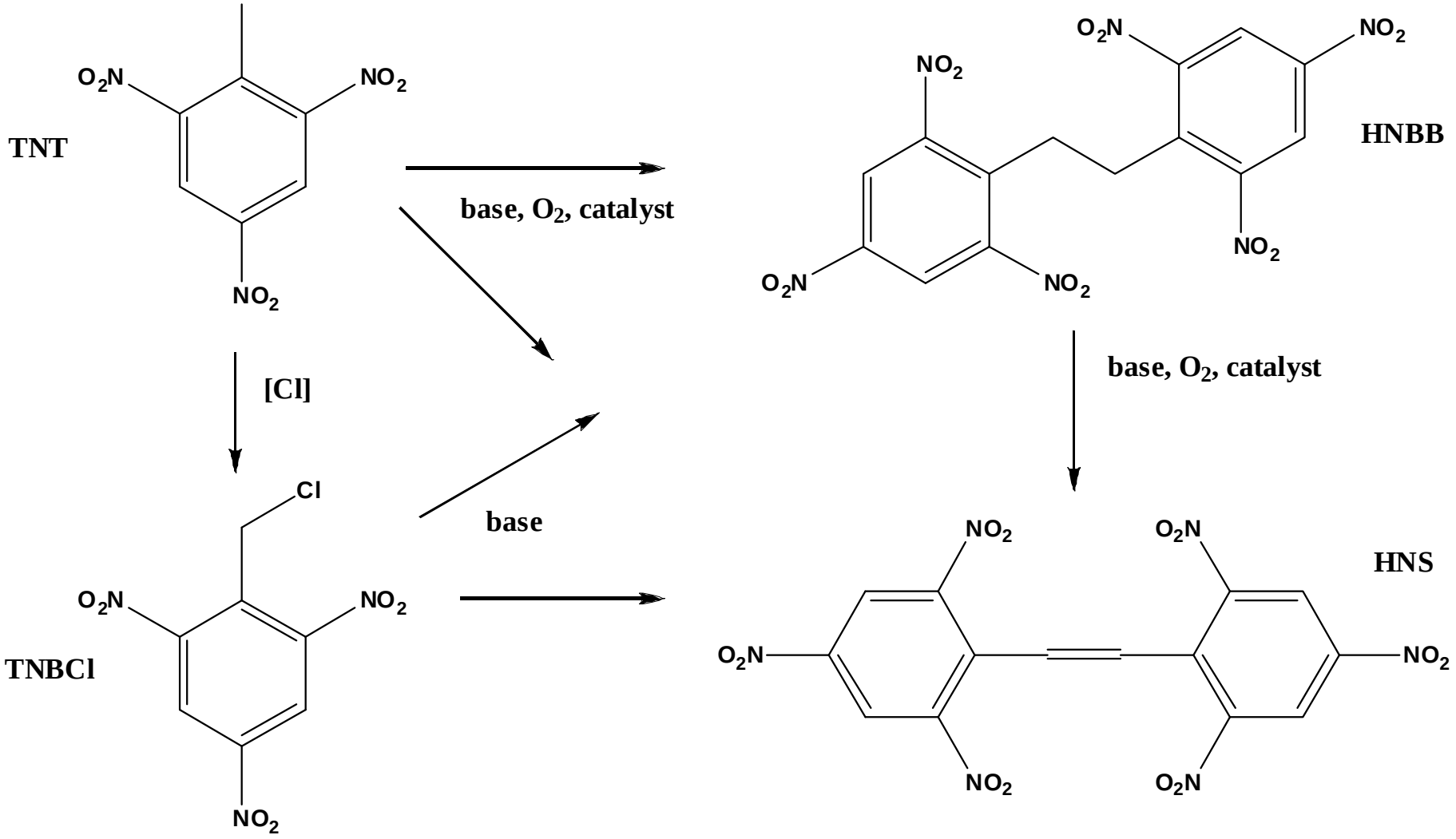
Program Objectives

- Viable Process for Manufacture of HNS at HSAAP
- Use Existing HSAAP Infrastructure
- Competitive Cost
- Meet Requirements of Oil and Gas Industries
  - Thermal Stability-Deeper Wells, Higher Temperatures
  - Formulation-amenable
    - Coated; Free Flowing; Bulk Density

