Nitrosamines and Thermal Degradation: Exploring Solvent Degradation with Mass Spectrometry

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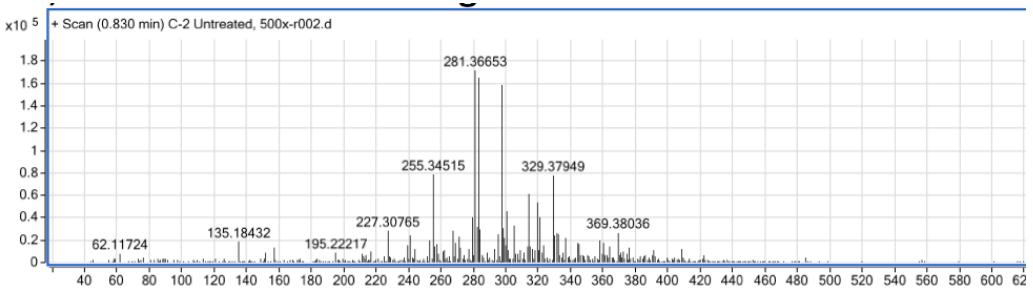
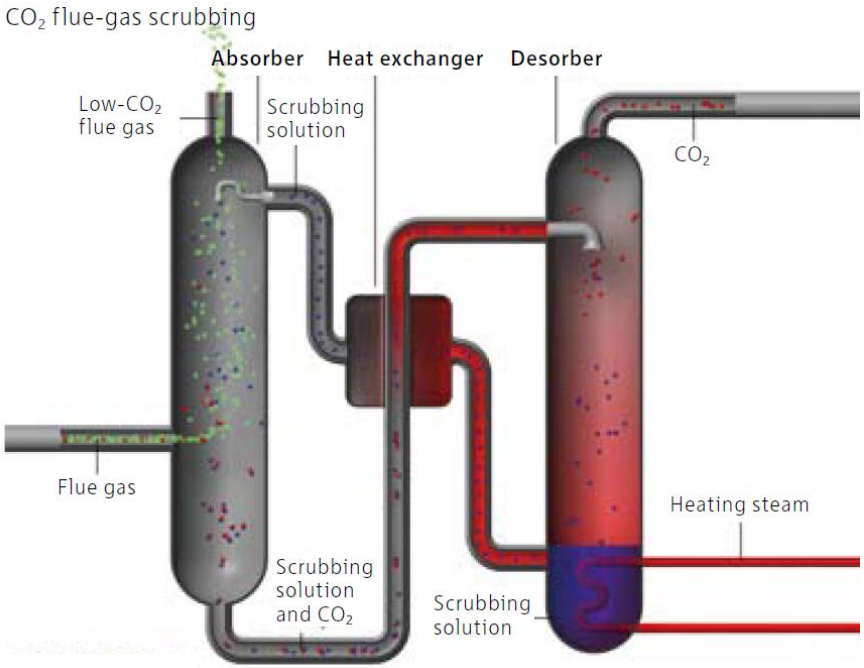
Outline

- Overview of Mass Spectrometry Methods
- Nitrosamines
  - Solid Phase Extraction (SPE)
  - Recovery and Analysis
- Thermal Degradation
  - Unknown Identification
  - Diamines
  - MEA
- Conclusion





MS Instrumentation

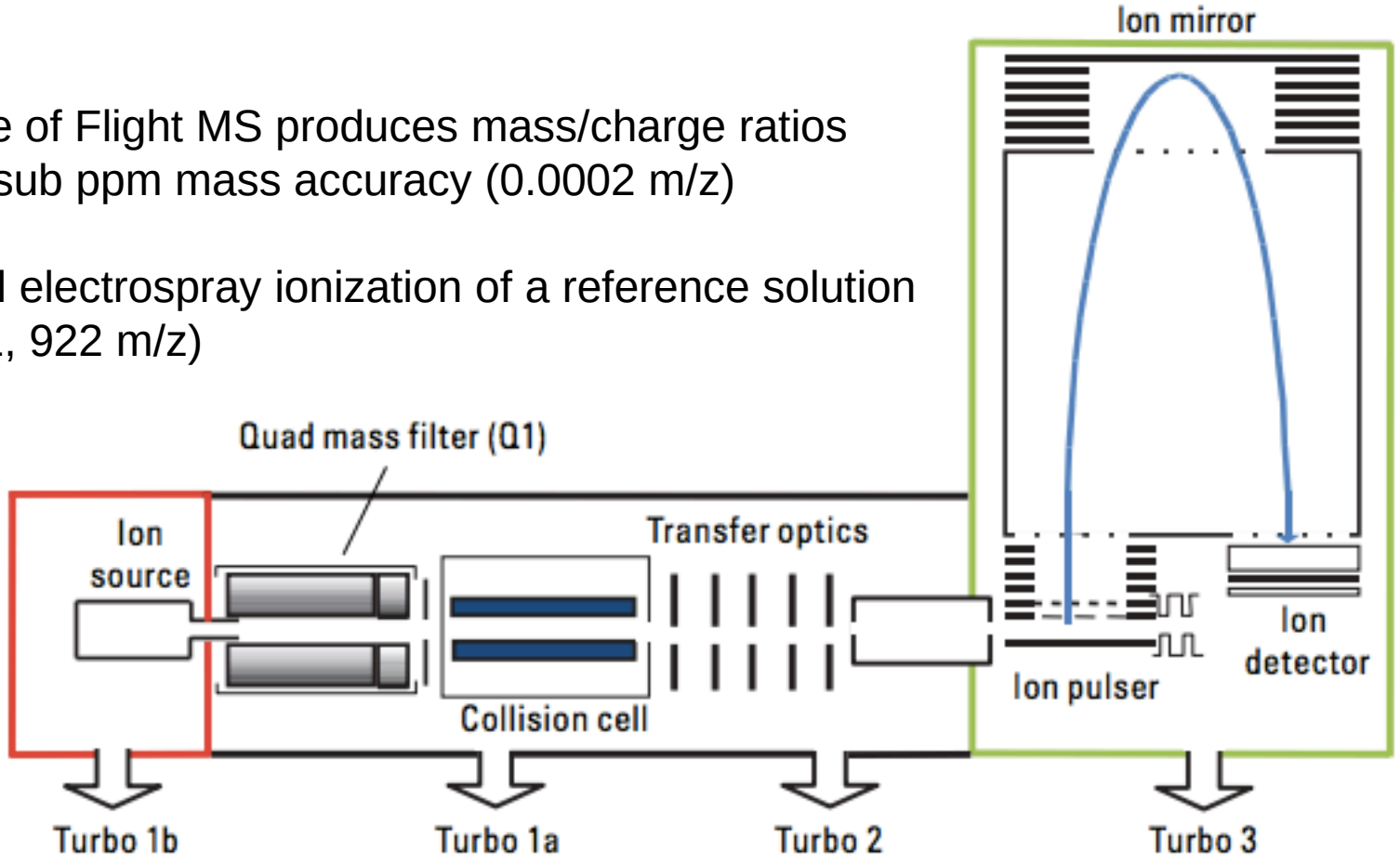
GC-MS
Good for Volatile Compounds
Nitrosamines, Aldehydes

HPLC-TOF-MS
Good for Aqueous Samples
Thermal, Oxidative
Nitrosamines and Aldehydes

Time of Flight Mass Spectrometry

•Time of Flight MS produces mass/charge ratios with sub ppm mass accuracy (0.0002 m/z)

