Headspace SPME-DART for Rapid Detection and Characterization of Explosives

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Presented October 1, 2014
SCIX 2014
Reno, NV

Program Goals

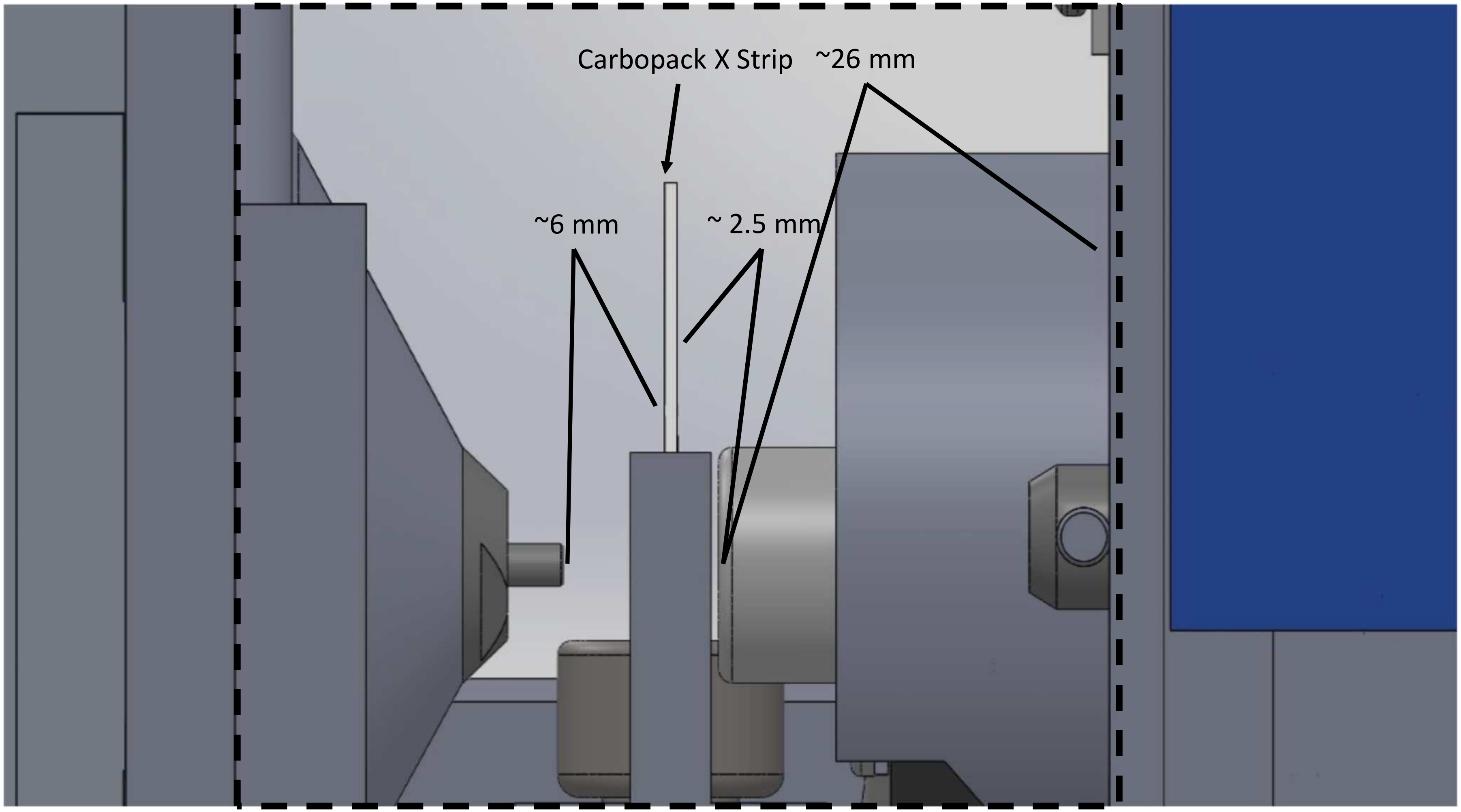
- Develop Rapid Headspace Sampling Technology using solid phase microextraction devices
- Complete rapid screening of the sample with DART-MS
- Produce mass spectra for development of Chemical Attribute Signatures for Explosives
- Examine various statistical methods for model development
- Assess model performance using known (modelled) and unknowns in blind study

1st step: Examine use of Passive Headspace

Conventional arson method

- Place sample in paint can with charcoal strips for GC/MS and sorbent coated screens for DART-MS suspended above
- Seal can and place in oven overnight – (30 minutes to overnight)
- For GC/MS: Remove charcoal strip from can, place in vial and add solvent (5 minutes) Place vial in autosampler equipped GC/MS and analyze (30 – 40 minutes)
- For DART-MS: Remove sorbent coated screen and analyze directly by DART-MS in (15 seconds)

DART to Carbopack X Strip to MSD Inlet Schematic



G12 Dart (grey) on the right; LRE (dashed line) in the middle; MSD (grey) on the right

Mass of molecules known to be present in common Smokeless Powders

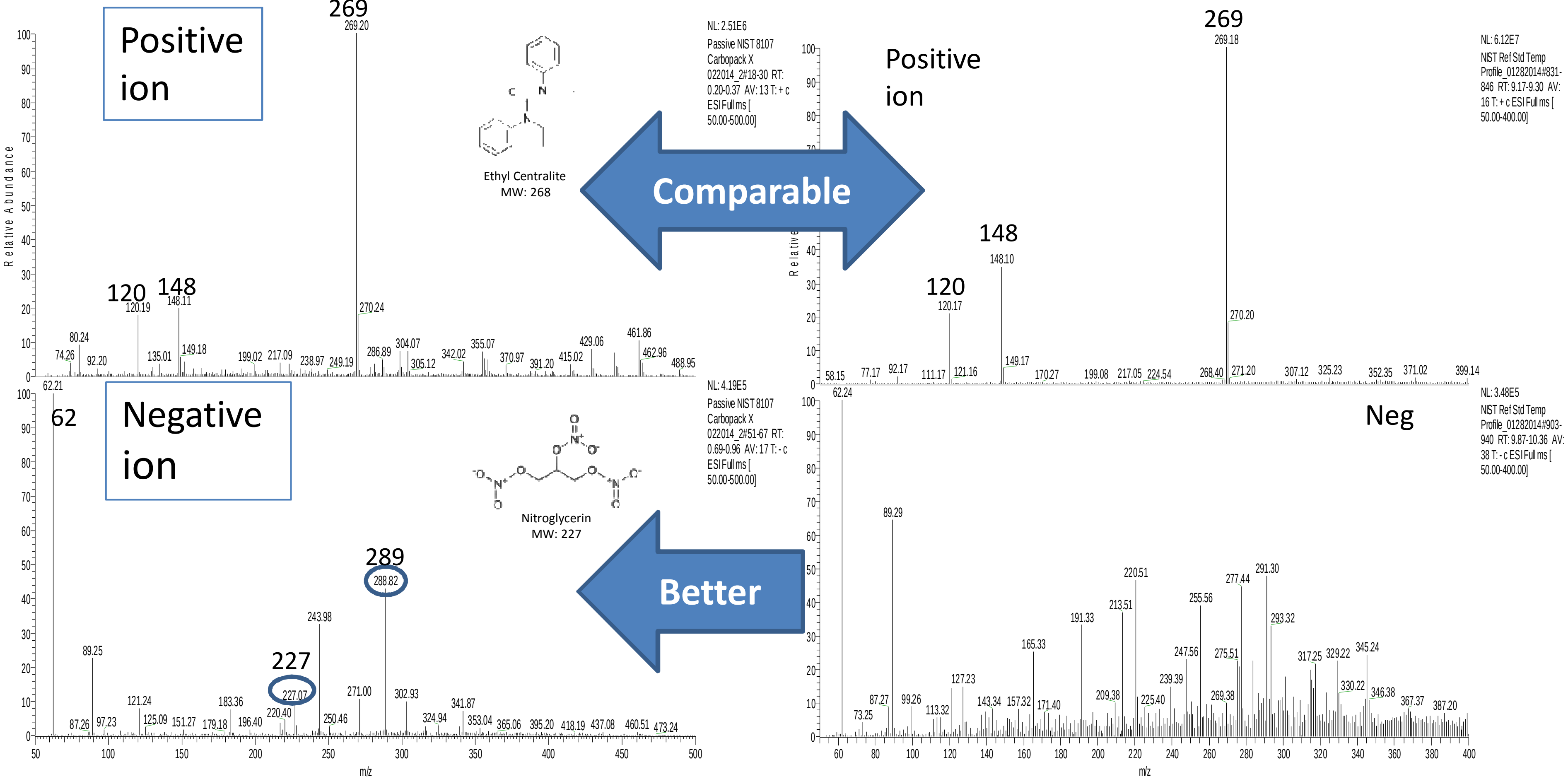
Compound	MW	Ion Mode	Precursor Ion (m/z)	Product Ions (m/z)
Diphenylamine	169.23	+	170	93, 65
N-Nitroso-diphenylamine	198.22	+	199, 337	169, 66
Dibutylphthalate	278.34	+	279	205, 149
Ethyl centralite	268.35	+	269	148, 120
Nitroglycerin	227	-	316, 303, 289, 262, 226	62, 46

Background: Could DART-MS detect the ions?