Known Routes

- Shipp Process: TNT, Bleach, THF, MeOH
- Duffin & Golding: TNT or HNBB, Base, O_2, Polar Aprotic Solvent (PAS)
- Duffin & Golding: TNT, $CuCl_2$, Carboxylate Base, PAS
- Gilbert: HNBB, O_2, Copper complex, Base, PAS
- Gilbert: HNBB, Halogenating Agent, Base, PAS
- Kompolthy: TNT or HNBB, O2, Copper complex, Base, PAS

Known Routes



Challenges

- In practice, all routes (1 or 2 step) have maximum 50% HNS yield

- Shipp process: sub-ambient, requires binary solvent system (THF/MeOH)
  - THF-expensive, toxic, flammable, peroxides
  - Recovery and make-up of THF/MeOH

- Other processes require Polar Aprotic Solvents; i.e., DMSO, DMF, HMPA
  - PAS are expensive and not recoverable in-house
  - PAS not recoverable externally with explosive residue

- Need 1 or 2 step process with low complexity, robust purification

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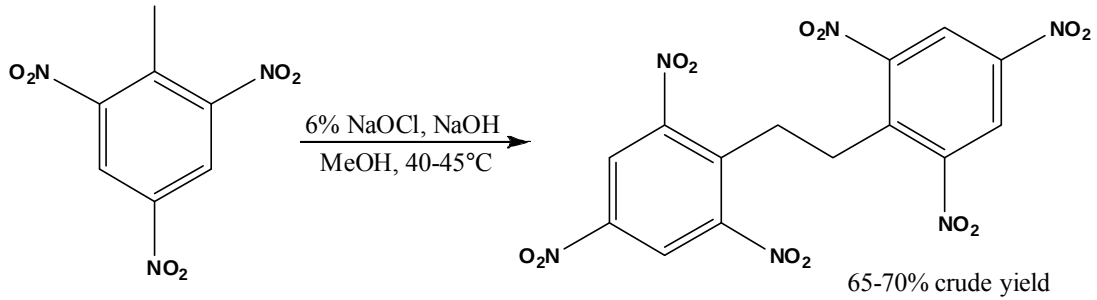
HSAAP Development Work

Two Step Process

Vary Shipp conditions to maximize HNBB

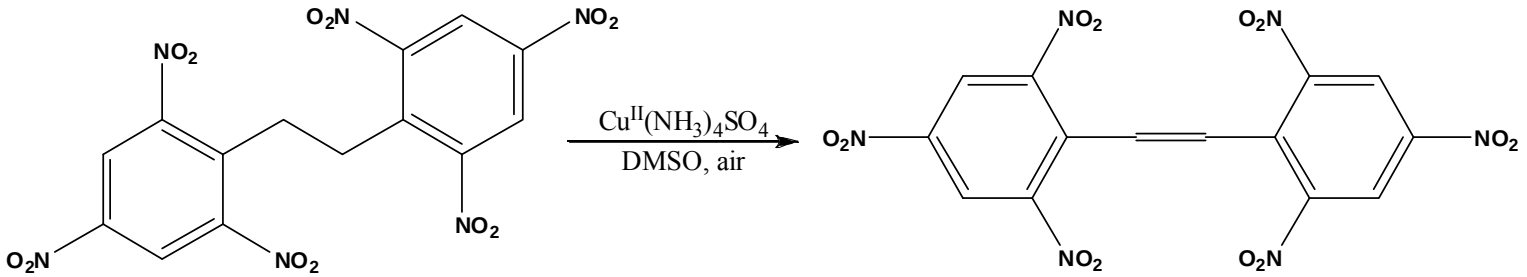
No THF, higher temperature, added base



65-70% crude yield
>90% HNBB, <7% TNT

Use Gilbert process to convert HNBB to HNS

DMSO, copper amine complex, air



ca. 90% crude yield
>90% HNS

Optimization-DOE

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TNT to HNBB

- NaOCl:base ratio-pH control
- Reaction temperature
- Maximum conversion within 30 min.
- Crude product used in next step

