Expanding the PAH Profile of Partially Combusted Microplastics Collected from the Marine Environment

Douglas Stevens[1], Bryan James[2], Christopher Reddy[3], Robert Nelson[3], Frank Dorman[1,2]

[1]Waters Corporation, Milford, MA
[2]Northeastern University; Boston, MA
[3]Woods Hole Oceanographic Institution; Woods Hole, MA
[4]Dartmouth College, Hanover, NH

X-Press Pearl Microplastics Spill

Fire and oil led to complex mixtures of PAHs on burnt and unburnt plastic during the M/V X-Press Pearl disaster

James, Bryan D., Christopher M. Reddy, Mark E. Hahn, Robert K. Nelson, Asha de Vos, Lihini I. Aluwihare, Terry L. Wade, Anthony H. Knap, and Gopal Bera. *ACS Environmental Au* (2023)

"The maritime disaster underscores **pyroplastic** as a type of plastic pollution that has yet to be fully explored, despite the pervasiveness of intentional and unintentional burning of plastic globally."

Pyroplastic MPs: Global Emission Sources

Waters™

- **Global waste plastic > 6.3 billion tons (1950-2015)**
  - Pilapitiya, "The world of plastic waste: A review." *Cleaner Materials* (2024)

- **Incineration**
  - 14% annual global plastic waste
  - Tan, "Reimagining plastics waste as energy solutions: challenges and opportunities." *npj Materials Sustainability* (2024)

- **Open Burn**
  - >20Mt annually in top 4 regions S Asia, SE Asia, SubS Africa, LA+Carib
  - Cottom, "A local-to-global emissions inventory of macroplastic pollution." *Nature* (2024)

- **Fires at wildland-urban interface (WUI)**
  - Schug, "The global wildland–urban interface." *Nature* (2023)

Toxicity and Forensics

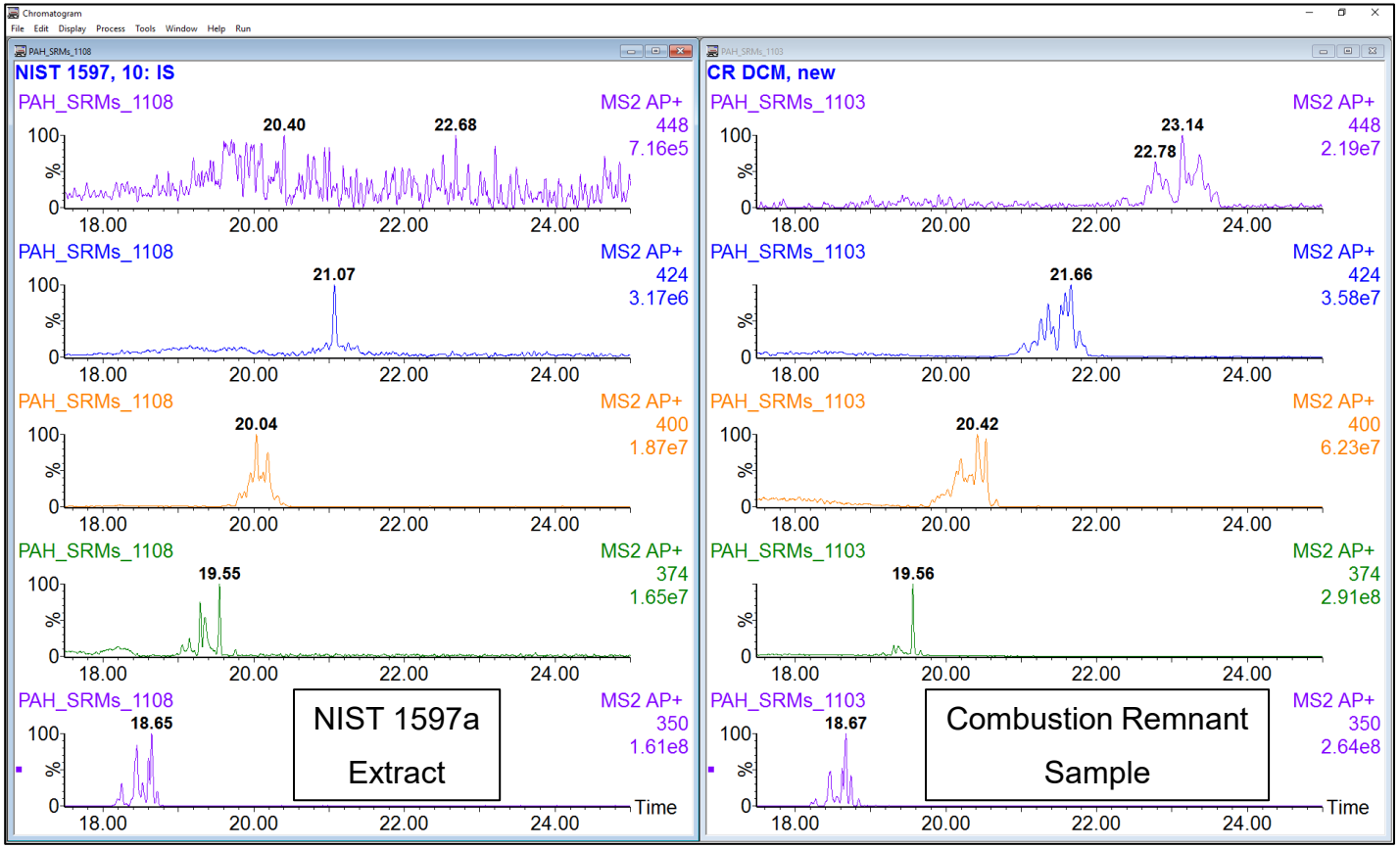
Waters™

- **PAH-based Markers**
  - **Individual PAH or PAH profiles may help identify source**
    - Ramdahl, "Retene—a molecular marker of **wood** combustion in ambient air." *Nature* (1983)
    - Simoneit, "Combustion products of **plastics** as indicators for refuse burning in the atmosphere." *EST* (2005)
    - James, "Fire and oil led to complex mixtures of PAHs on burnt and unburnt plastic during the M/V X-press pearl disaster." *ACS Environmental Au* (2023)
    - Zhang, "Contribution of **Coal Tar** Sources to Polycyclic Aromatic Compounds and Associated Ecological Risk in Lake Ontario Sediments: Inference from a Novel Marker." *EST* (2025)