Comparison of Heated Passive Headspace and Dissolution

Heated Passive Headspace
Carbopack X; 150°C for 30 min

Dissolved in Acetone
2 flakes in ~ 1 mL

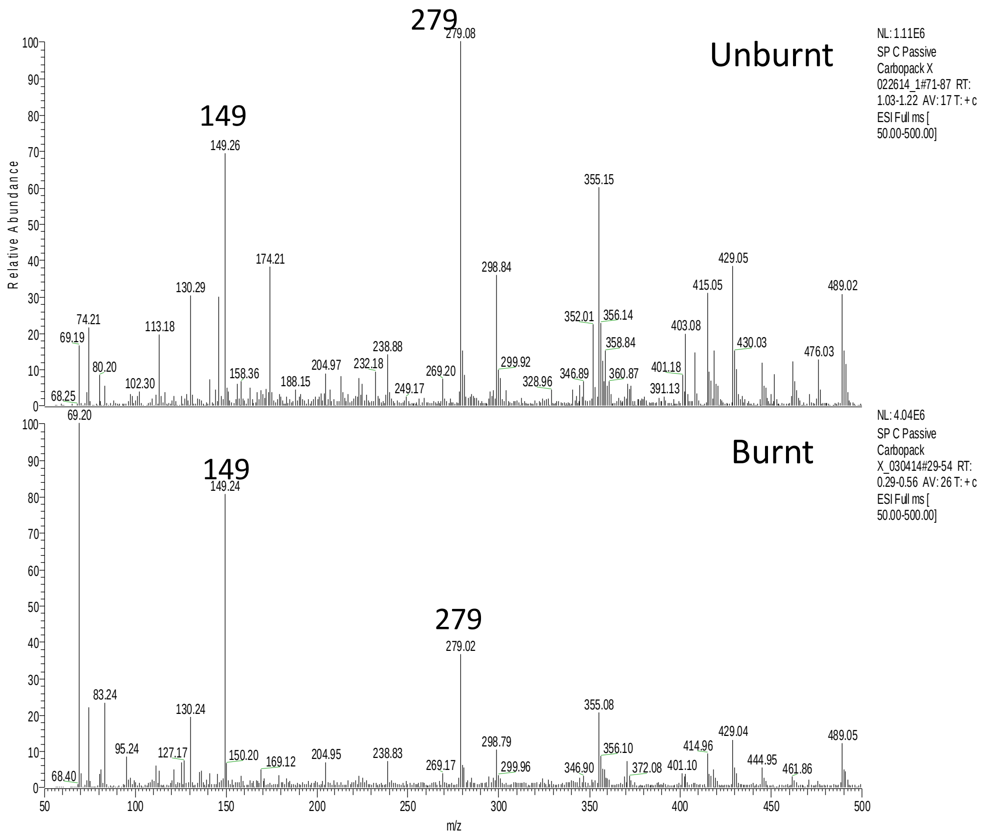


NIST RM 8107

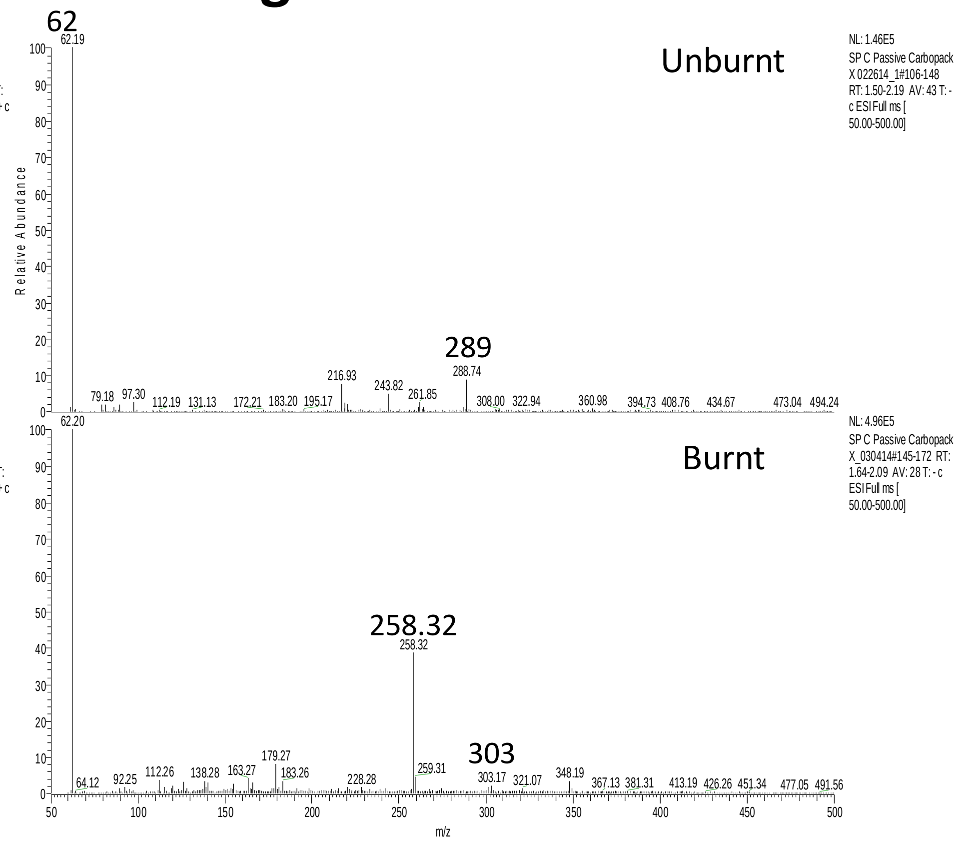
What could DART-MS detect post-activation?

Comparison of Unburnt (top) vs Burnt Smokeless Powder

Positive Ion Mode



Negative Ion Mode



Smokeless Powder C

Passive Headspace Results

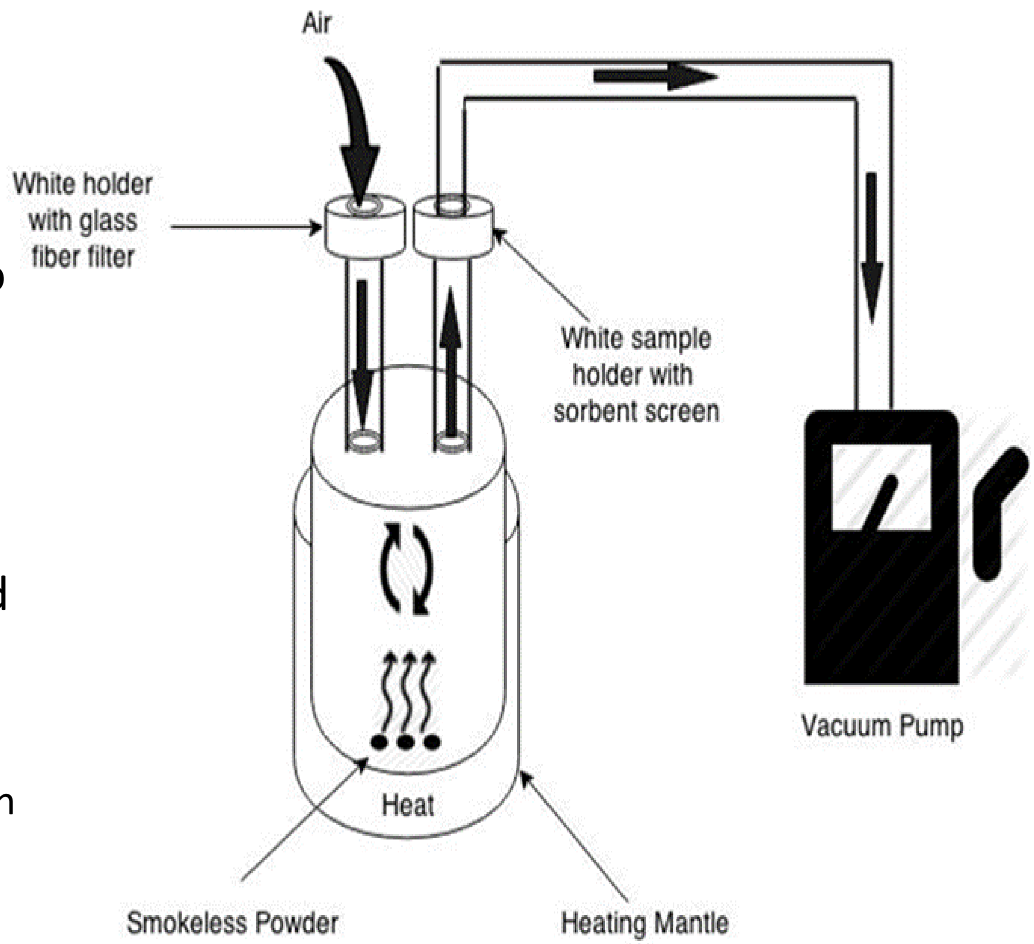
- Carbopack X screens capable of retaining all smokeless powder analytes for DART-MS
  - Different Smokeless Powders yield different spectra
  - Headspace yielded better S/N in some cases
    - Negative Ion mode for nitroglycerine (NG)
  - For 30 minute method analytes were not observed at 100°C so higher temperature was needed
  - At higher temperature some powders thermally decomposed
  - More fragment ions observed as temperature was raised

Faster Method Desired Examined – Dynamic Headspace

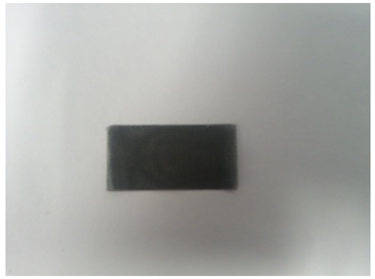
Rapid sampling method

- Utilize paint can with modified lid to permit air flow through
- Place ~ 5 mg sample in can on weighing pan and seal can
- Place can in pre-heated jacket at to 110°C jacket
- Start vacuum and sample for 5 minutes with gas flowing through sorbent coated screen in holder
  - Temp and time optimized
- Remove sorbent coated screen and transfer to DART-MS for analysis
  - He Temperature: 300°C
  - Alternating POS; NEG ion
  - Thermo EXACTIVE + at 35K resolution