HNBB to HNS

- Copper catalyst mole% optimized
- Increased temperature; reaction times reduced from 24 hrs. to 3 hrs.
- Eliminate aqueous quench, reaction liquor can be reused up to 5 times
  - Add ca. 10% fresh DMSO and catalyst charge

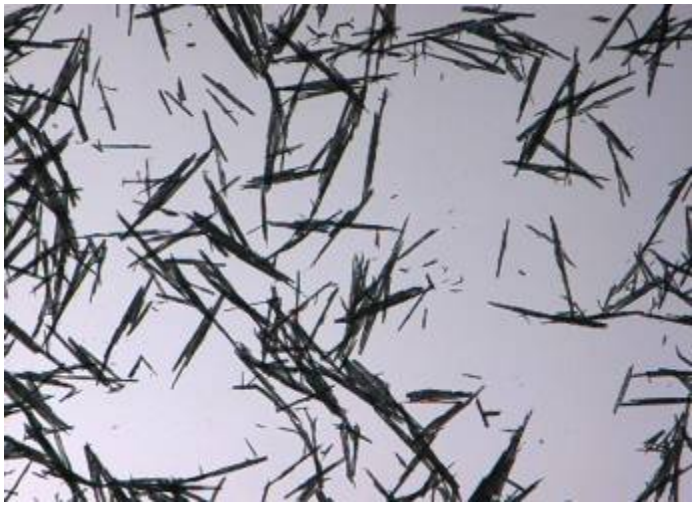
Purification-Recrystallization

- Crude HNS has dark brown color, contains 8-10% HNBB
- HNS has poor solubility in common solvents
- Recrystallization from PAS/anti-solvent adds significant cost
- Results in needle-like morphology
- Product failed Thermal Stability Testing

Material was used for coating trials assuming worst-case morphology

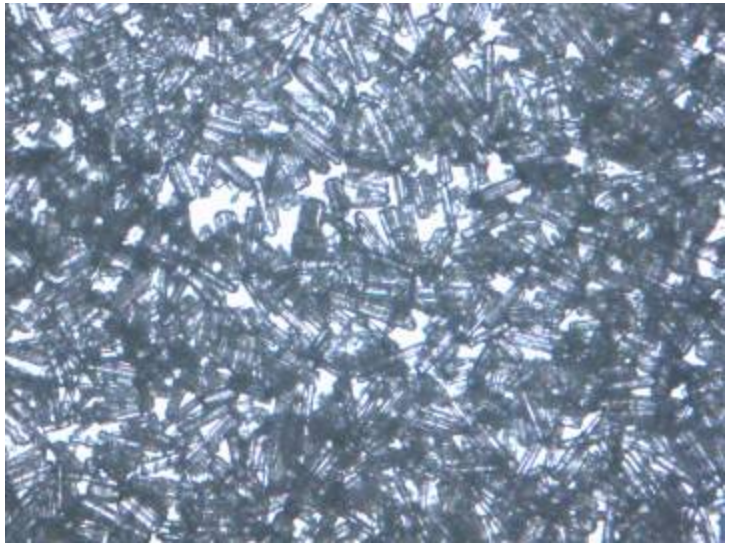
HNS Coating Trials

- Granulation/coating process for HNS with needle morphology
- Pump aqueous slurry through high shear mixer