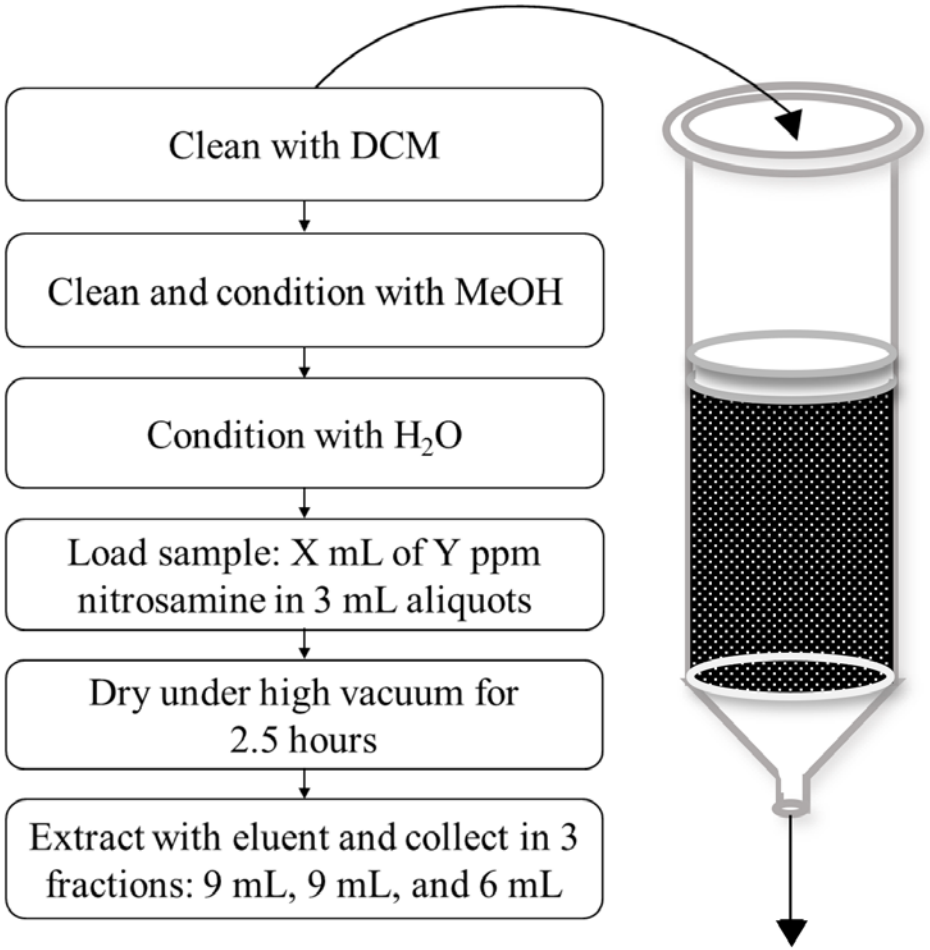
•Dual electrospray ionization of a reference solution
•(121, 922 m/z)



Nitrosamine Analysis

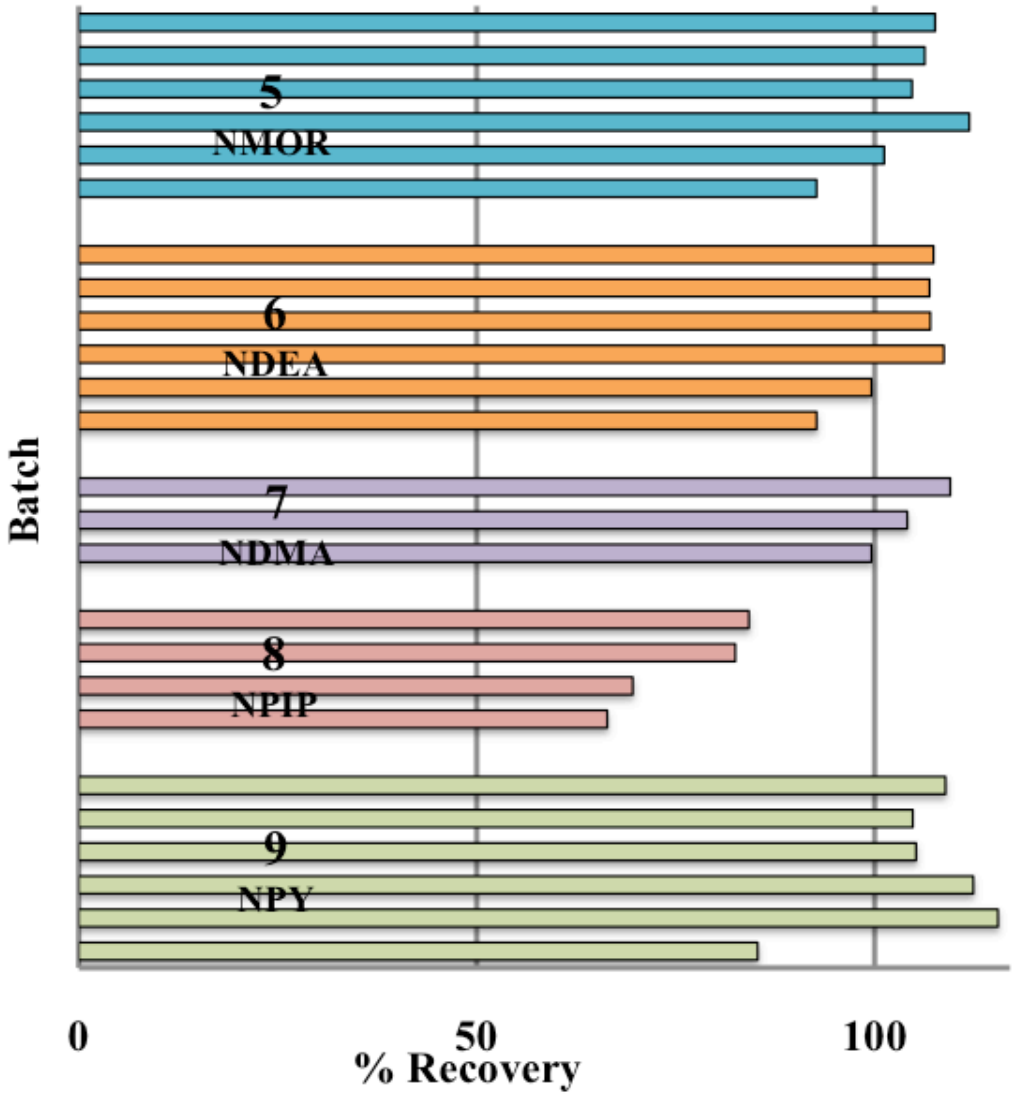
- Two samples types
  1. Liquid
     - Nitrosamines are collected in 30 wt% MEA.
  2. Gas
     - Nitrosamines are collected in 0.1% sulfamic acid.
     - SASK Power is using a similar methodology.

Solid Phase Extraction (SPE)



- Activated carbon cartridges with specific affinity for nitrosamines (EPA 521)
- Separate the nitrosamines from the concentrated amine matrix
- Sample pre-concentration leading to lower limits of detection

Percent Recovery of solid phase extracted nitrosamines - MEA



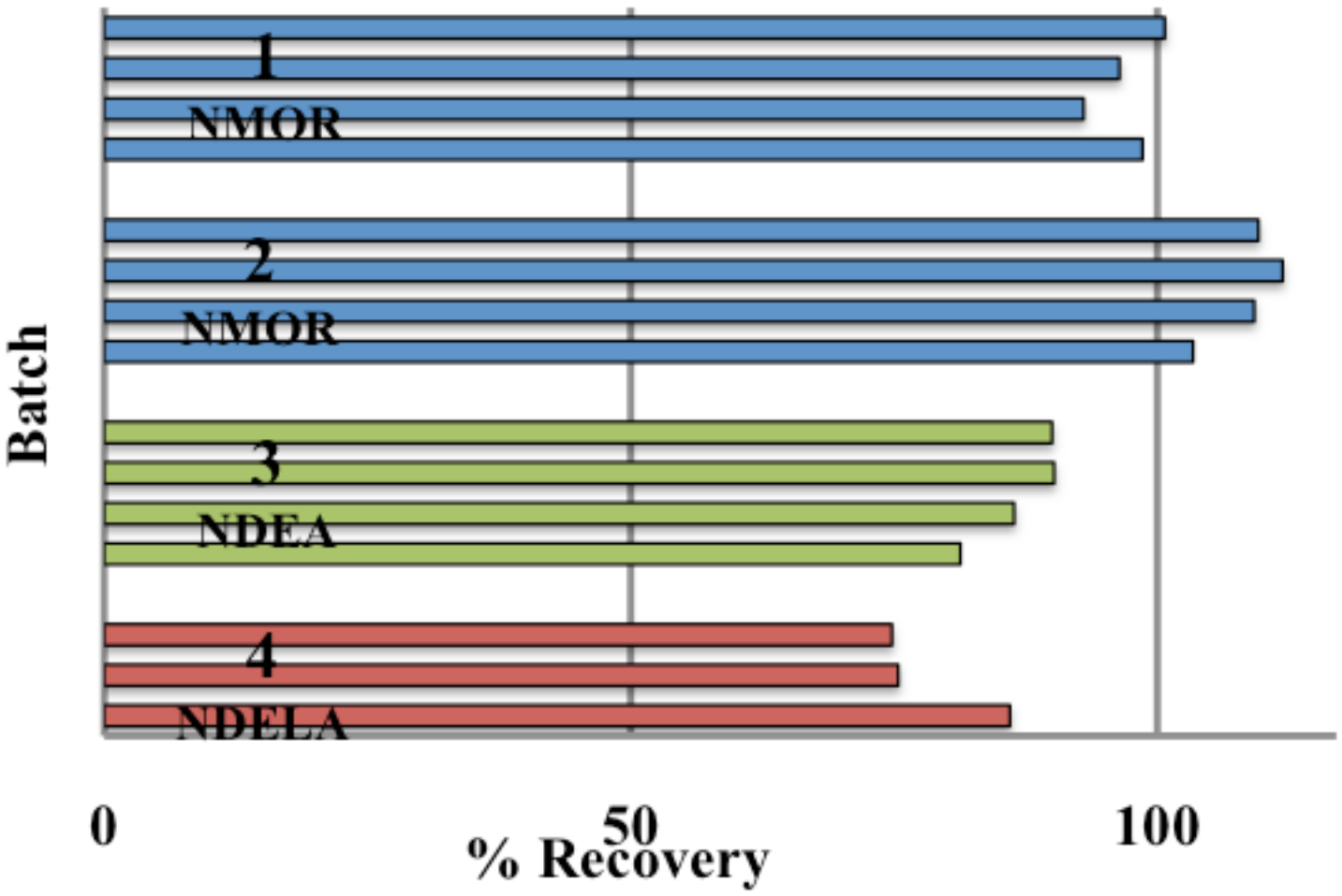
- 30% MEA (C/N=0.4) spiked with the nitrosamines
- Eluent: DCM
- Good reproducible recovery with DCM over a range of different nitrosamine concentrations