SPME-DART device



Dynamic Headspace Collection System

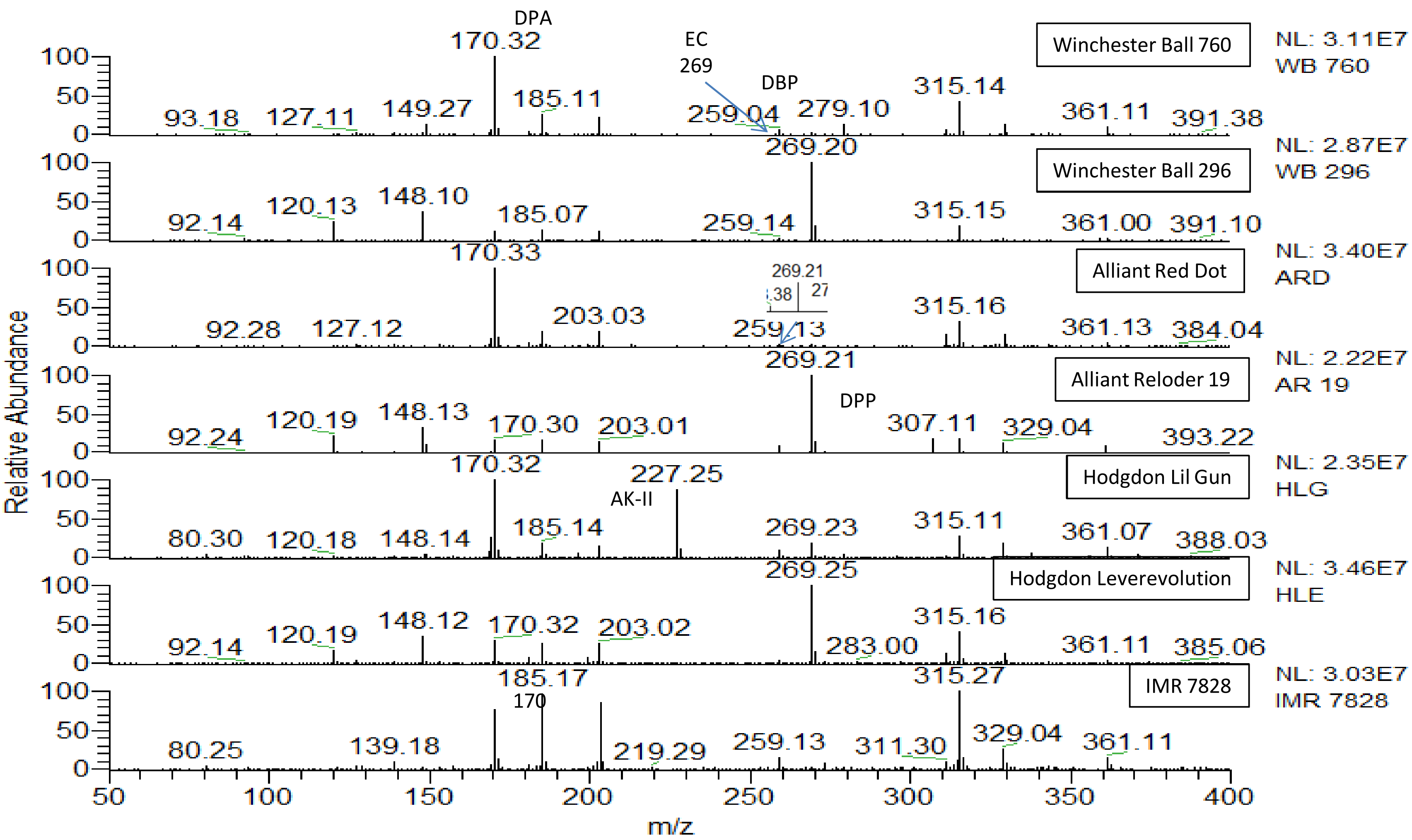


Carbopak X,
Carboxen 369
Tenax
Nanocarbon
75x75 wire /in.
coated meshes
tested initially

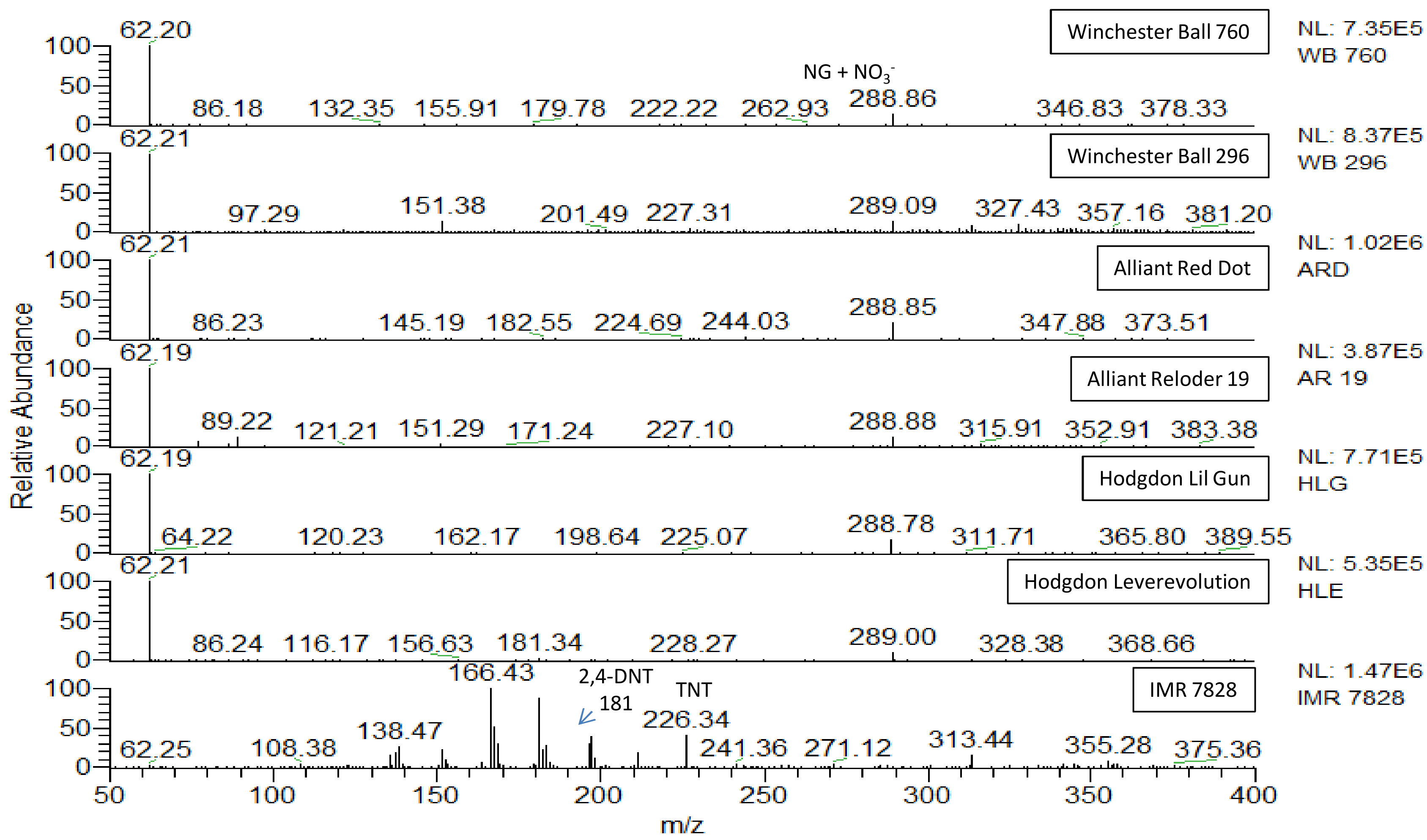
Carbopak X
results used for statistical study

Leland Legacy portable pump set to 3L/min, SKC trace filter collectors hold screen

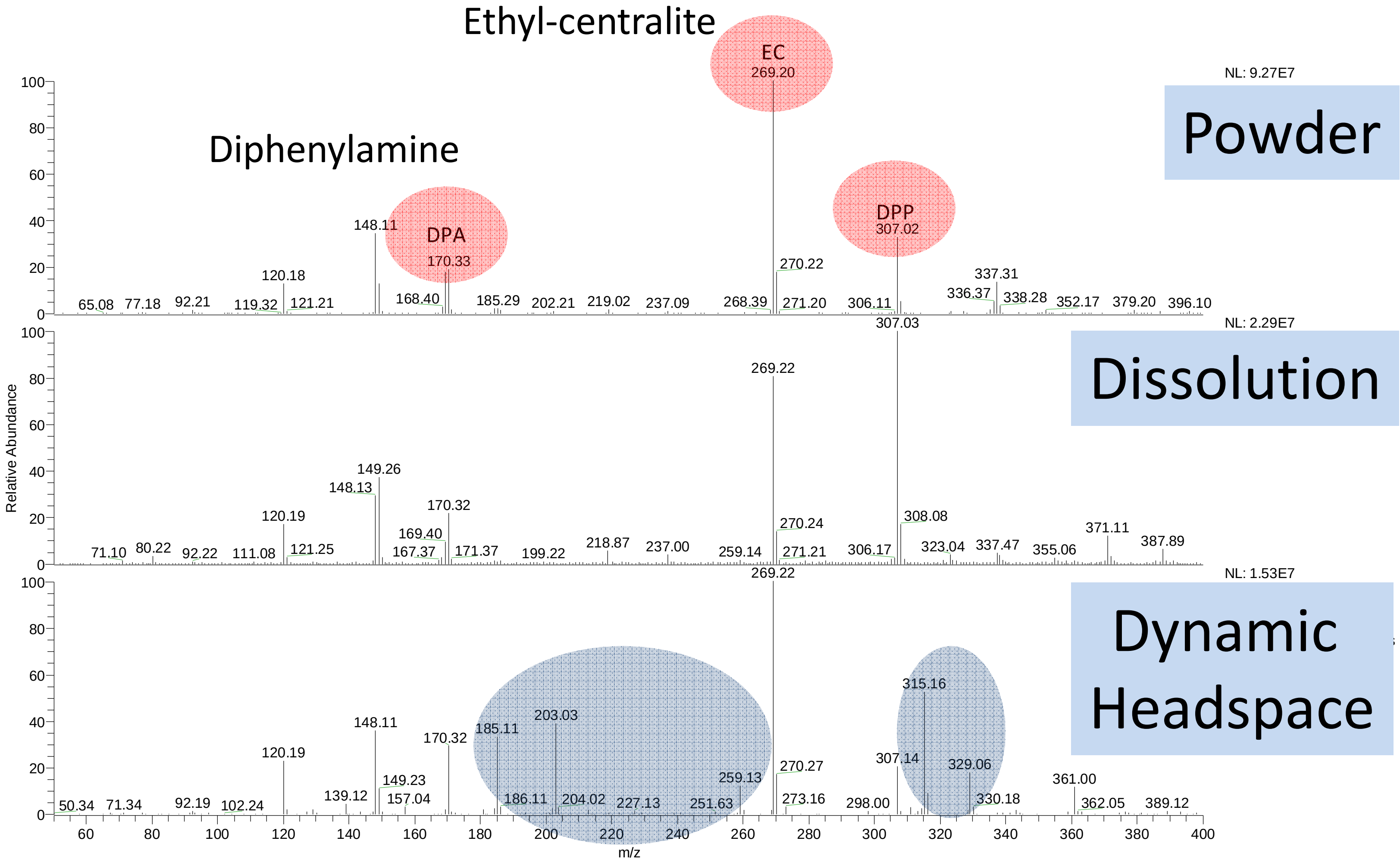
Comparison of 7 Different Smokeless Powders – Positive ion