- **Toxicity of PAHs**
  - **Toxic Equivalent Factor (TEF) of HMW PAHs can be 10 – 30 v BaP**
    - Aquilina, "Evaluation of the cancer risk from PAHs by inhalation: Are current methods fit for purpose?" *Environment International* (2023)

Looking Back: HMW PAHs GC-APCI MS

Waters™



Limitations Imposed by GC/MS

Waters™

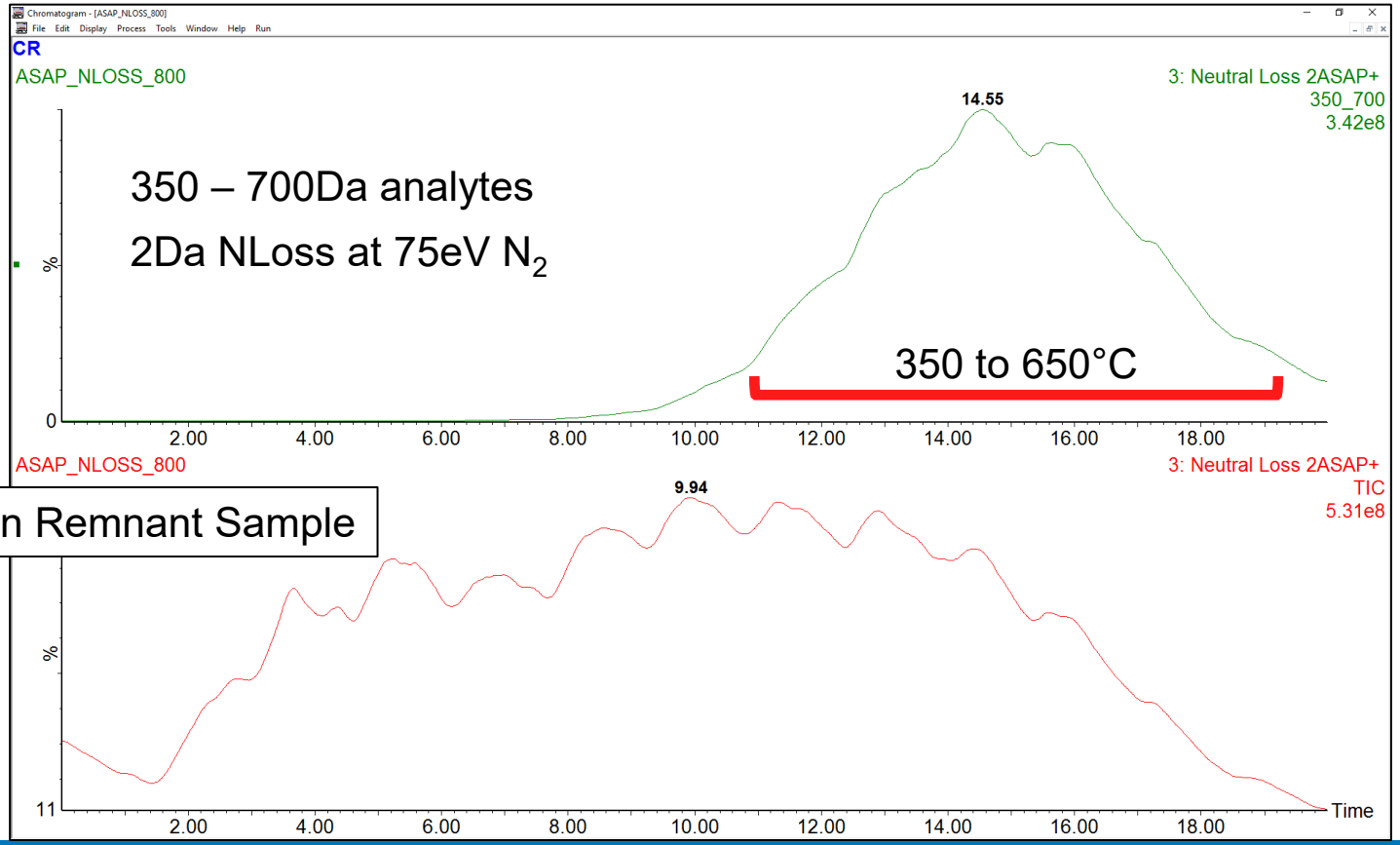
- **Upper temperature limit of column**
  - High temp columns 400°C - excessive bleed and column deterioration
- **Injection port discrimination**
  - High boiling analytes less efficiently transferred to column
- **Maximum carrier gas flow rate into MS**
  - Increased carrier flow reduces elution temp but vacuum source GC/MS have limited ability to tolerate high flow

Atmospheric Solids Analysis Probe (ASAP)