Application to a Mixture of Different Nitrosamines

Table 1. Initial and final composition and volume of 0.1% sulfamic acid Batch solutions

Batch	Nitrosamine	Extraction solvent	Initial sample volume (mL)	Final sample volume (mL)	Concentration (ug)	ΔV
5	NMOR	DCM	20 mL	~17.5 mL	10-200	1.14x concentration
6	NDEA	DCM	20 mL	~17.5 mL	10-200	1.14x concentration
7	NDMA	DCM	20 mL	~12.5 mL	5-50	1.6x concentration
8	NPIP	DCM	20 mL	~12.5 mL	5-100	1.6x concentration
9	NPY	DCM	20 mL	~17.5 mL	10-200	1.14x concentration

Percent Recovery of solid phase extracted nitrosamines - Sulfamic



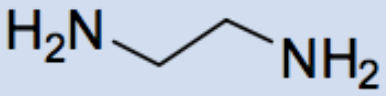
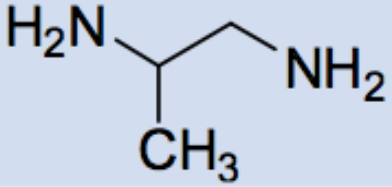
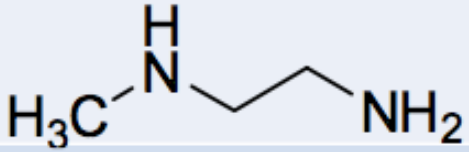
- 0.1% Sulfamic acid spiked with the nitrosamines
- Eluent: DCM or Acetone
- Good reproducible recovery with DCM over a range of different nitrosamine concentrations

Application to a Mixture of Different Nitrosamines

Table 2. Initial and final composition and volume of benchmark 30 wt% MEA Batch solutions

Batch	Nitrosamine	Extraction solvent	Initial sample volume (mL)	Final sample volume (mL)	Concentration (ug)	ΔV
1	NMOR	DCM	100 mL	~17 mL	10-100	5.9x concentration
2	NMOR	DCM	40 mL	~16.5 mL	20-400	2.4x concentration
3	NDEA	DCM	40 mL	~16.5 mL	20-400	2.4x concentration
4	NDELA	Acetone	20 mL	~16.5 mL	200	2.4x concentration

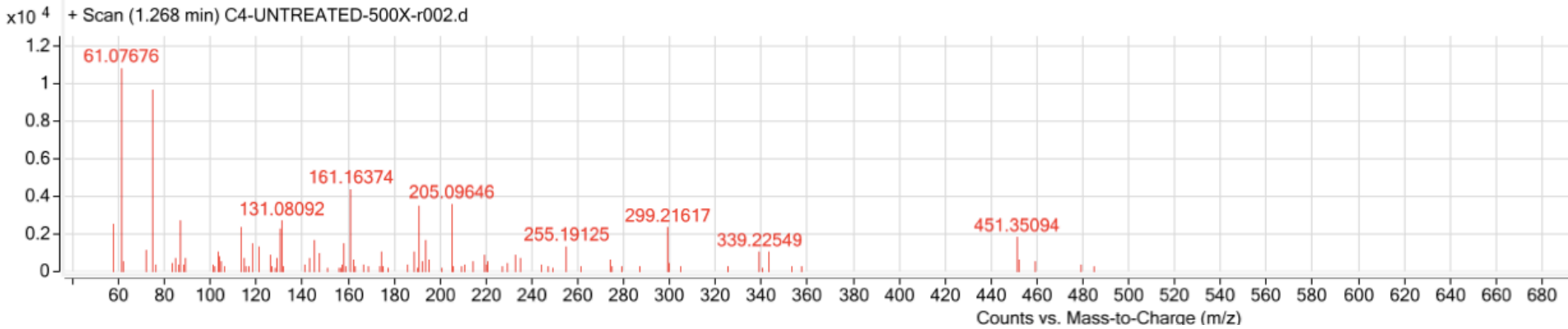
Thermal Degradation of Diamines

Diamines
Ethylenediamine (EDA) 
1,3-Diaminopropane (1,3-DAP) 
1,2-Diaminopropane (1,2-DAP) 
N-methylethylenediamine (MEDA) 

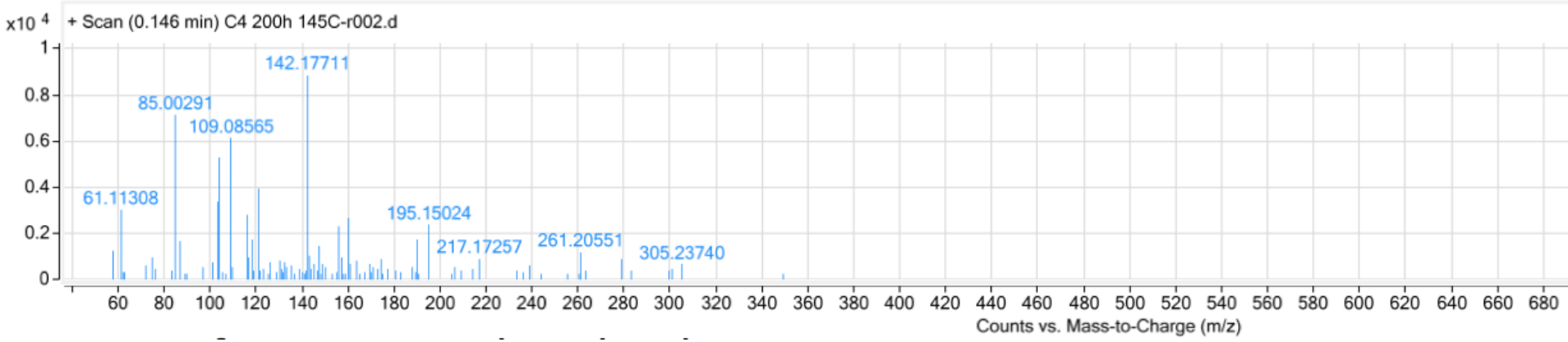
- Loaded amine solution (2.5M, C/N 0.4)
- 125°C, 135°C, 145°C
- 100-200 hours heating
- Un-heated solution as a reference blank