Comparison of 7 Different Smokeless Powders - Negative ion

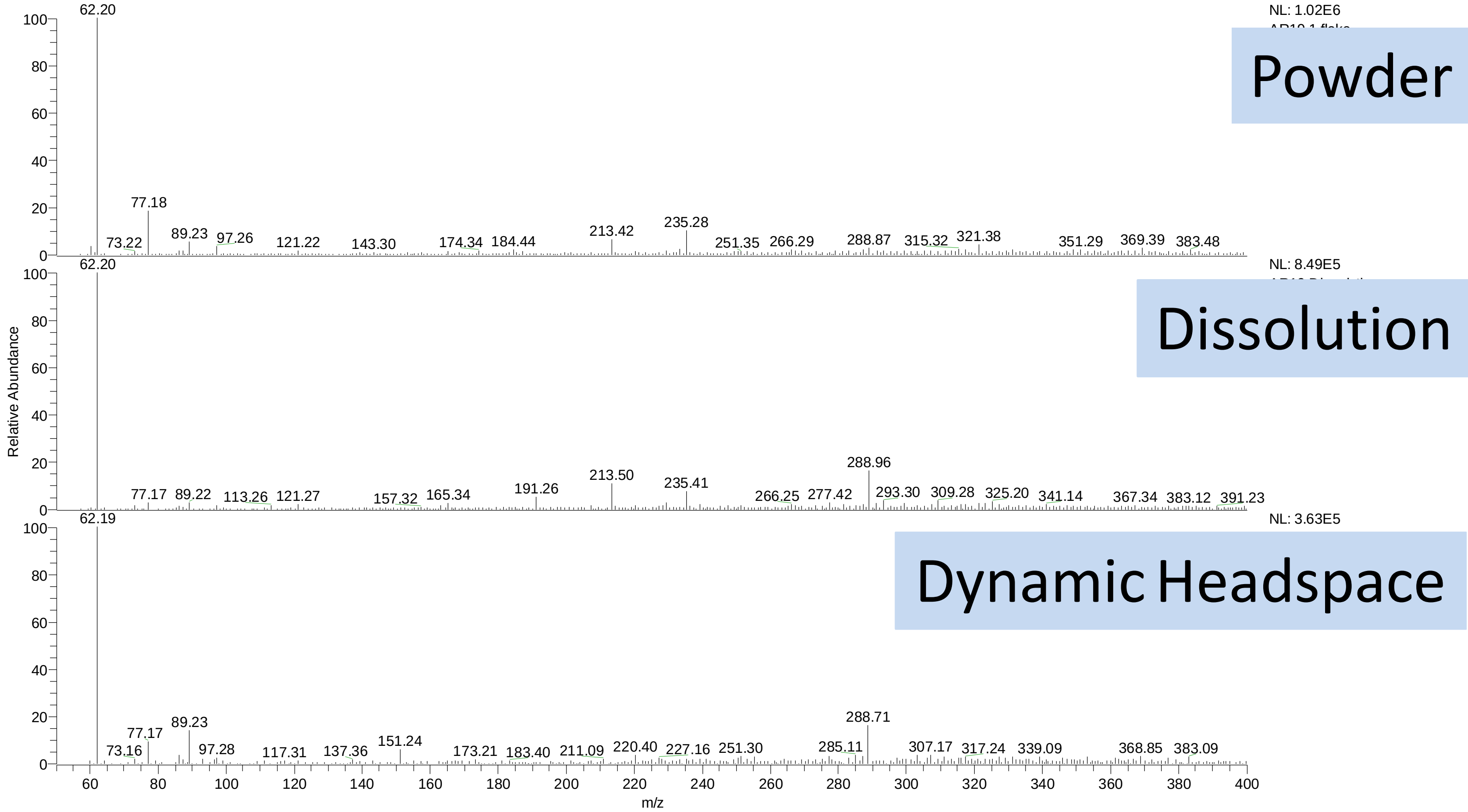


Alliant Reloder 19



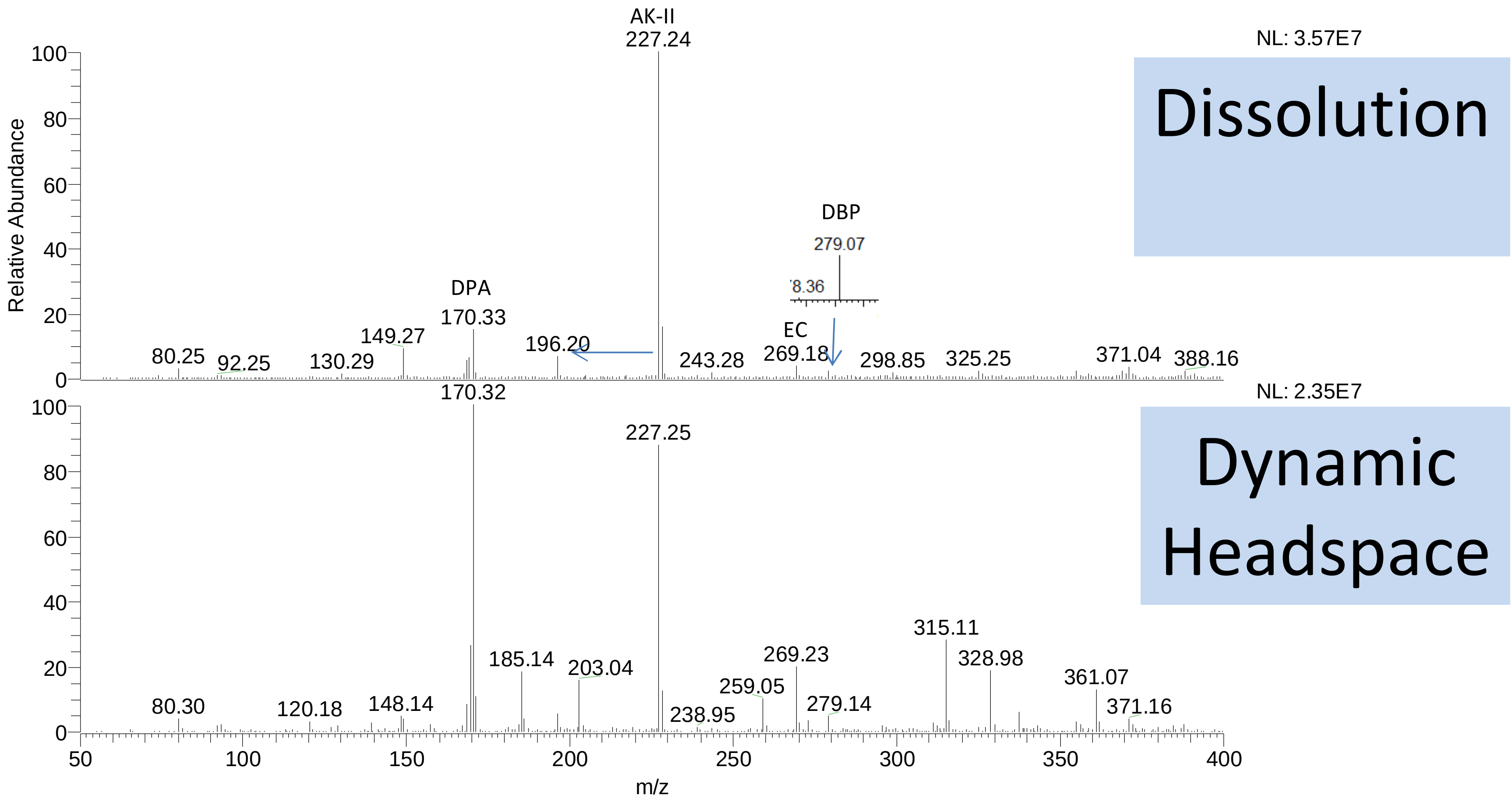
Positive Ion Mode

Alliant Reloder 19