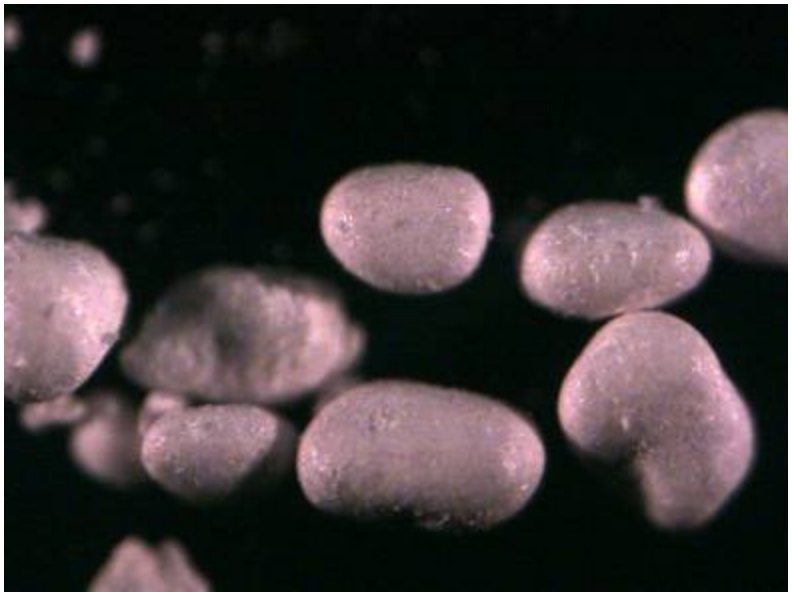
Starting Material (100x Magnification):
Length: 400 – 800 micron
Width: 12 – 20 micron