Waters™

Broad Coverage of HMW PAHs

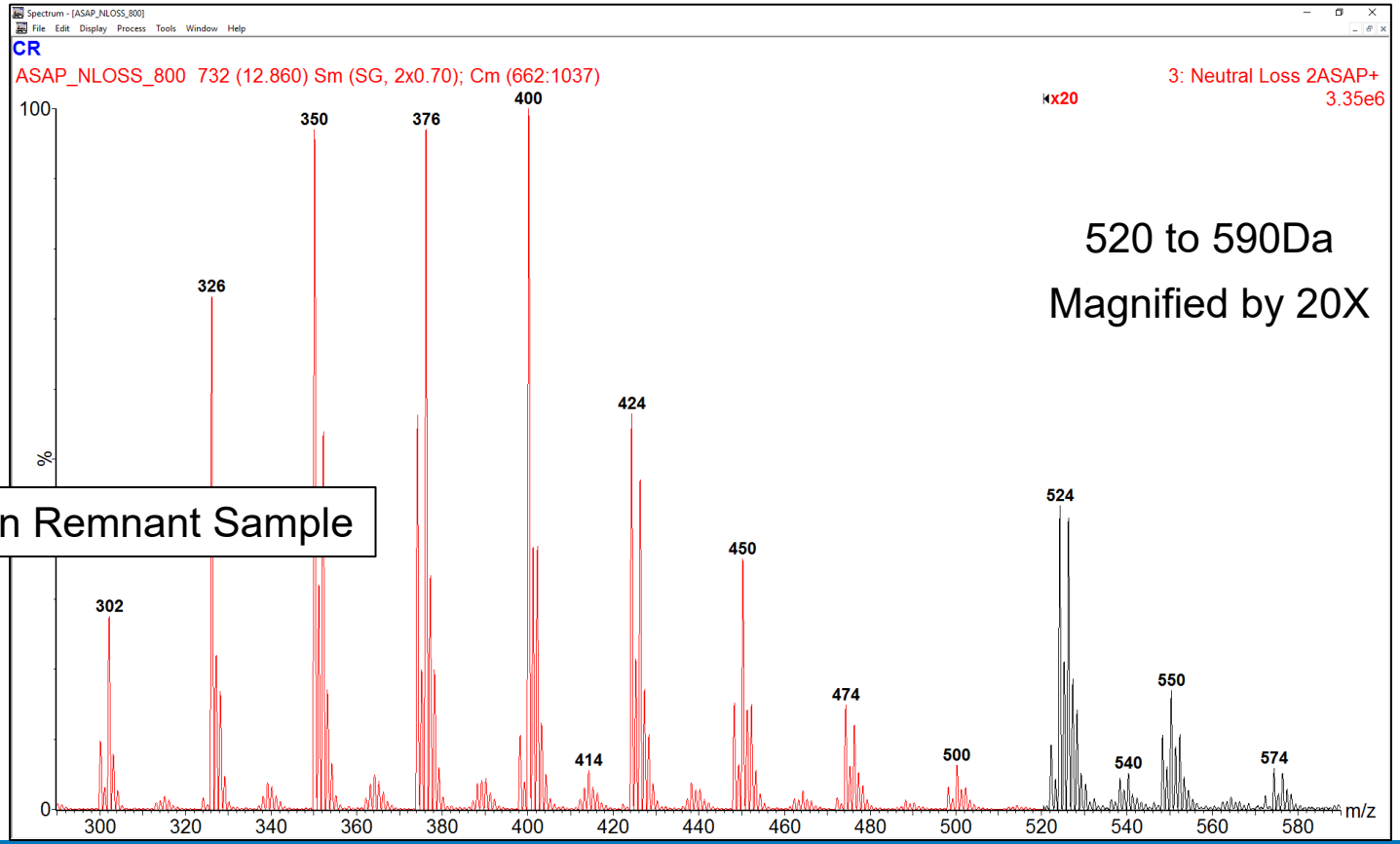
Waters™



Combustion Remnant Sample

Spectral Abundance and Distribution of HMW PAHs