Negative Ion Mode

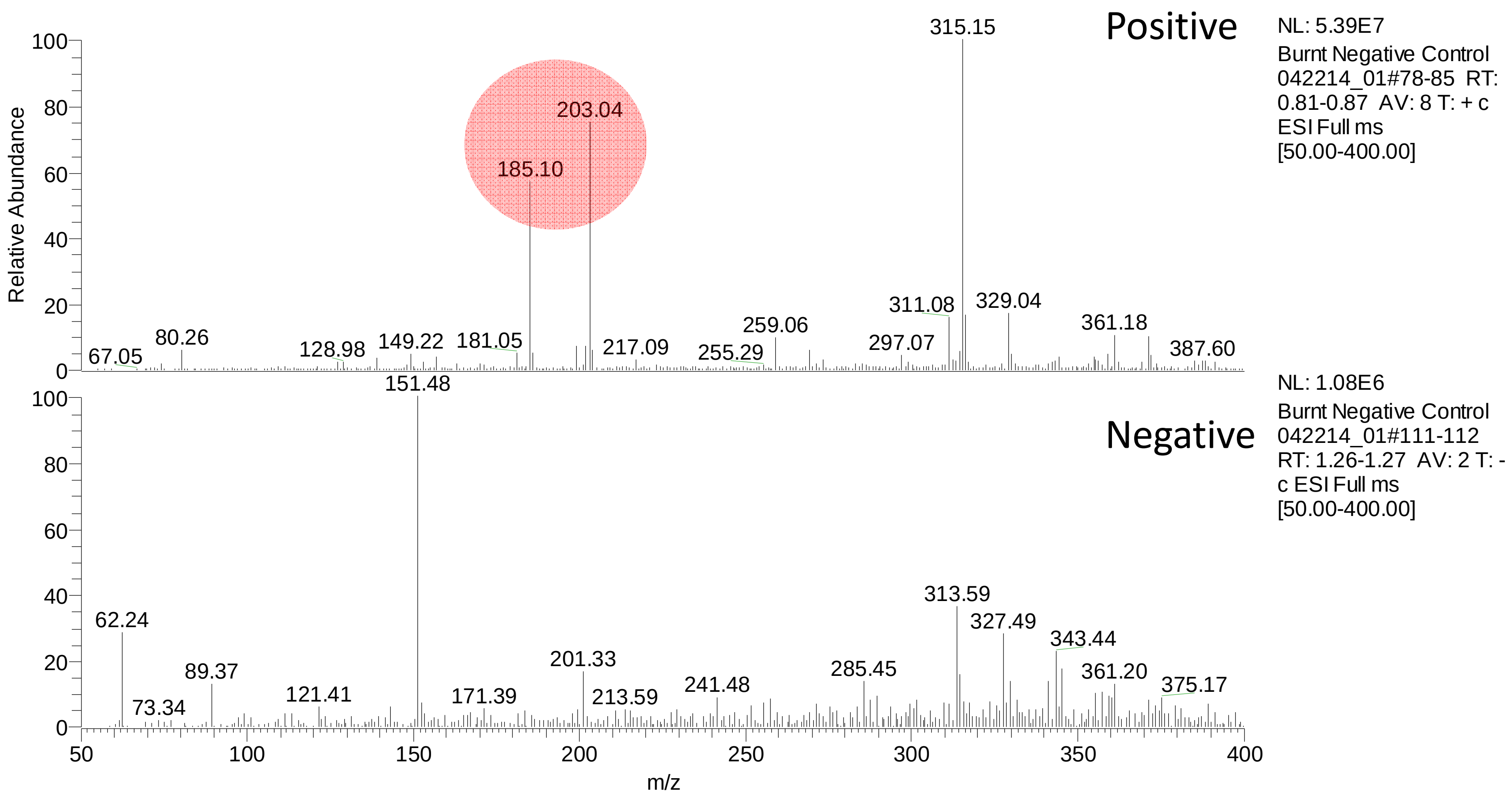
Hodgdon Lil Gun



Positive Ion Mode

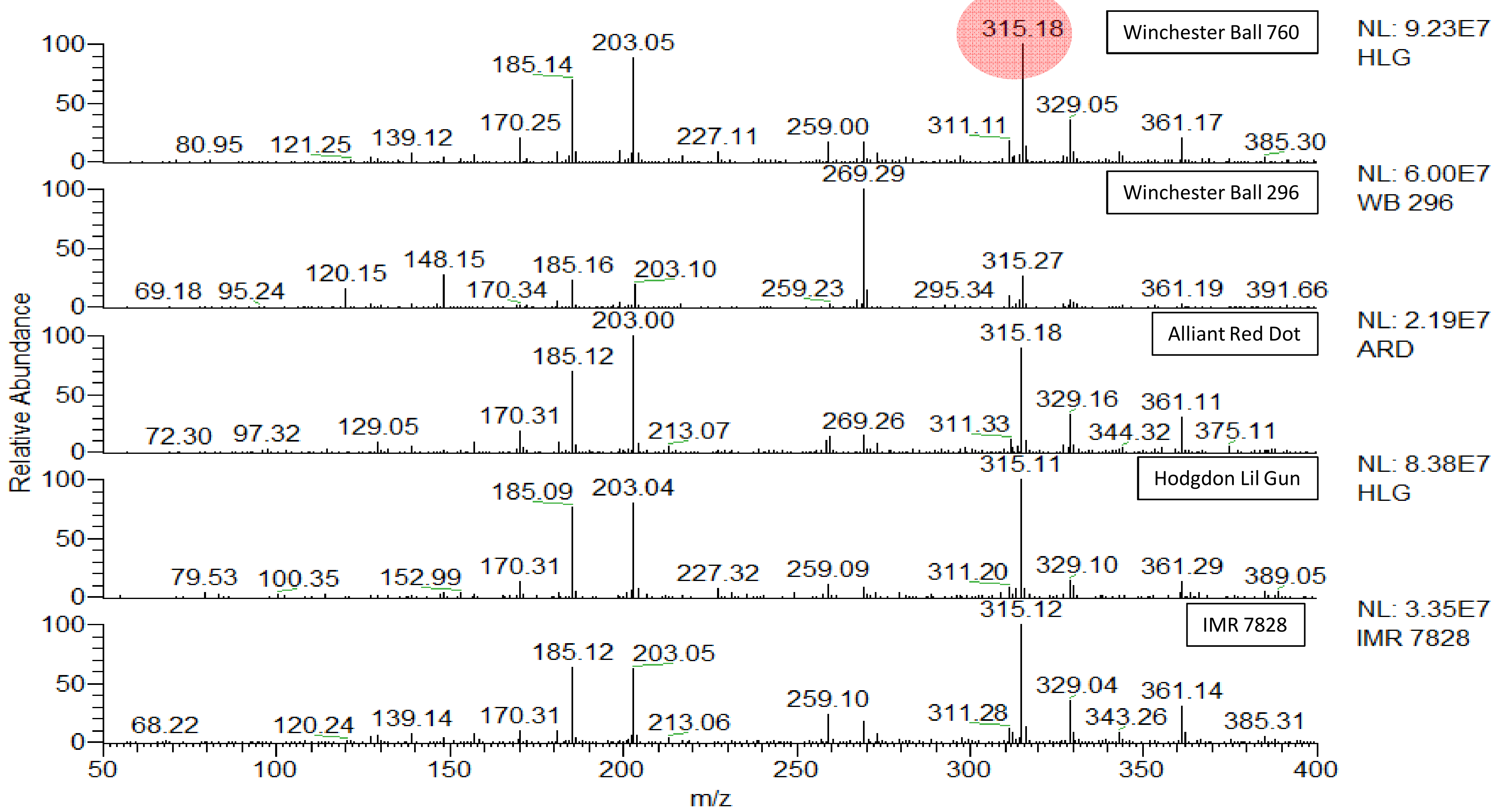
Dynamic Headspace Sampling of <u>Burnt</u> Smokeless Powder