Ground HNS (400x Magnification):
Length: 150 – 300 micron
Width: 12 – 20 micron

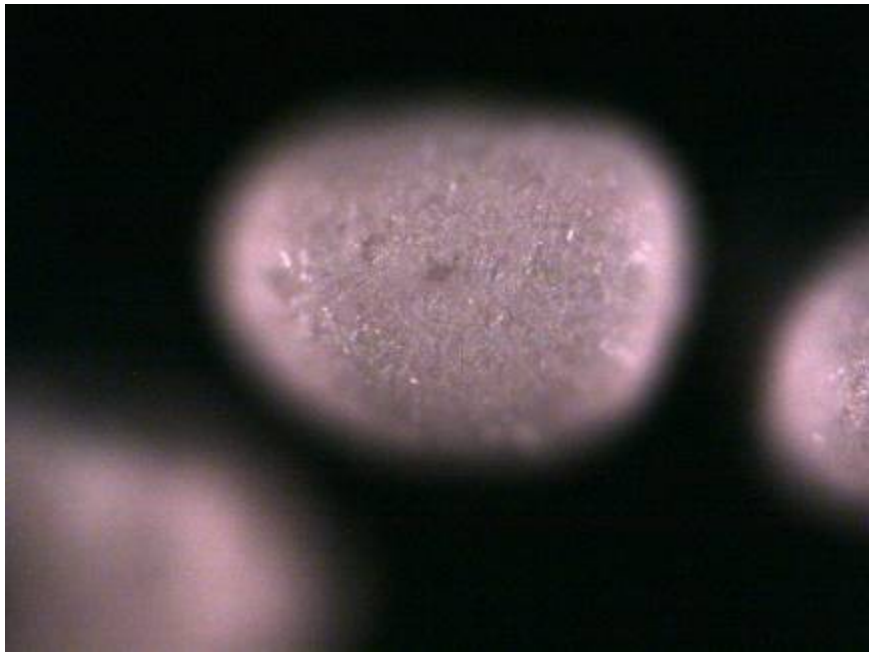


HNS Coating Trials

40x Magnification



100x Magnification



Purification-Digestion

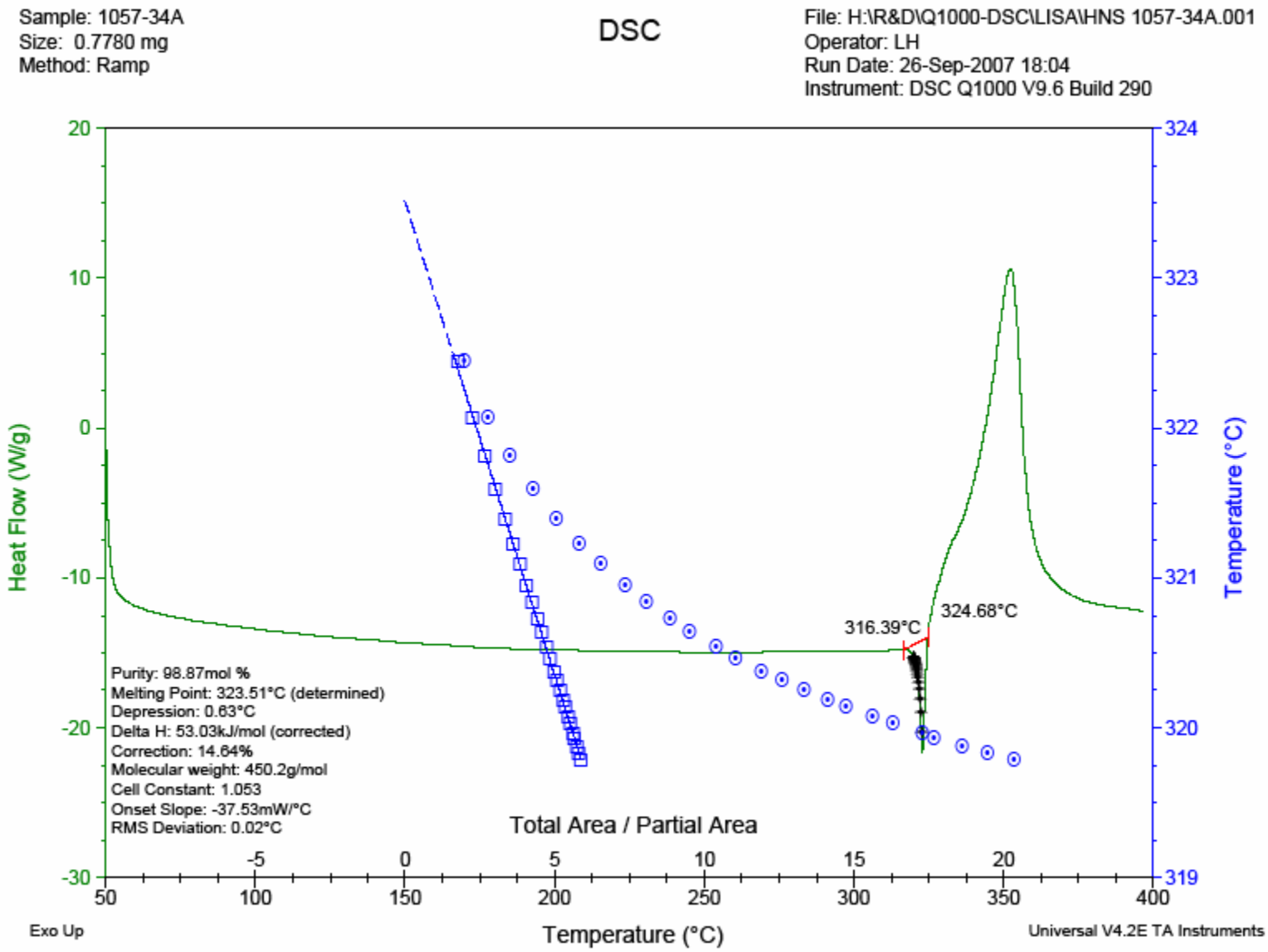
- Digestion in refluxing 55% HNO_3
- Hot water wash, acetone rinse
- >90% recovery