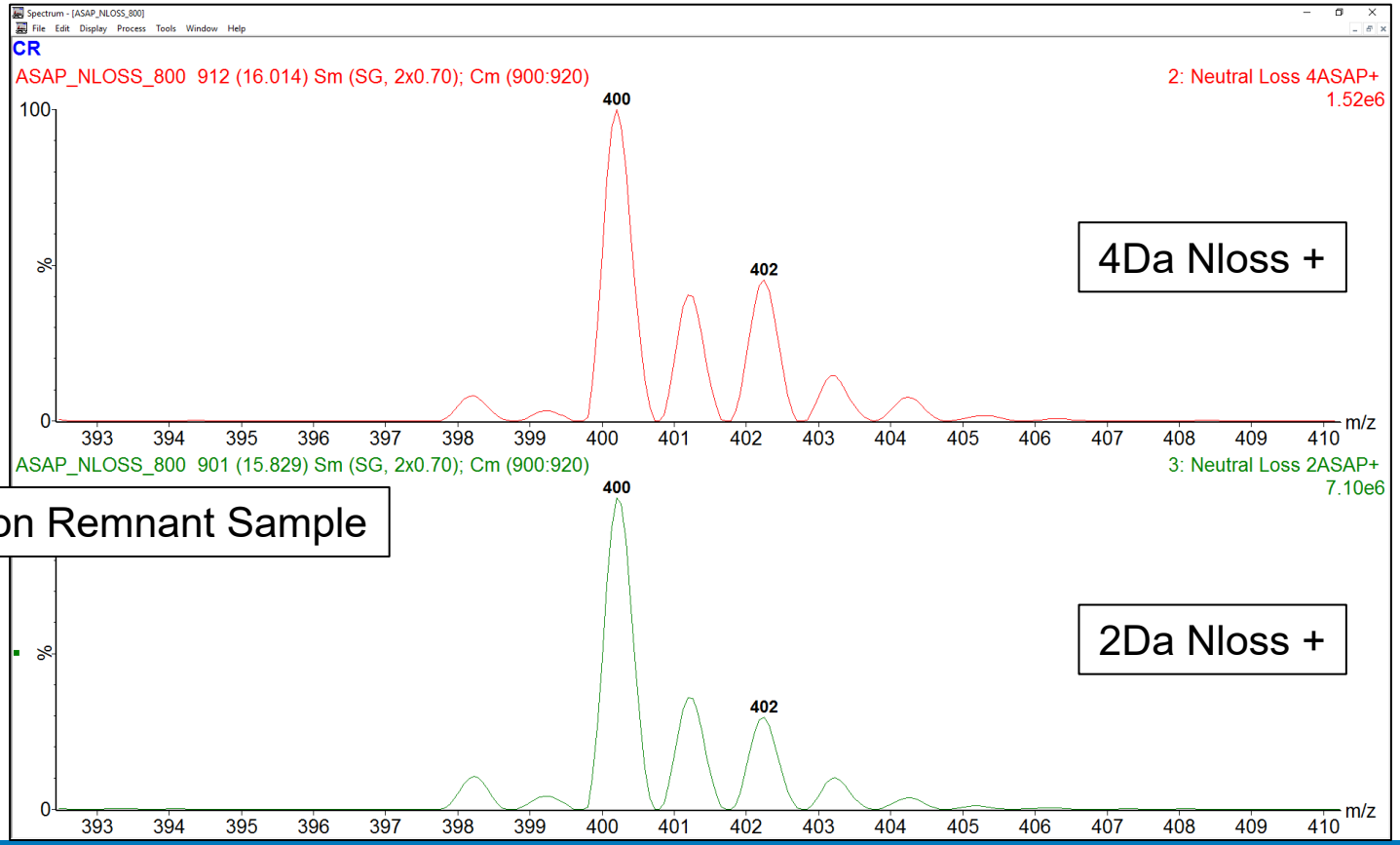
Waters™



Combustion Remnant Sample

Focusing on a Narrow Cut

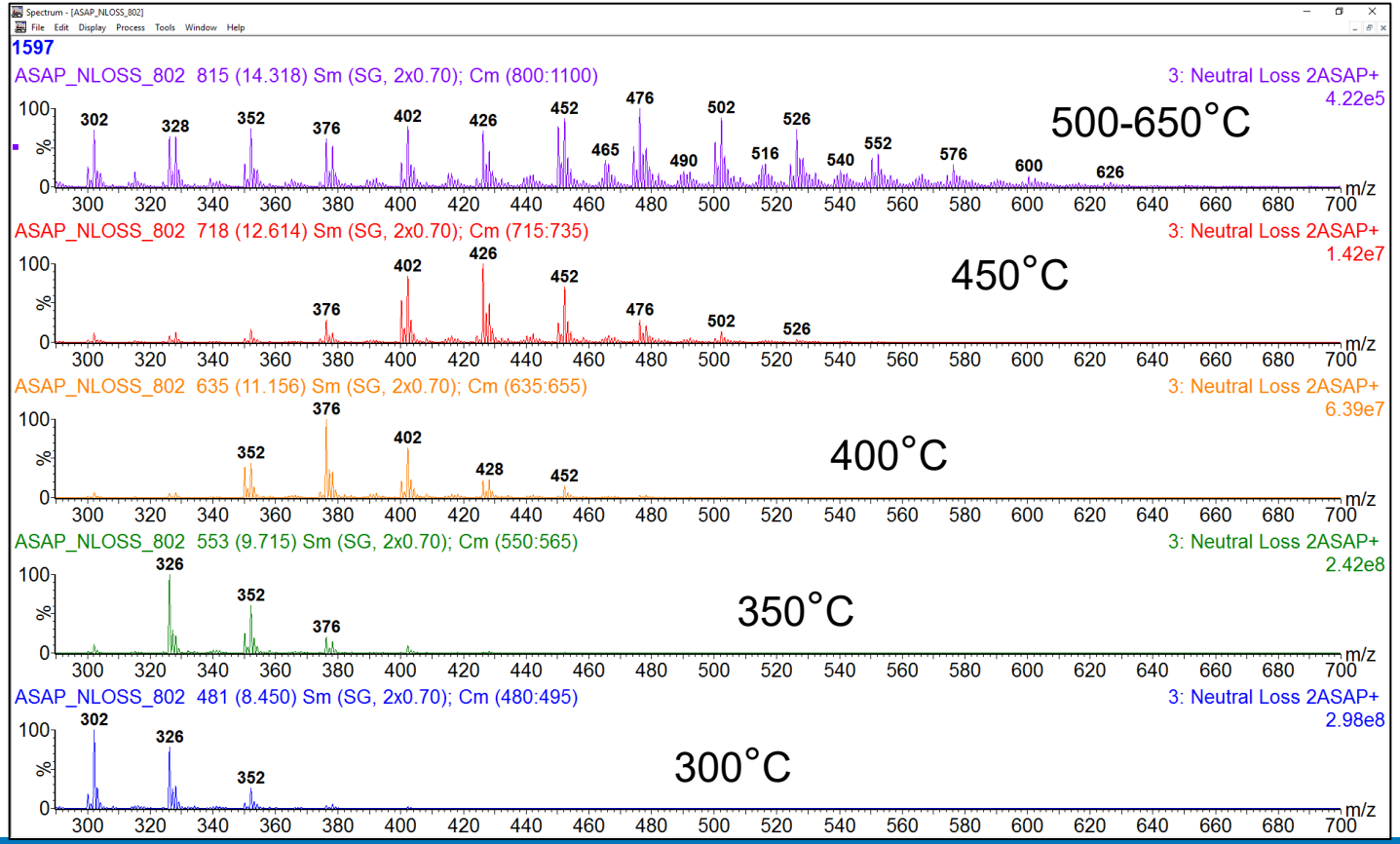
Waters™