Negative Control for Dynamic Headspace

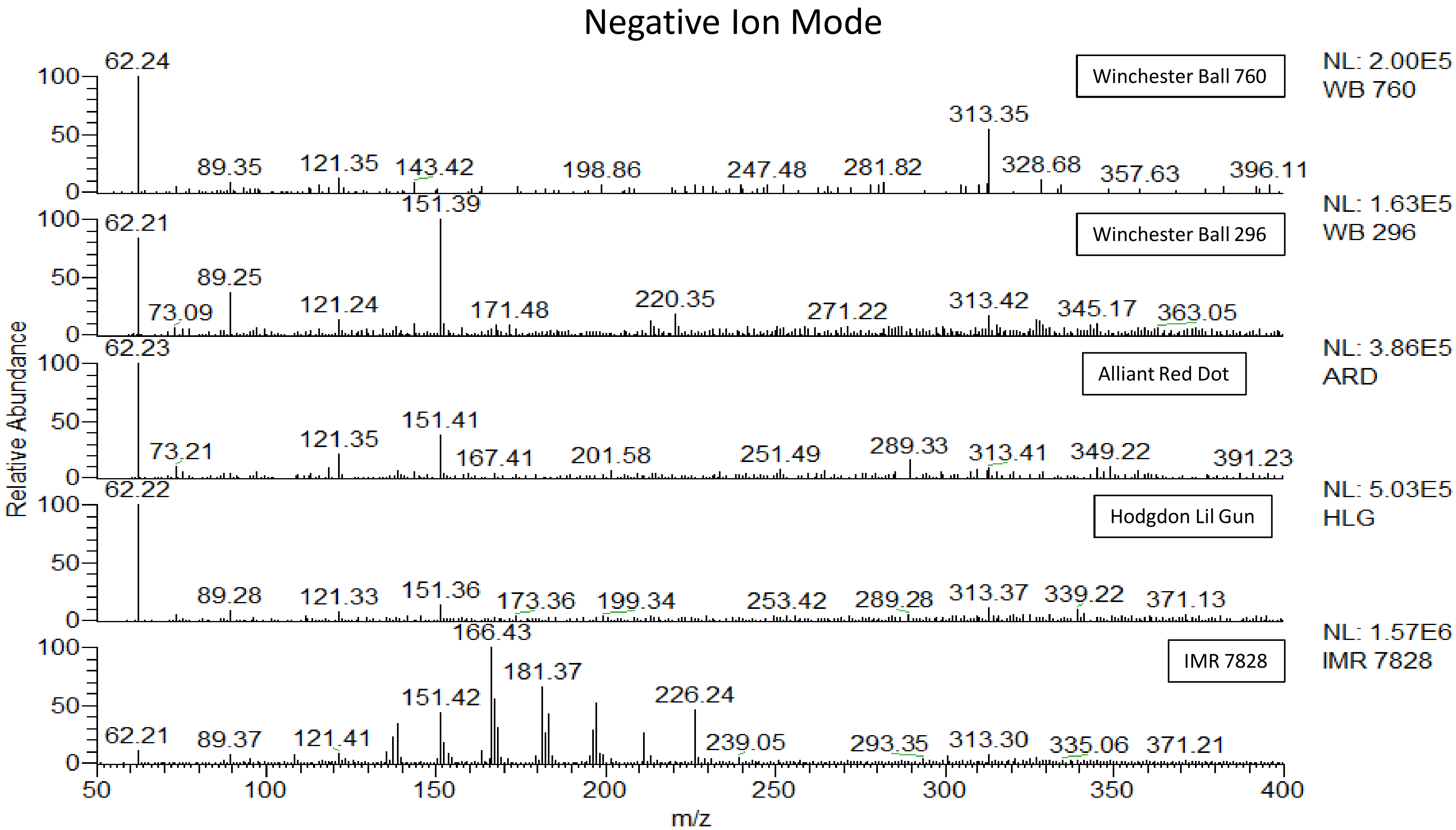


Comparison: 5 Burnt Smokeless Powders

Positive Ion Mode

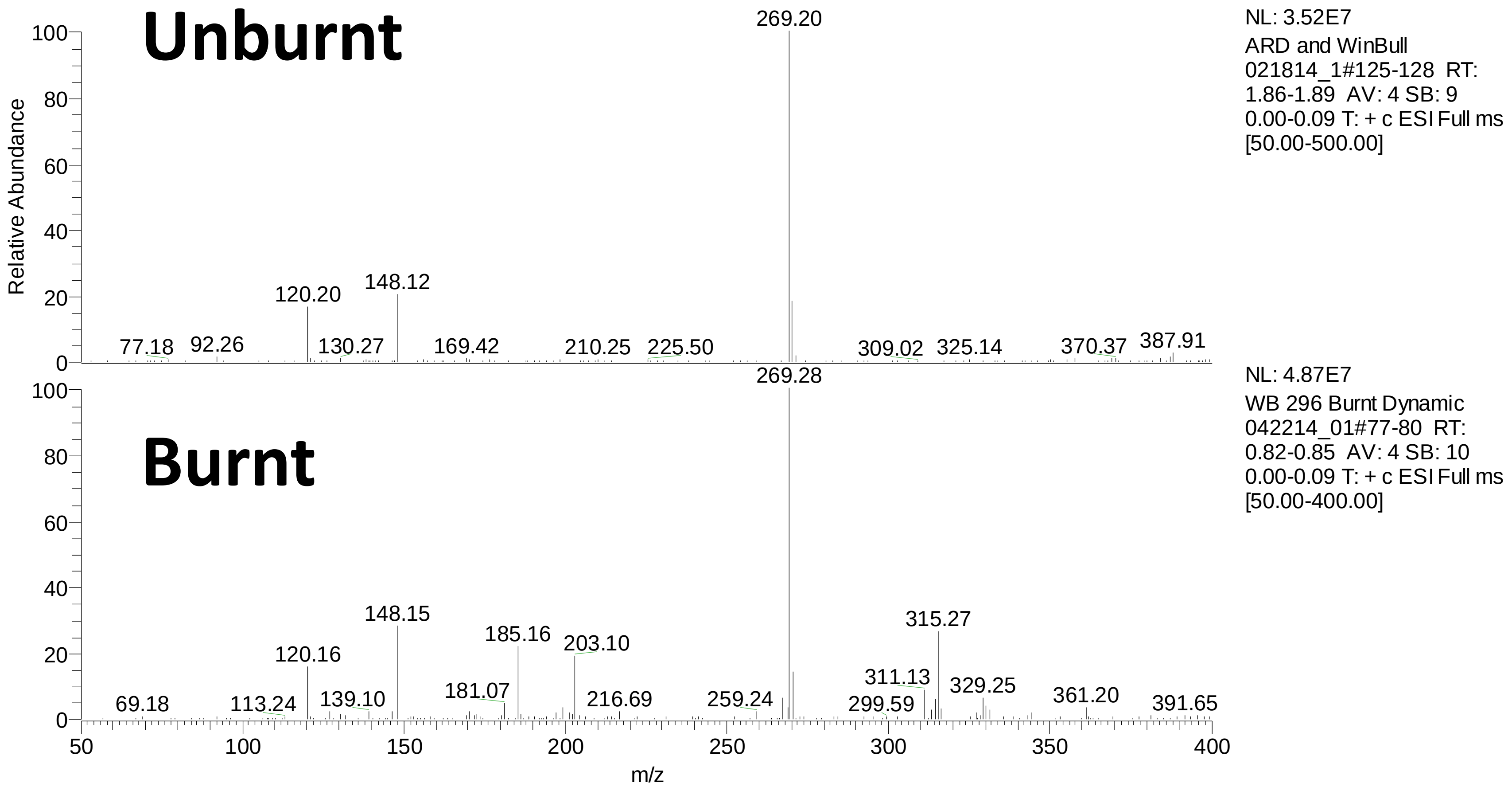


Comparison: 5 Burnt Smokeless Powders



Winchester Ball 296

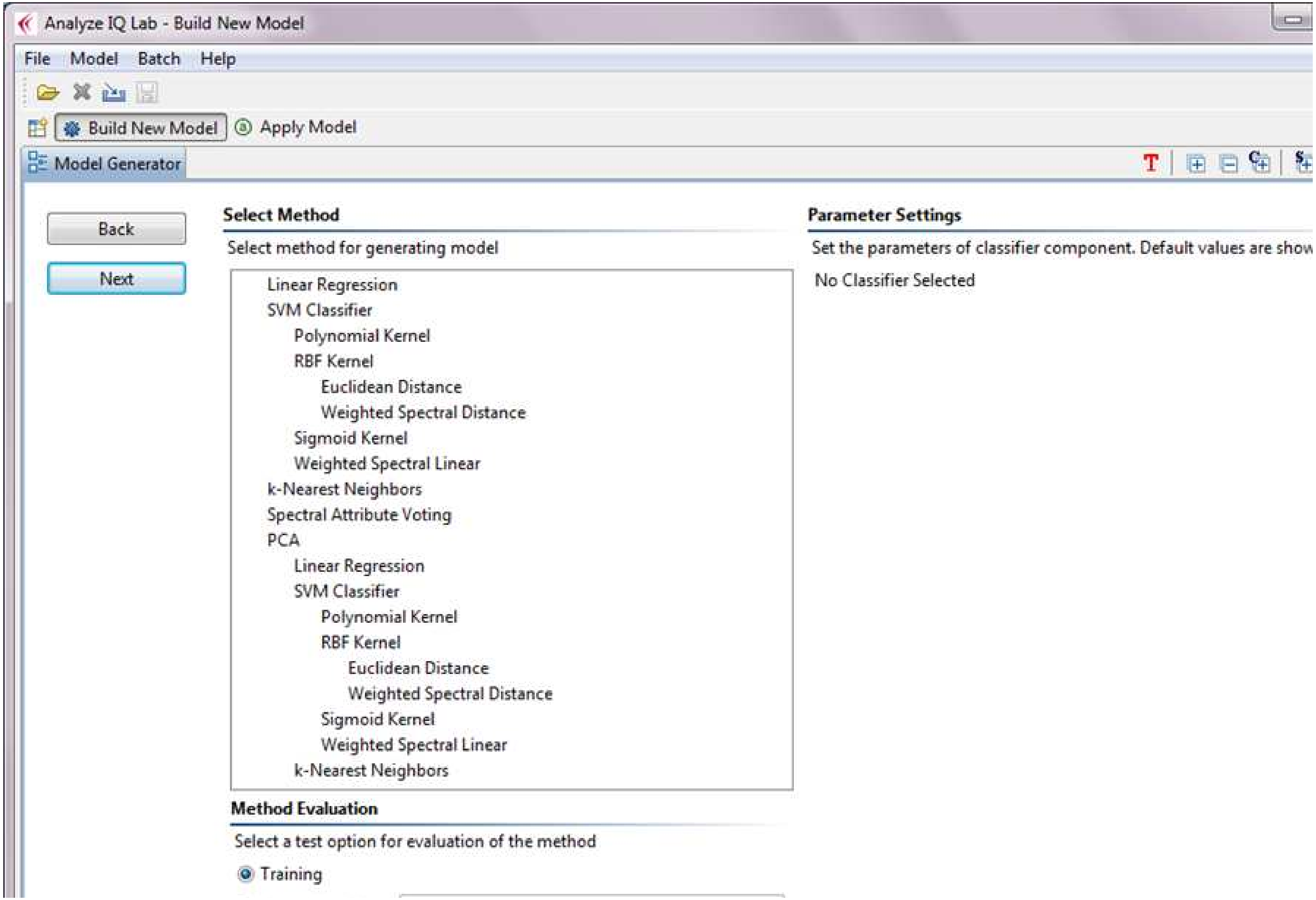
Positive Ion Mode



At this point we went statistical

User Interface for Analyze IQ Statistical Analysis Program

Analyze IQ User interface



Experimental flow and interface of Analyze IQ Lab program for statistical analysis into the system architecture.