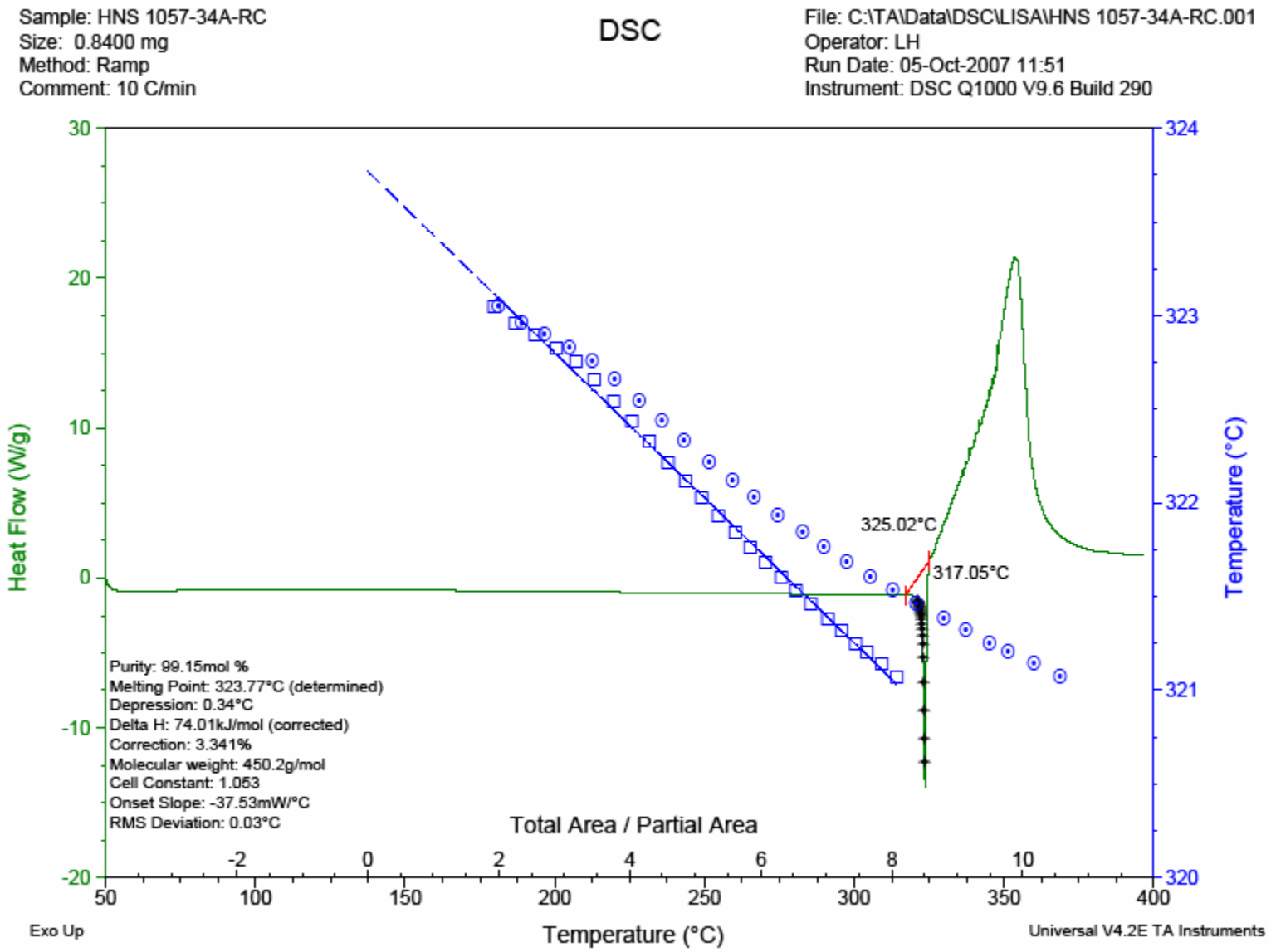
- Provides pale yellow solid, small particle size
- Passes VTS/ampule test requirement: 260 °C for 140 min.; 2.00 cc/g max.

Analytical Challenges

- ❖Primary requirement is thermal stability
- ❖HPLC method requires ultra-pure standard
- ❖Low accuracy/reproducibility with current method

- ➢DSC can quantify (not identify) level of impurities
- ➢Valid for samples of purity $\geq$ 98.5%
- ➢Attempt to correlate DSC purity with thermal stability





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Conclusions and Future Work

- Viable 2 step process for HNS identified
- Robust purification process identified
- All material processed passes thermal stability test
- Coating process which even works on undesirable morphology identified

- Continue optimization of first step towards TNT conversion
- Optimize PAS usage in second step
- Optimize coating/granulation for digested HNS
- Continue examining modifications to Shipp process

HNS manufacture at HSAAP by 2nd quarter 2008