Combustion Remnant Sample

Time/Temperature Step Summed Spectra

Waters™



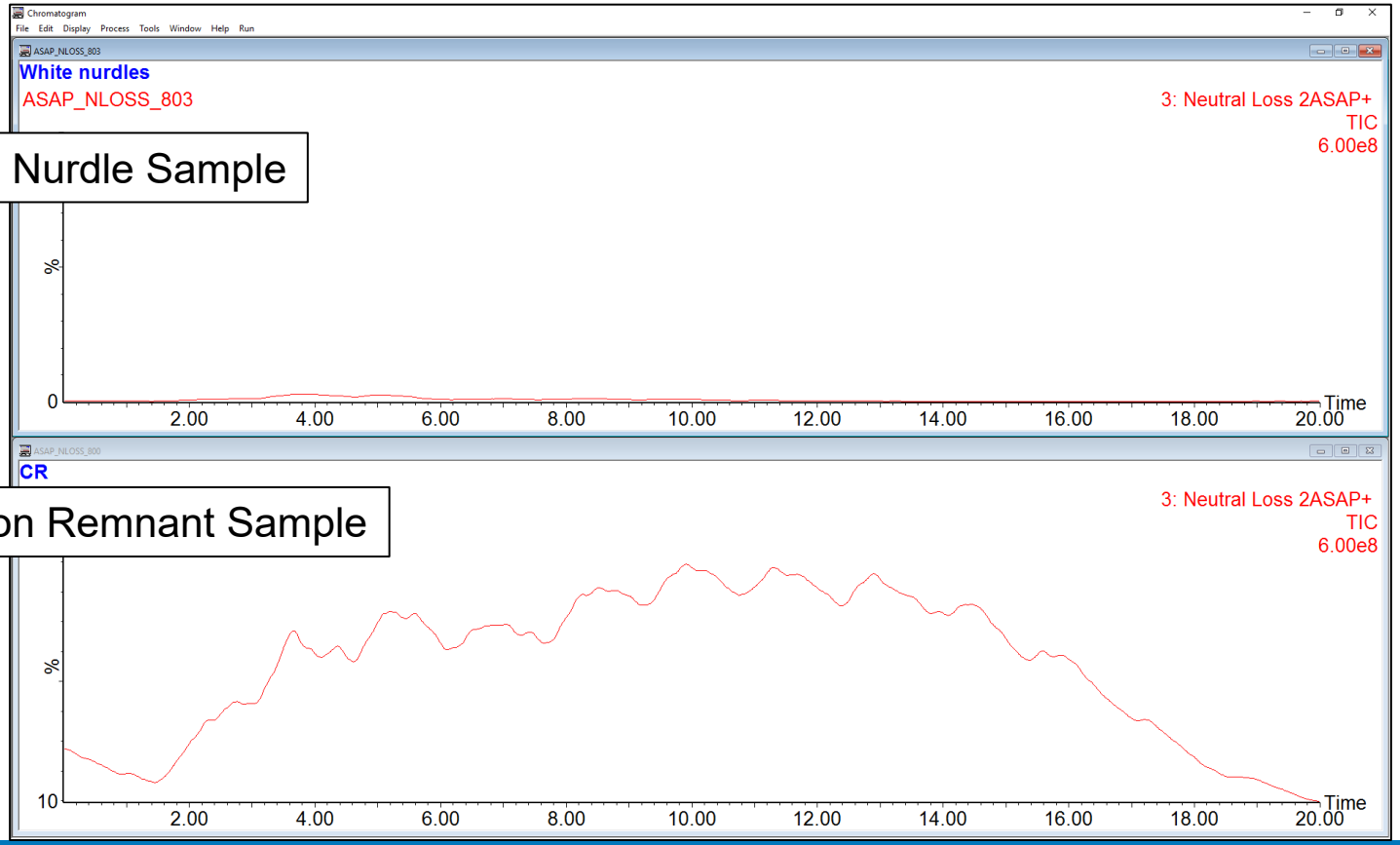
NIST SRM 1597a