Product Identification - EDA

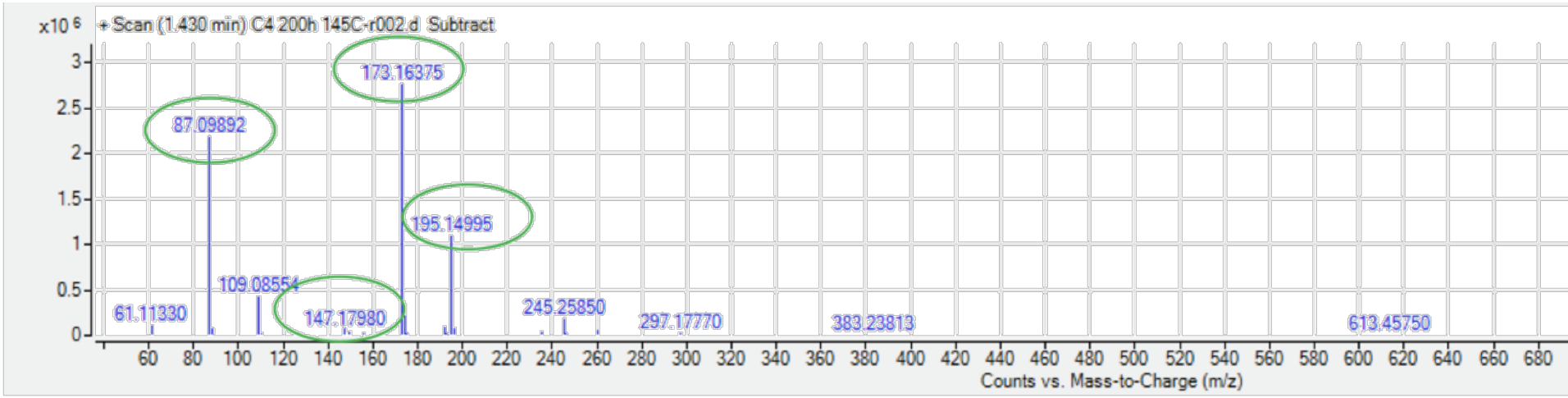
A. EDA TIC before heating



B. EDA TIC after 145C, 200h



Product Identification - EDA

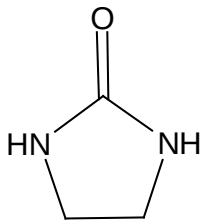


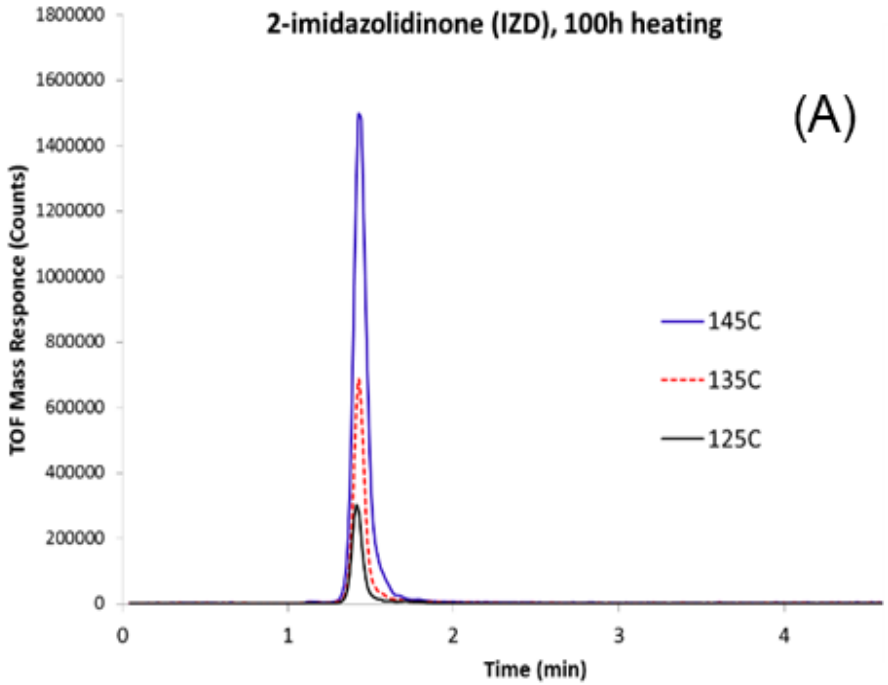
Actual [M+H]+ (m/z)	Formula Generated	Calculated $[M+H]^+$ (m/z)
87.09892	$C_3H_6N_2O$	87.0553
147.17980	$C_5H_{14}N_4O$	147.124
173.16375	$C_7H_{16}N_4O$	173.13969
195.14995	Poor molecular match	195.1499