Background operations of Analyze IQ in blue. Graphical user interface in red

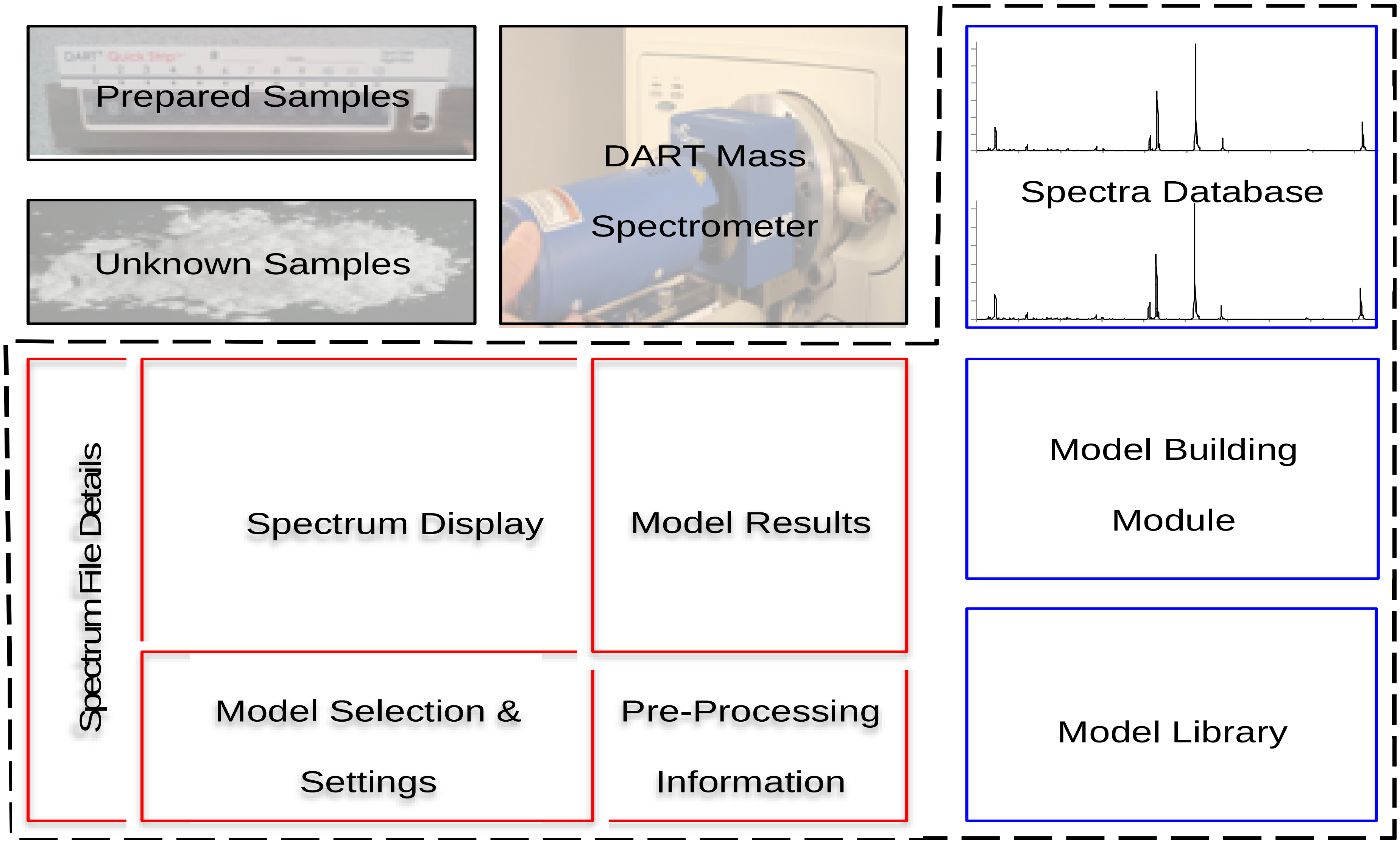


Table 2: Percentage cross-validation error of different machine learning methods and pre-processing methods with PCA used to build the algorithm to classify Alliant Reloder 19 smokeless powder

	Pre-processing Technique					
Method	Smooth	First Derivative	Normalize	# of PC	# (or average) incorrect	% Error
Linear Regression	Yes	No	Yes	100	5	3.33
Polynomial Kernal SVM	Yes	No	Yes	50	10.2	5.67 (C=0.1)
RBF Kernel SVM Euclidean Distance	Yes	No	Yes	50	21.4	11.89 (C=1)
RBF Kernel SVM Weighted Spectral Distance	Yes	No	Yes	5	33.2	18.44 (C=1, σ=0.01)
Sigmoid Kernel SVM	Yes	No	Yes	50	69	38.33 (C=10)
Weighted Spectral Linear SVM	Yes	No	Yes	100	13.8	7.67 (C=0.1)
K-Nearest Neighbors	Yes	No	Yes	50	19	10.56 (k=3)

Examination of Results of Statistical Analysis

- Models from original training set were built without post-processing of SPME DART mass spectra
  - 30 samples were used to build each model
  - Models were built for 3 different powders
  - Models were tested against new samples processed in same manner
    - Low numbers of false negative and false positive reported
    - Provided that a model for the powder existed in the data sets differentiation was achievable
    - When unknown powders were included in the blind study high number of both false negative and false positives

Examination of Results

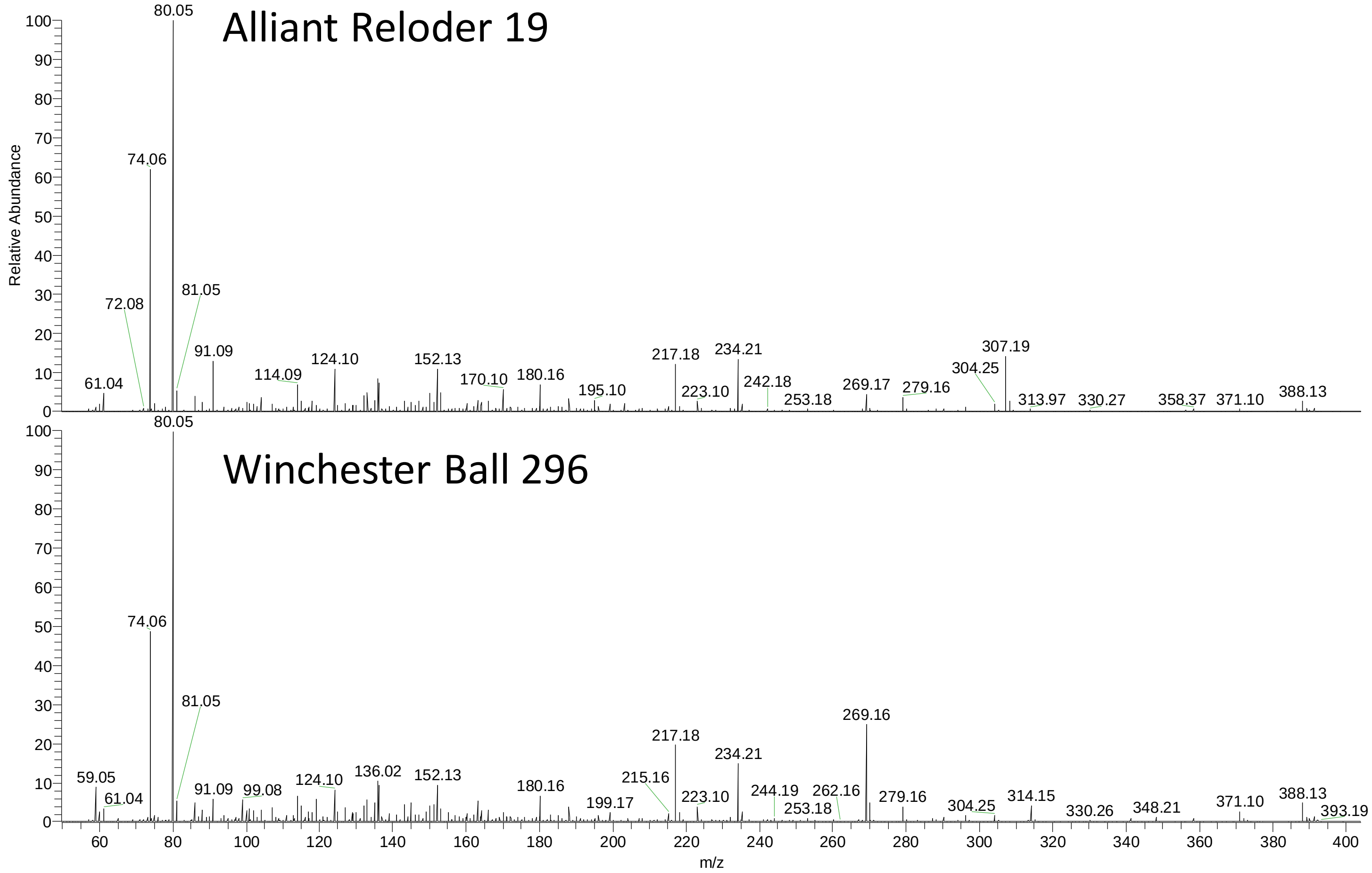
- Manual examination of data completed in order to investigate why the models failed to differentiate
  - Investigate individual spectra used to built models
    - Postulation was made that where spectra were similar due to large number of background ions being similar the statistical model were being differentiated by a few unique ions
    - Potential that the models were matching the modelled powders due to the large number of common background ions

Examination of Results of Statistical Analysis

- Decided to attempt improvement of the data by employing standard background subtraction of the mass spectra
  - Reprocessed spectra used to build original statistical models
  - Enhanced the appearance of signal from most explosive components (Figure 2)
  - Alliant Reloader (Figure 3)
  - Winchester Ball 296 (Figure 4)