Comparison of PAH Levels in Unburned and Burned Plastic

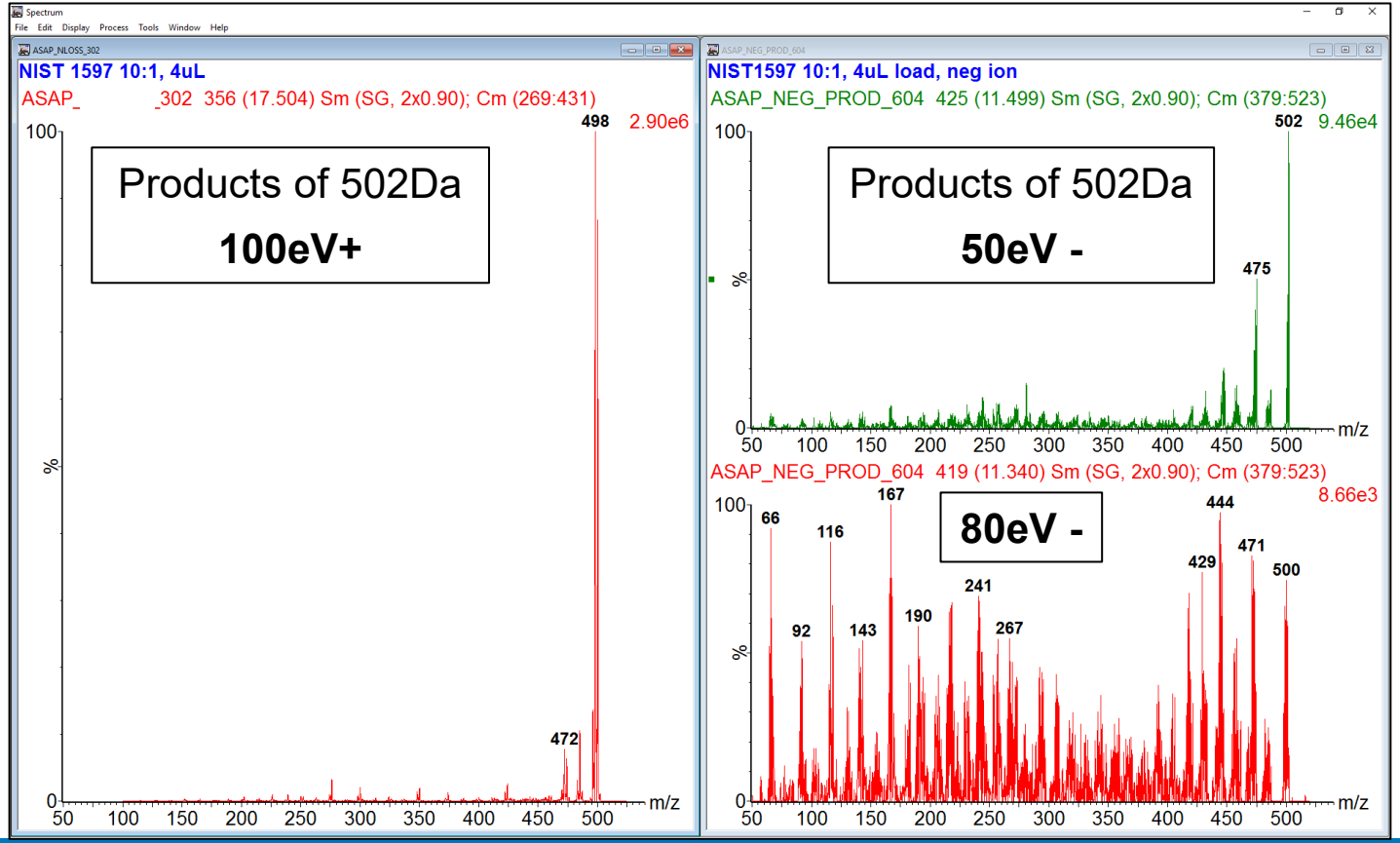
Waters™

White Nurdle Sample

Combustion Remnant Sample

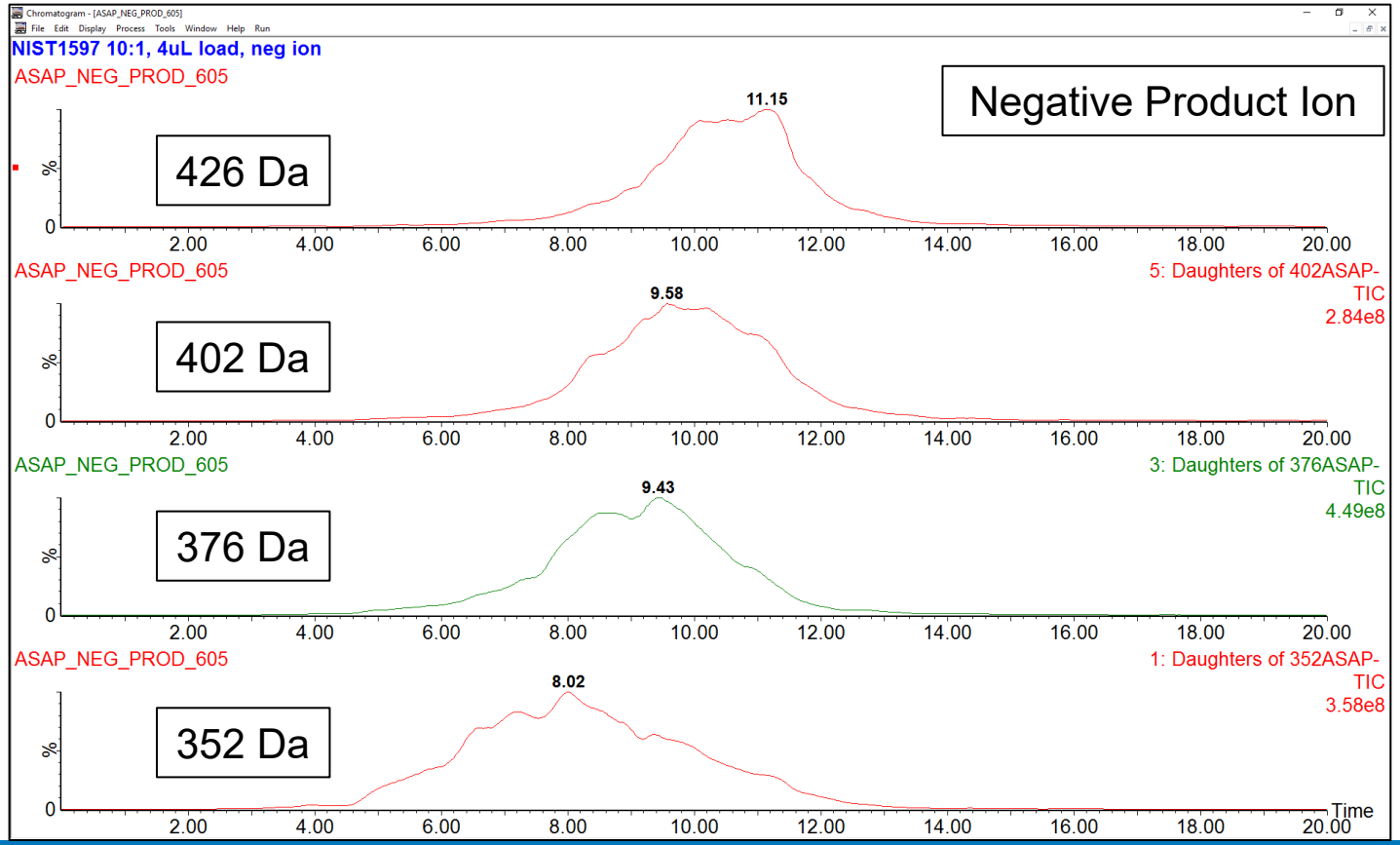