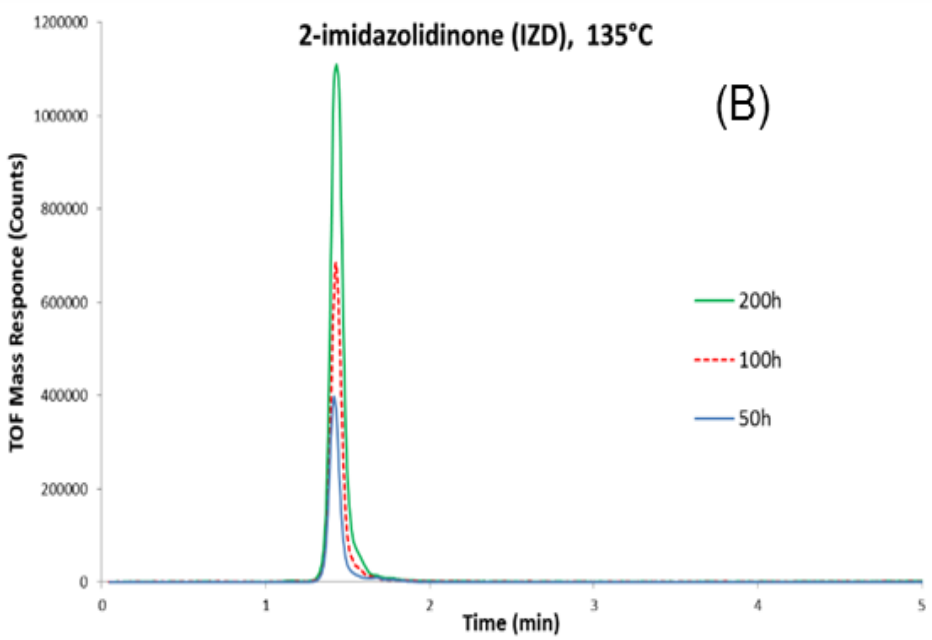
Product Identification - EDA

Extracted Ion Chromatograms (EIC) from MS data

$C_3H_6N_2O$	87.0553 m/z



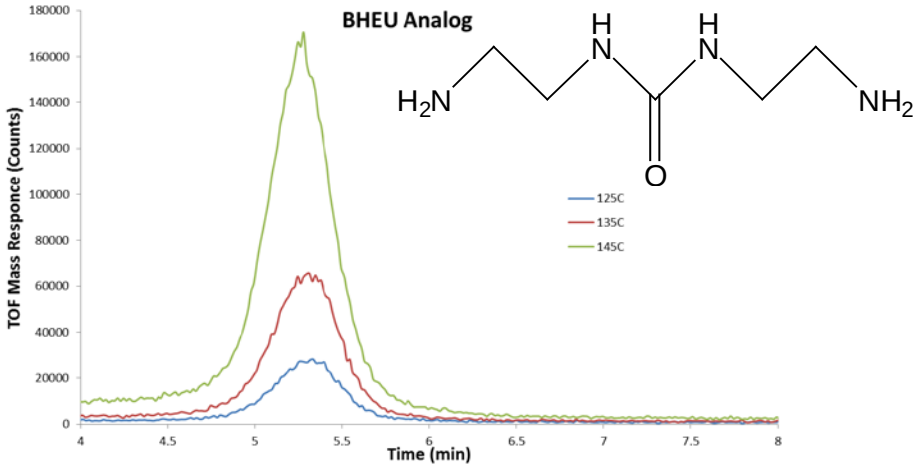


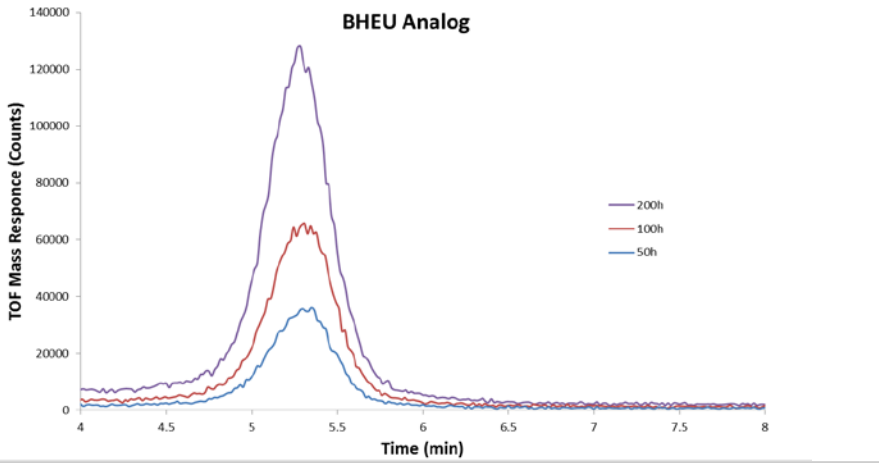


Product Identification - EDA

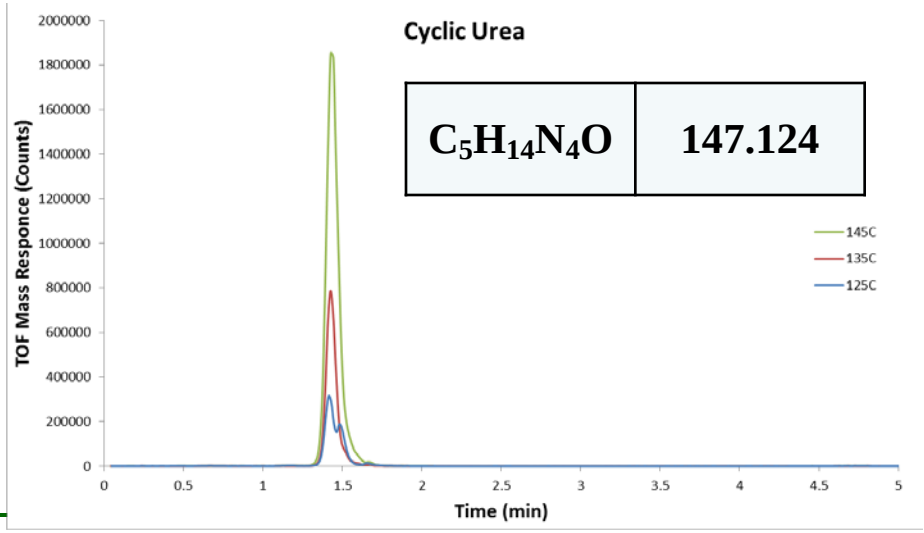
Extracted Ion Chromatograms (EIC) from MS data