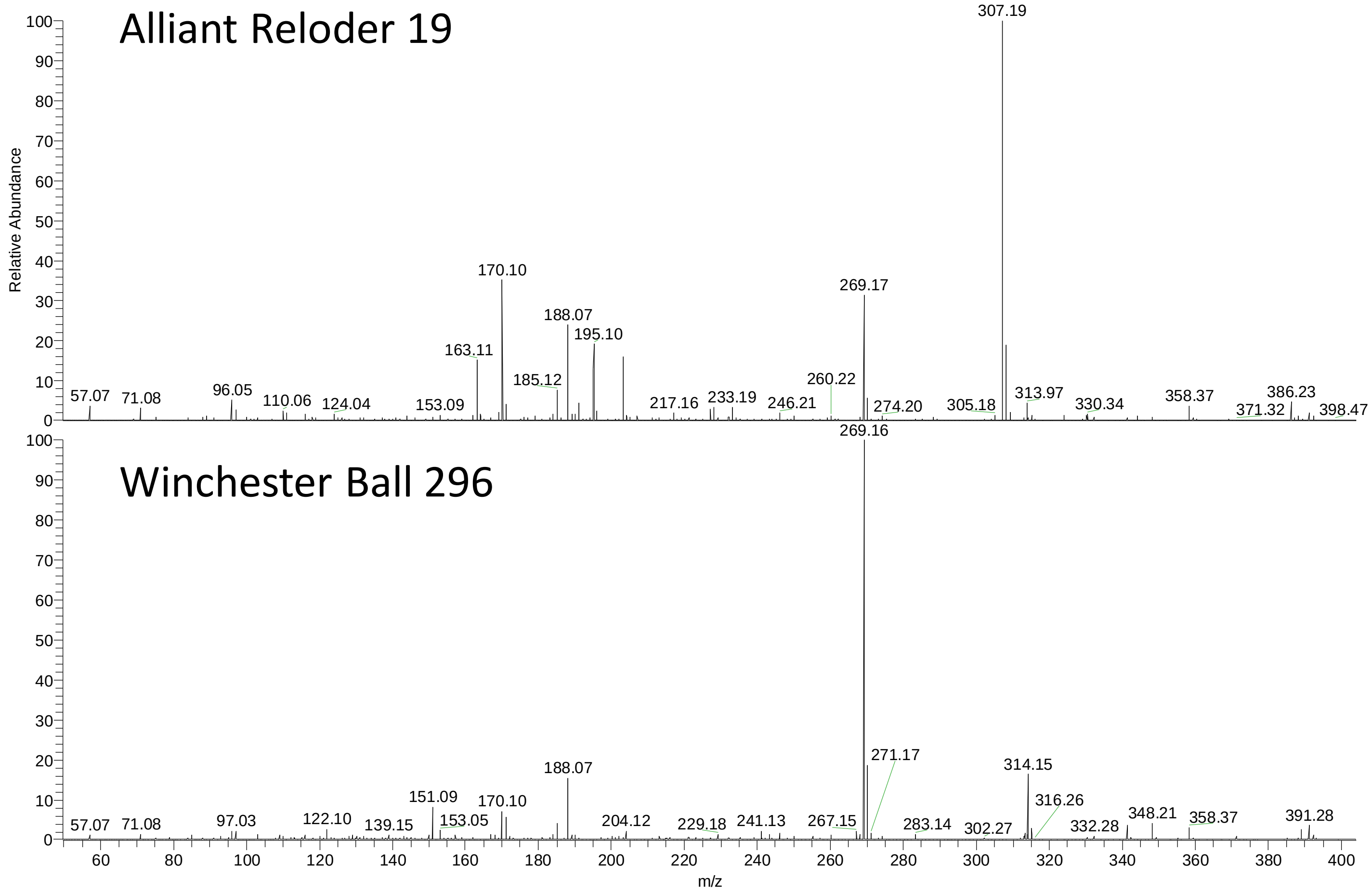
Comparison of 2 Smokeless Powders

Dynamic headspace data without background subtraction



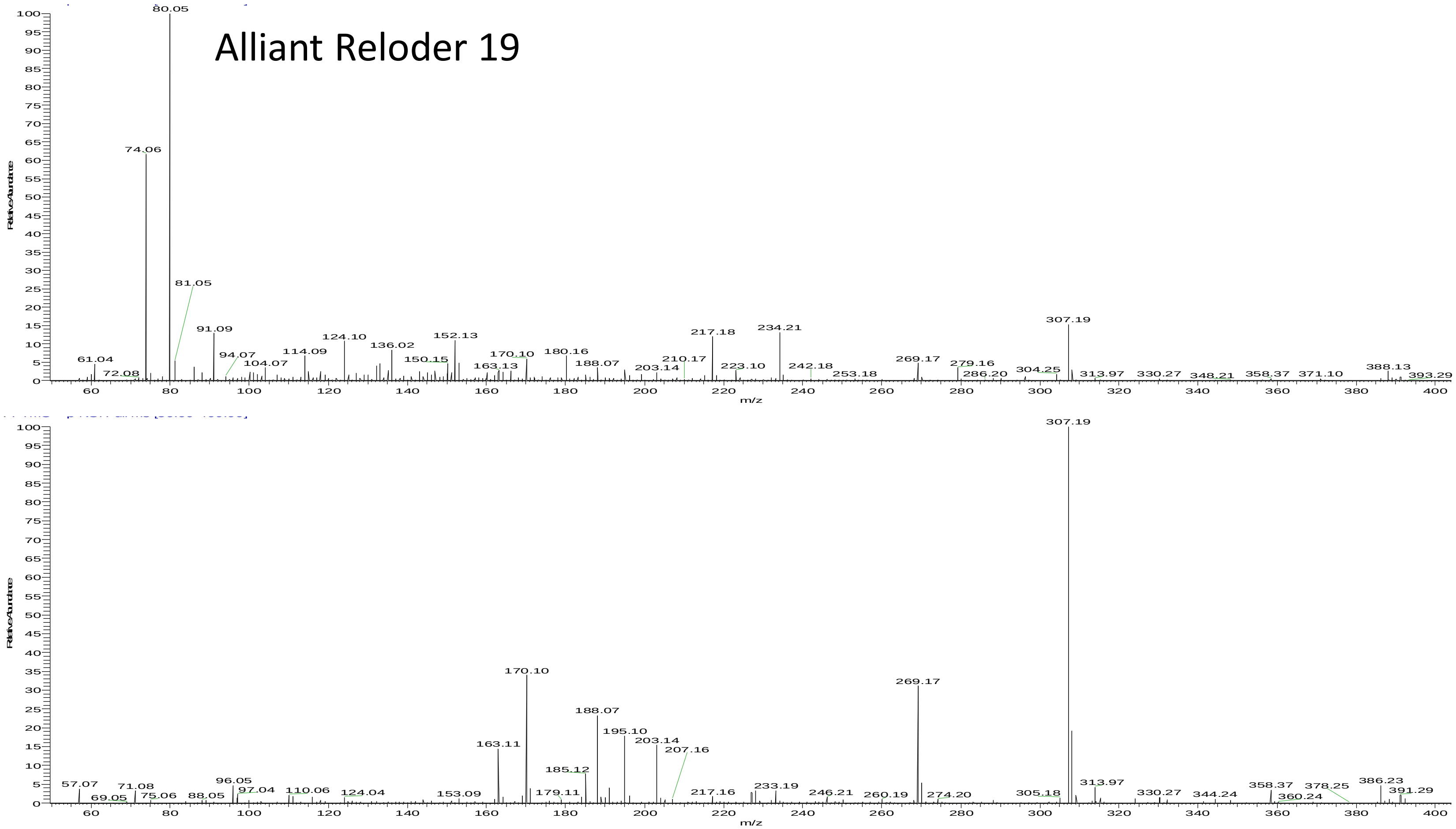
Comparison of 2 Smokeless Powders

Dynamic headspace data with background subtraction



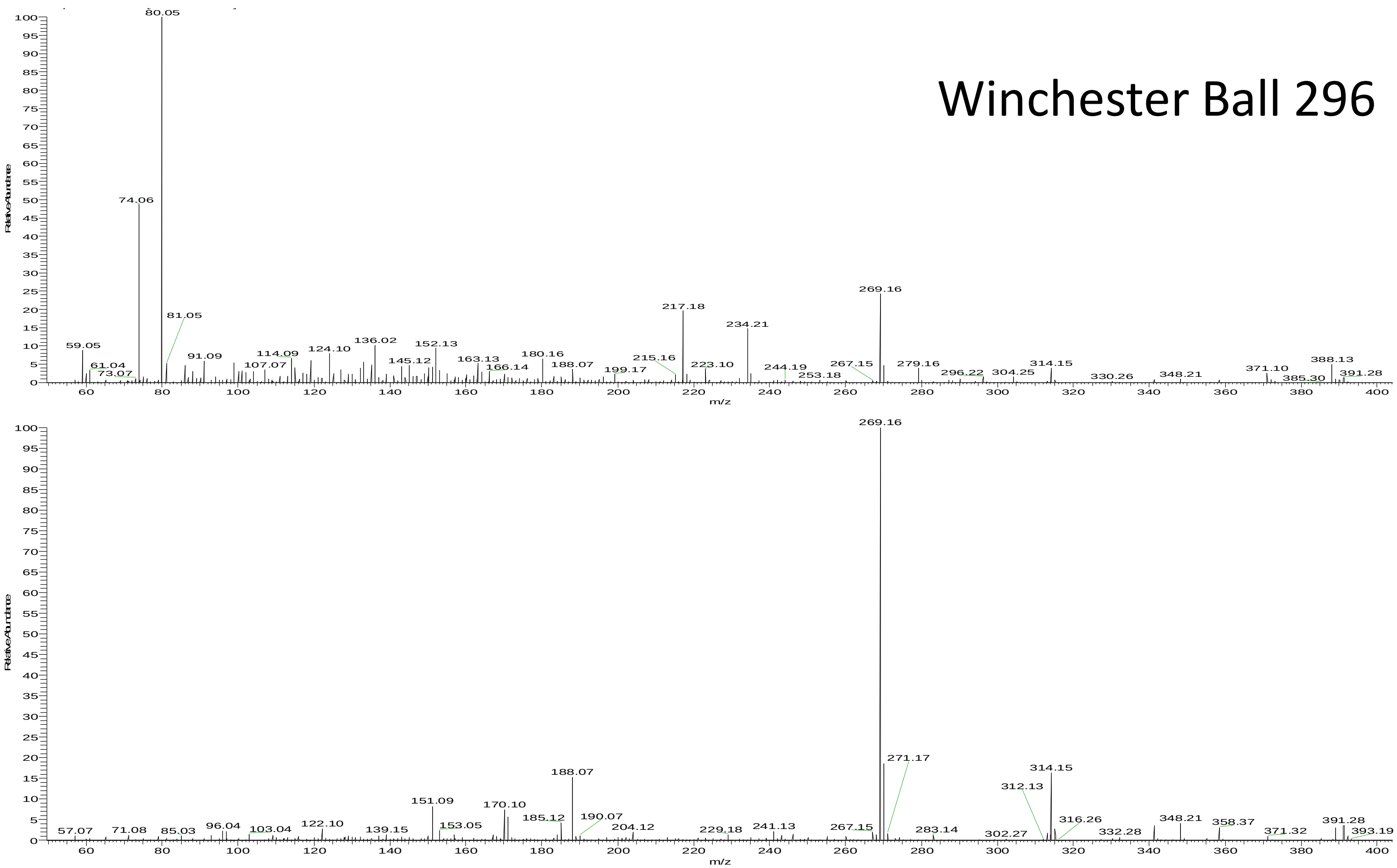
Alliant Reloder 19 Smokeless Powder

Without (top) and with background subtraction (bottom)



Winchester Ball 296

Without (top) and with background subtraction (bottom)



Conclusion: SPME DART and Spectrum Processing

- A Dynamic Headspace device has been used to complete sampling of explosive powders (burnt and unburnt) for analysis in 5 minutes post-sampling
- DART-MS of the SPME coated wire mesh yield good quality mass spectra in 15-20 seconds
- 30 samples were prepared for each statistical model thus a model can be built rapidly in under 3 hours.
- SPME-Headspace DART permits rapid determination of powder type using untreated mass spectra provided that a statistical model for the powder has been determined
- SPME-Headspace DART permits rapid differentiation of powder type with capability for distinguishing knowns from unknowns provided that background subtracted mass spectra are utilized to generate statistical models.
- Post-explosion analysis for presence of exploded residue on objects is possible by using background subtracted data for model building

The author thank DHS Forensics for funding under BAA--13--007

Contract title: Sample Collector for Rapid Direct Ionization in Real Time