Comparing Acquisition Modes/Polarity



NIST SRM 1597a

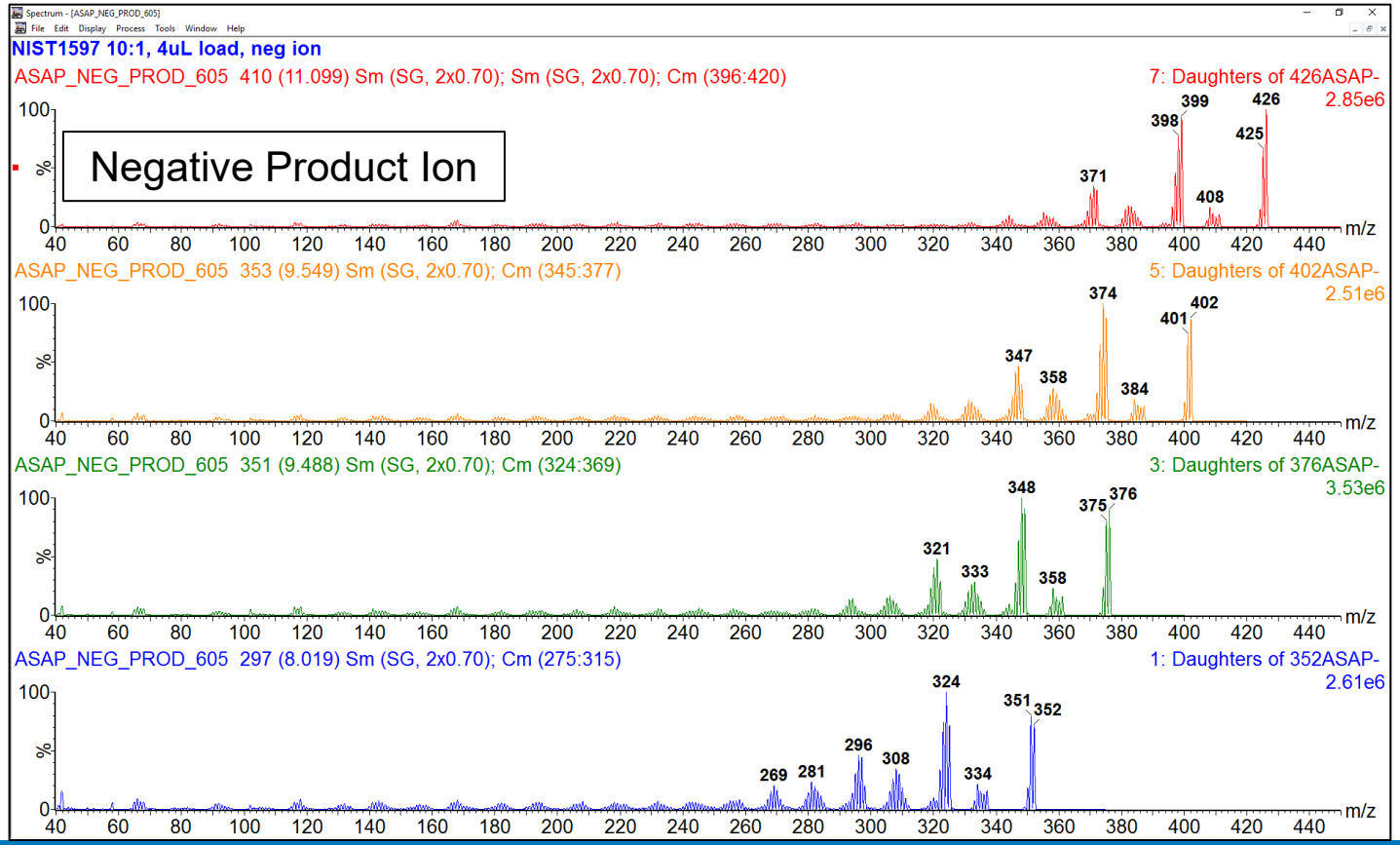
Single Analysis Targeting Multiple HMW PAHs