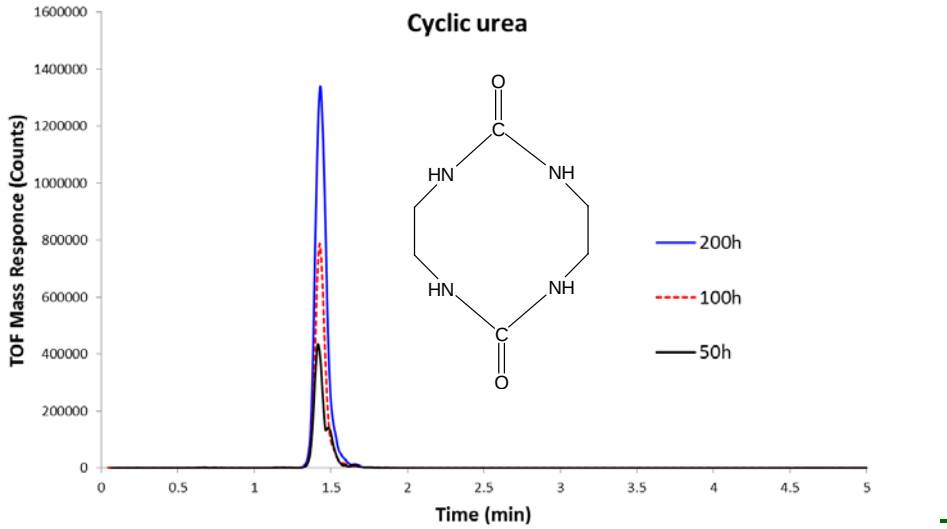
$C_7H_{16}N_4O$	173.13969





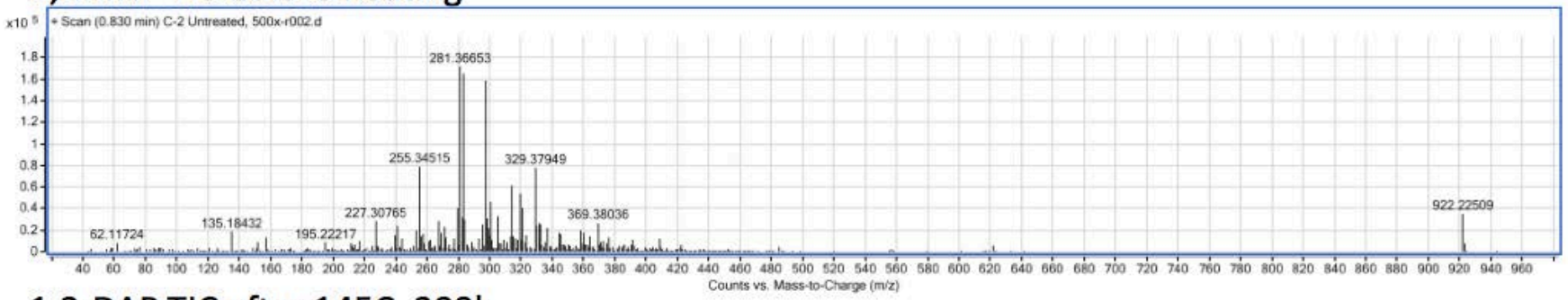
$C_5H_{14}N_4O$	147.124



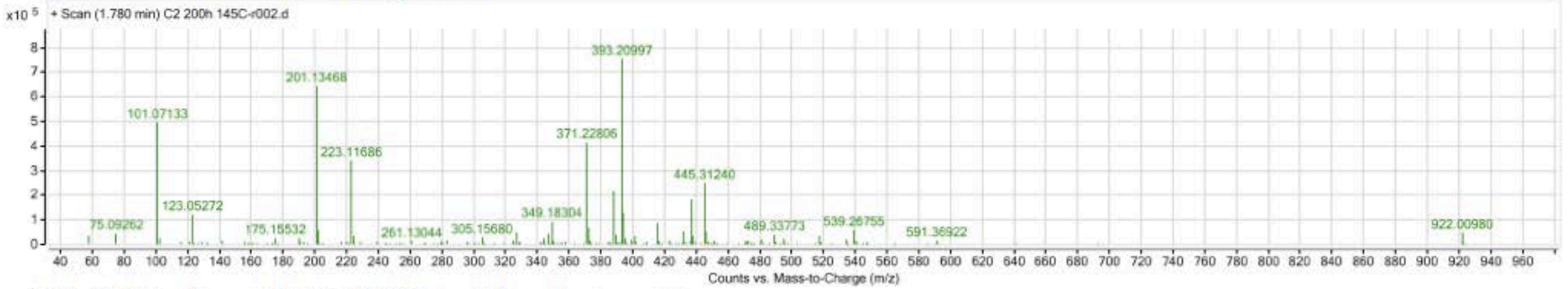


Product Identification – 1,2-DAP

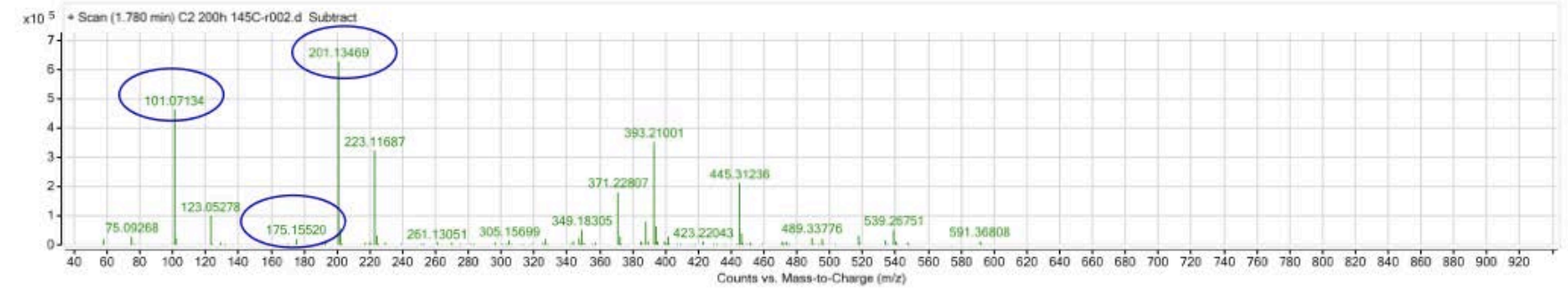
1,2-DAP TIC before heating



1,2-DAP TIC after 145C, 200h



1,2-DAP after 145C, 200h with substraction



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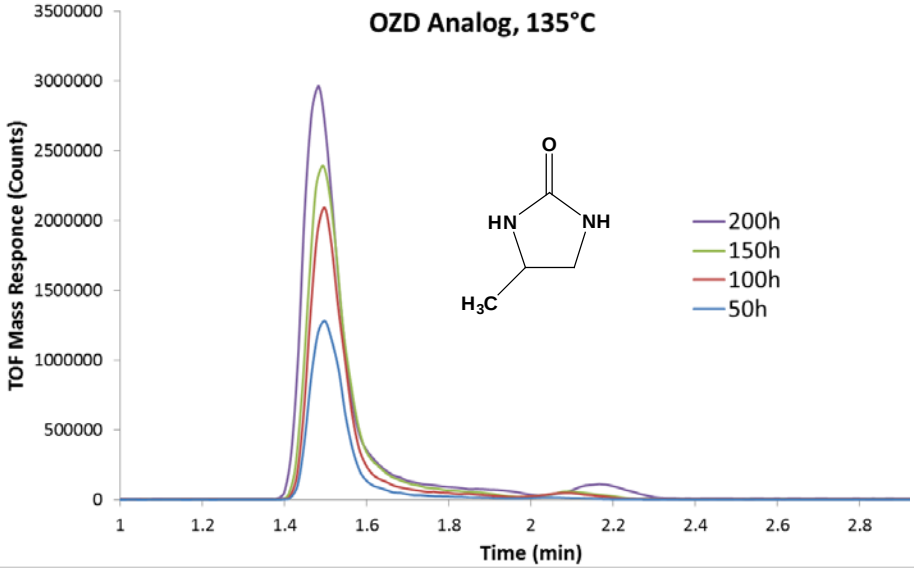
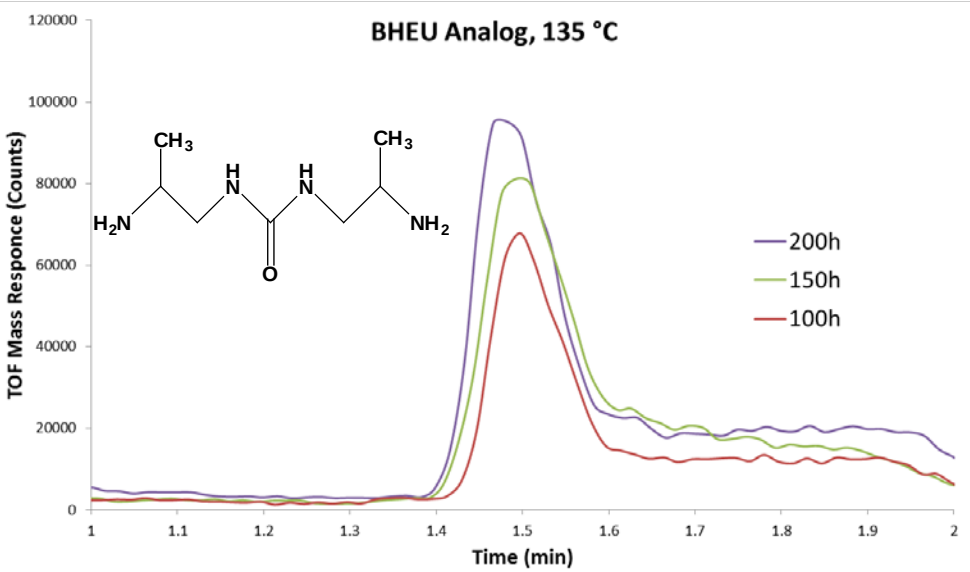
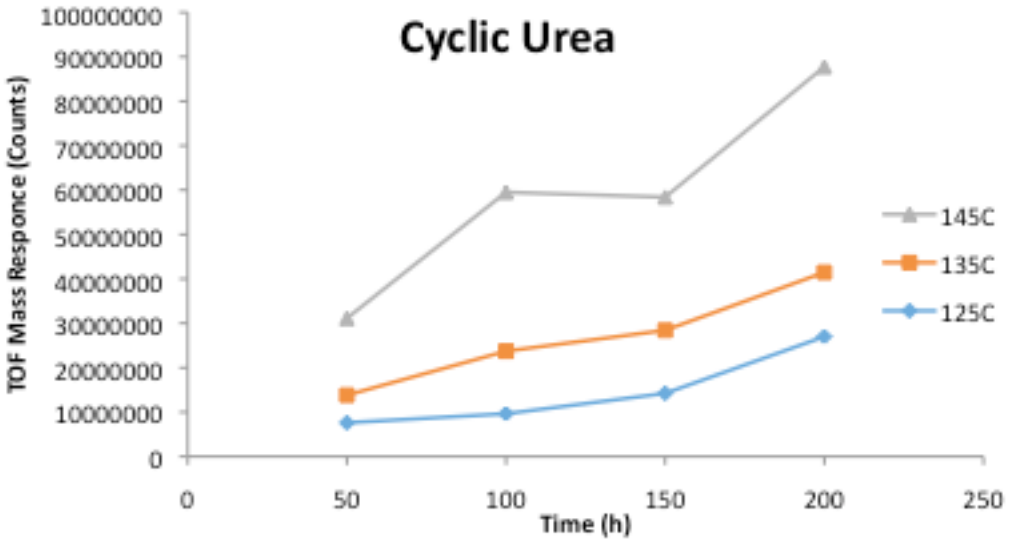
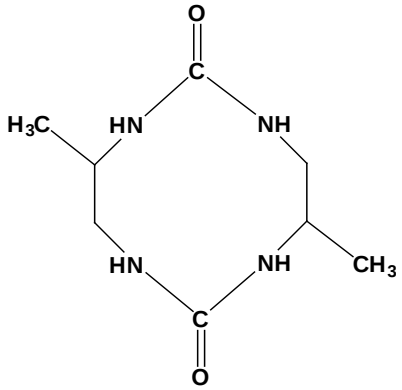