NIST SRM 1597a

Rich Fragmentation for Multiple Target Analytes

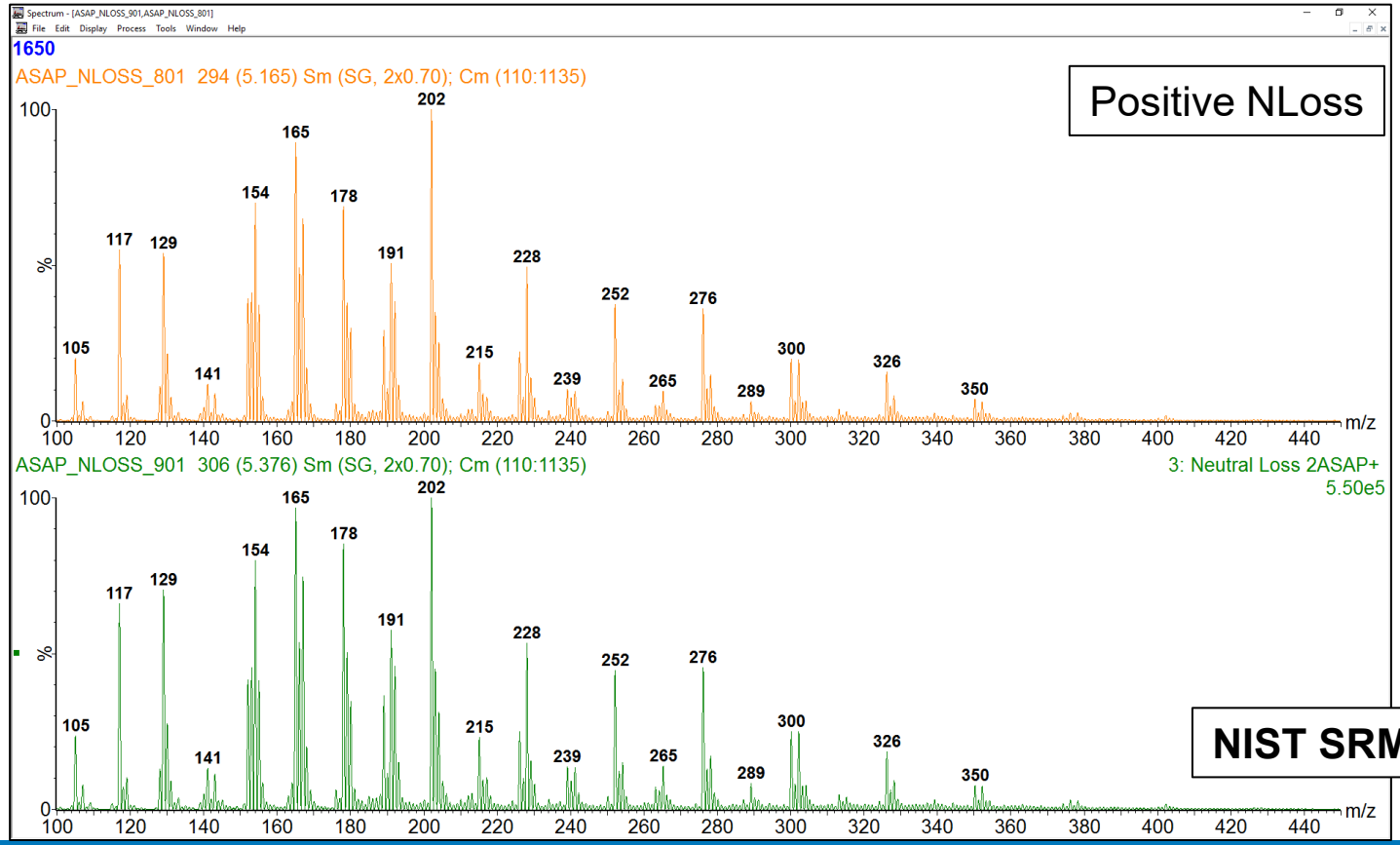
Waters™



NIST SRM 1597a

Diesel Particulate SRM – Solid Analysis

Waters™



Benefits and Limitations of Probe Analysis

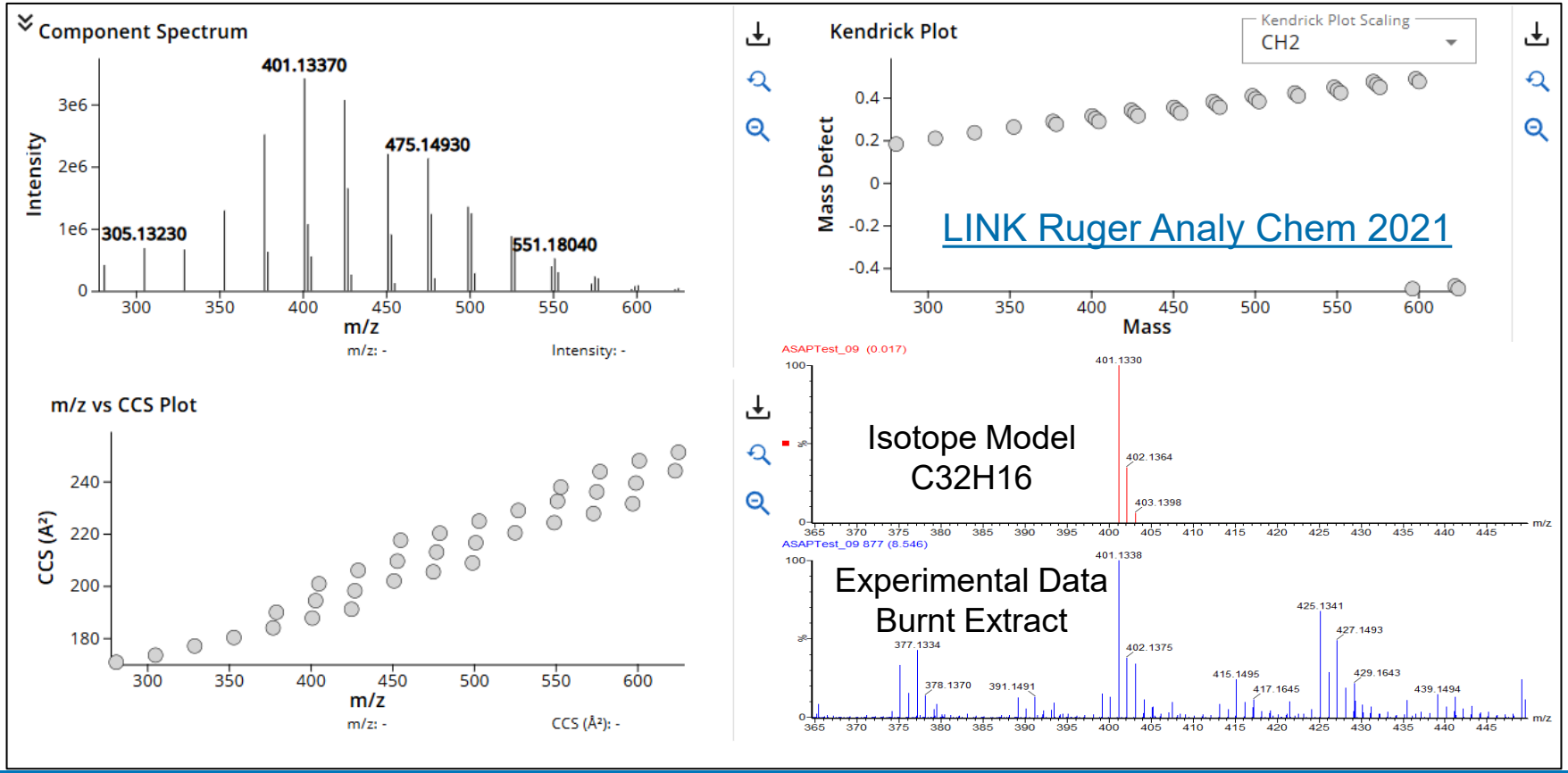
Waters™

- **Benefits**
  - Access to high boiling point analytes
  - Compatible with multiple acquisition modes
  - Simple sample prep and operation
  - Analysis of insoluble components
  - Faster analysis

- **Limitations**
  - No separation of individual analytes
  - Reduced sensitivity - higher concentration internal standards required
  - Manual operation

Probe IMS Analysis: Burnt Sample

Waters™



Conclusions

Waters™

- Analysis of HMW can be extended to 600Da using direct probe introduction for more comprehensive sample characterization
- Probe analysis shows good agreement with GC-APCI data up to 424Da
- Multiple tandem quadrupole MS/MS acquisition modes and polarity can be acquired concurrently based on the goals of the analysis – Nloss, Products, MRM, positive and negative
- Analysis of insoluble sample components enabled
- Adaptable to IMS HRMS

Acknowledgements

- Sarah Dowd
- Michael McCullagh

Thank You! Questions?