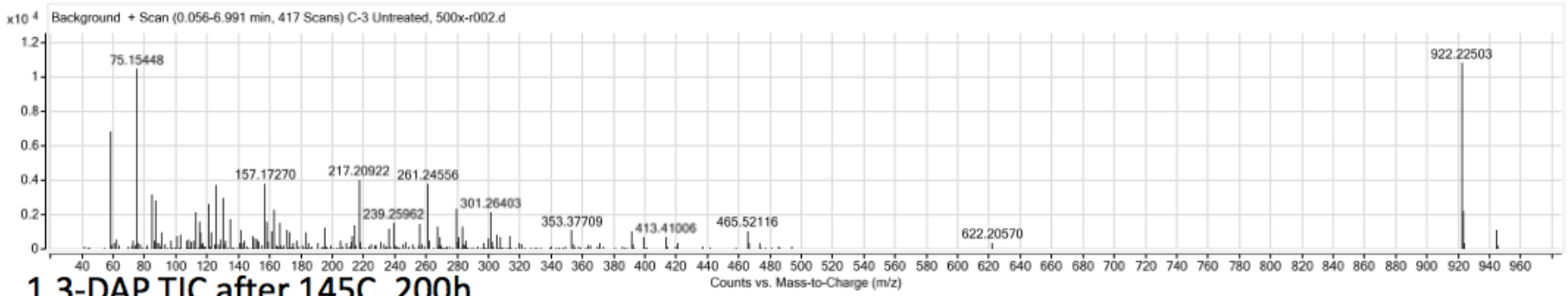




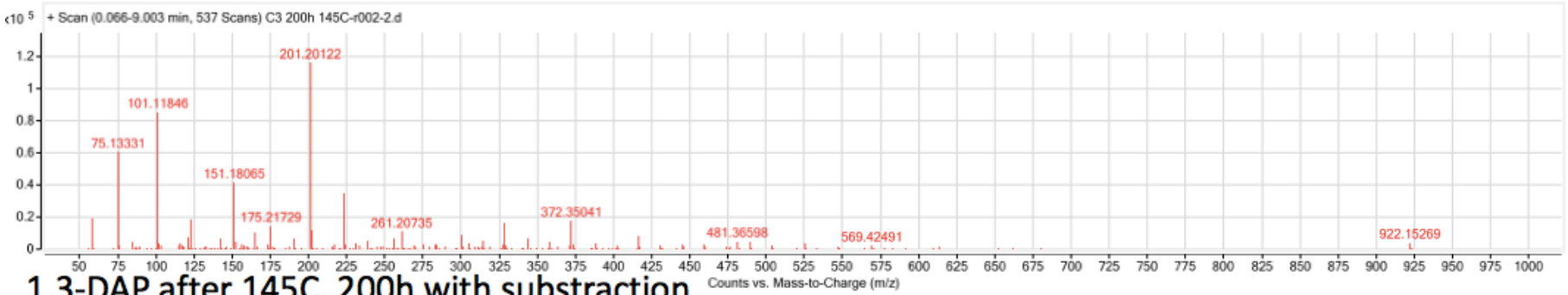


Thermal Contribution – 1,3-DAP

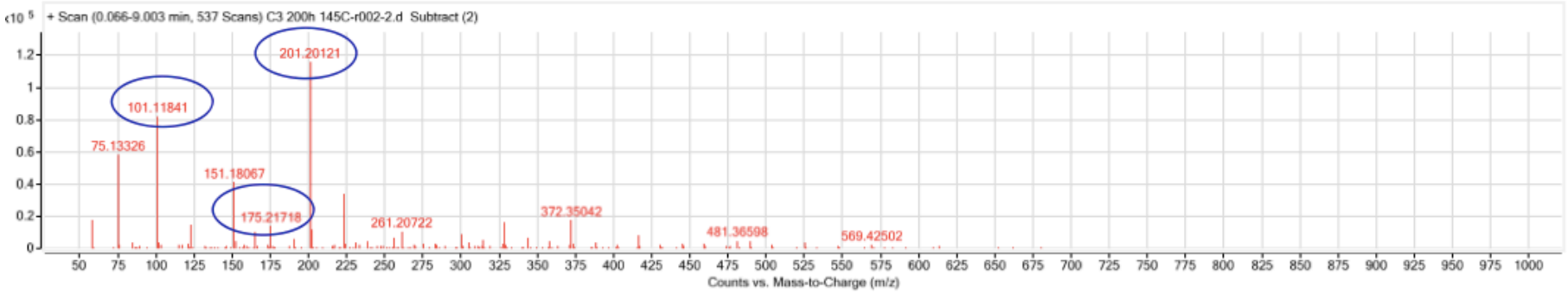
1,3-DAP TIC before heating



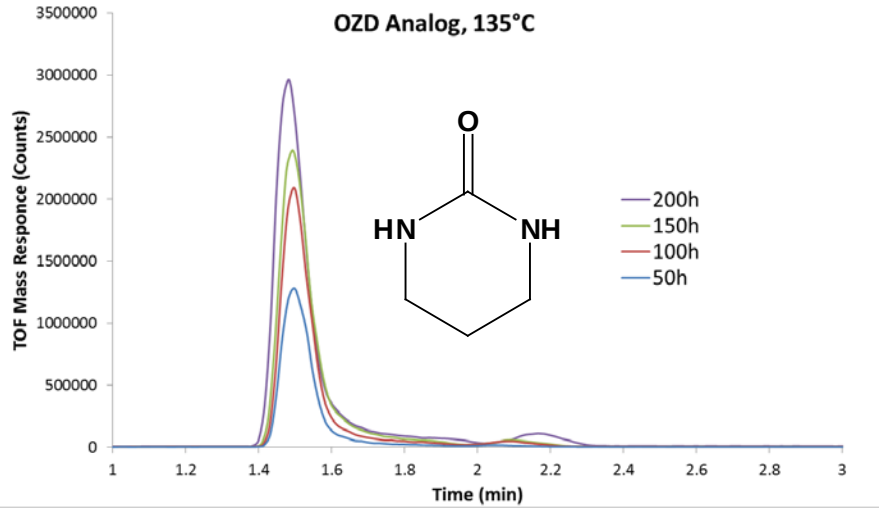
1,3-DAP TIC after 145C, 200h

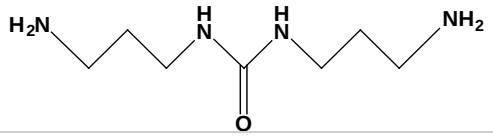


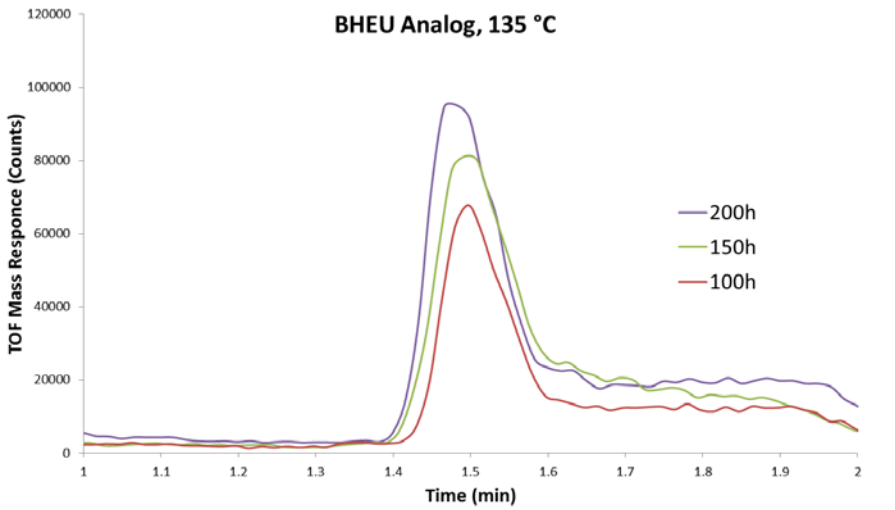
1,3-DAP after 145C, 200h with substraction

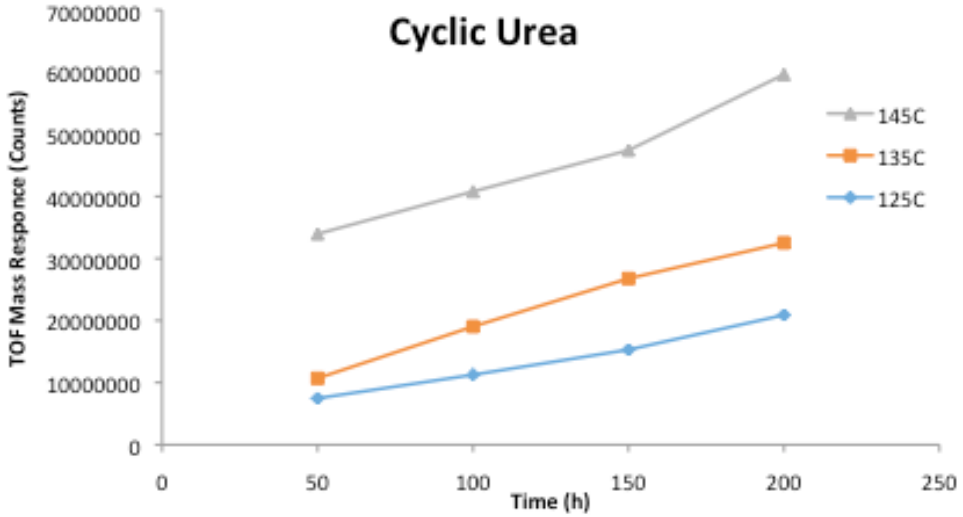


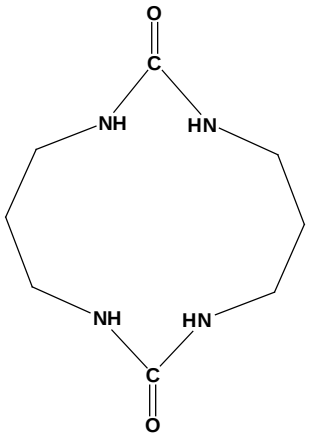
Product Identification – 1,3-DAP





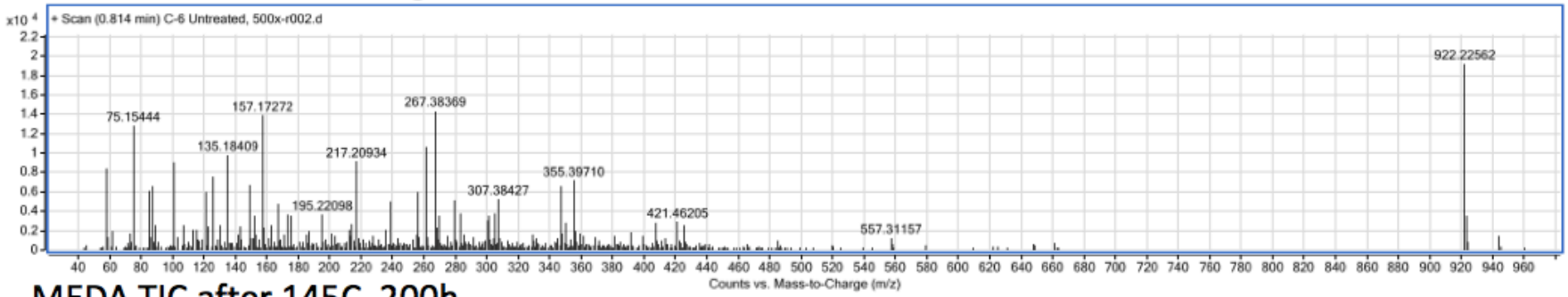




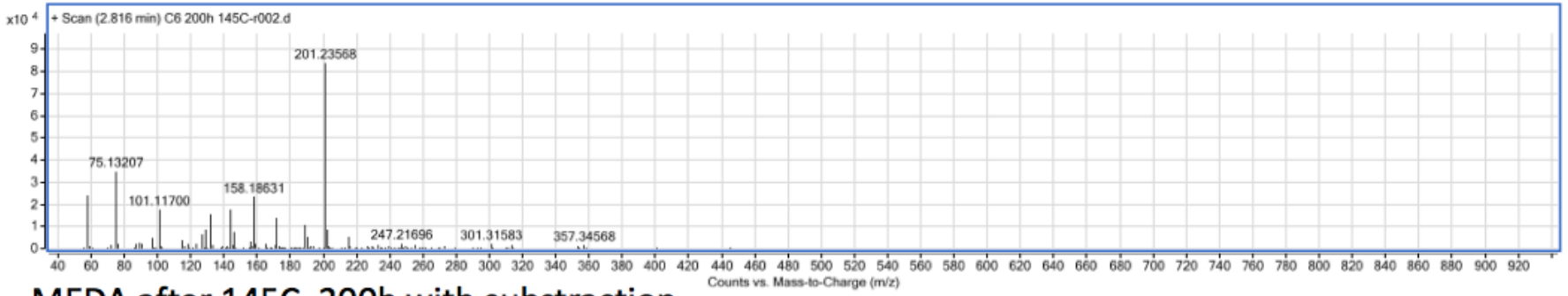


Product Identification – MEDA

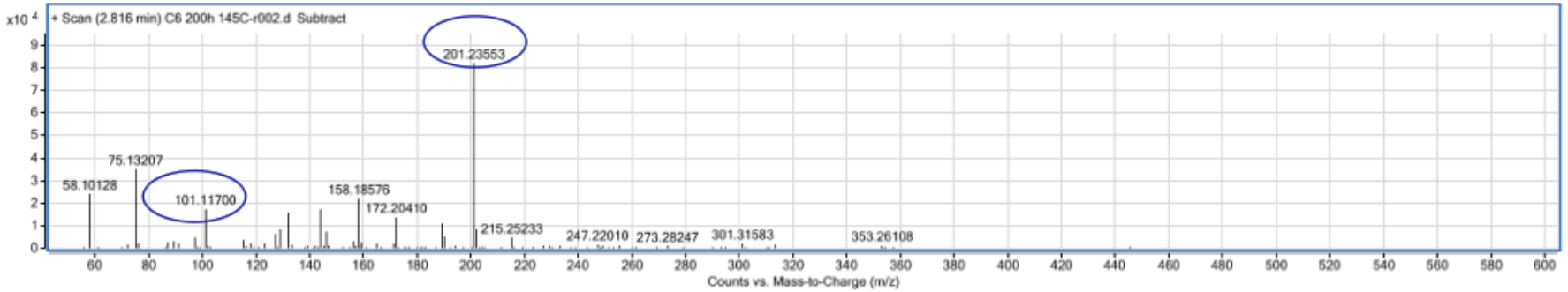
MEDA TIC before heating



MEDA TIC after 145C, 200h



MEDA after 145C, 200h with substraction



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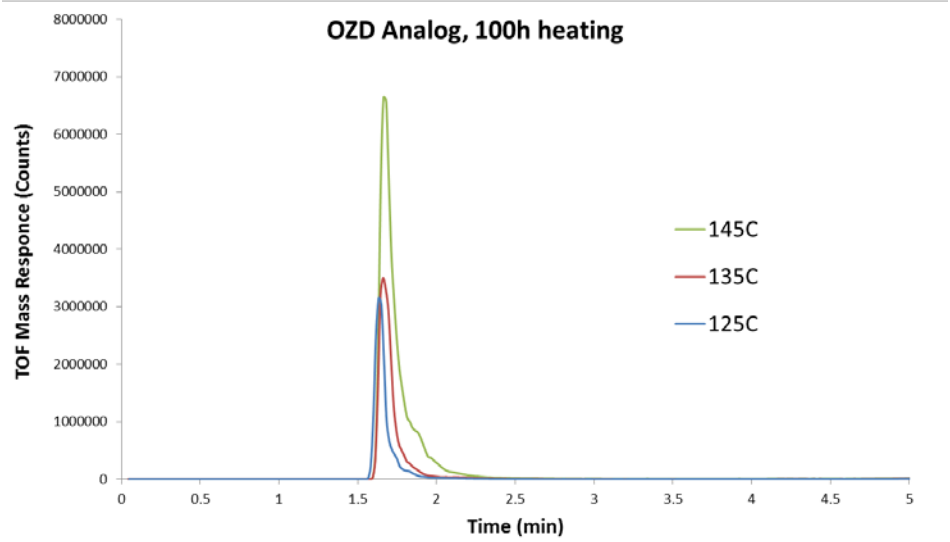

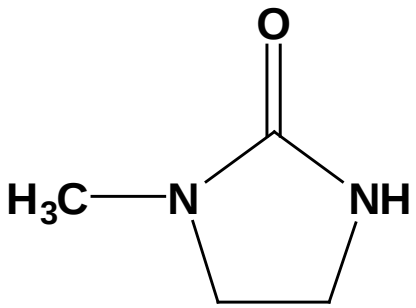

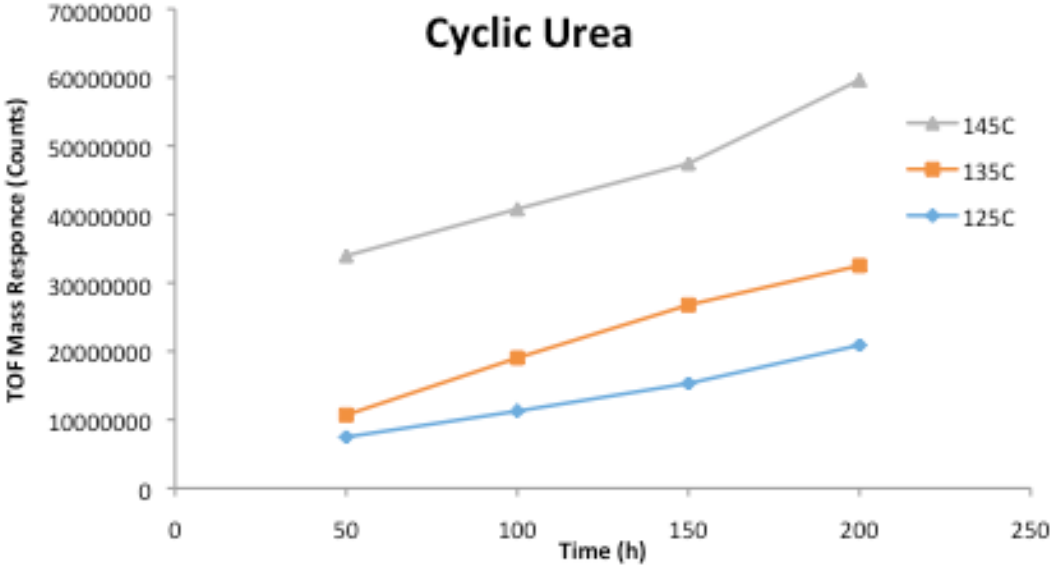

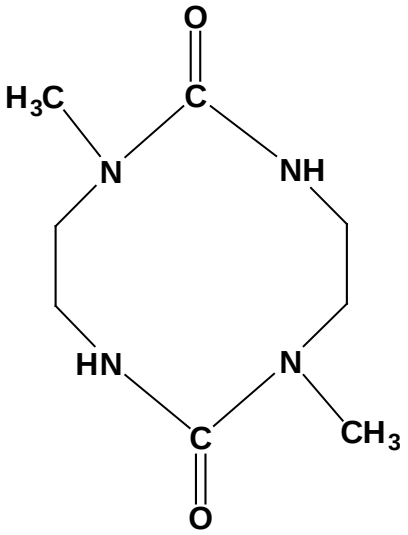

Acknowledgement

Carbon Management Research Group Members,

PPL companies

A unit of American Electric Power

and US National Energy Technology Laboratory (NETL)

[Analytical method development support for this work provided under DE-FE 0007395]