THE USE OF DIRECT ANALYSIS IN REAL TIME (DART)-MS FOR THE DETECTION OF PESTICIDES IN FOOD SOURCES

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BMSS Annual Meeting
September 6, 2010

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Overview

- **Direct Analysis in Real Time (DART) Technology**

- **Traditional Sampling – DIP-it Tips**
  - Limitations:
    - Difficulty reproducing the ionization exposure time, sample positioning and object size
    - Programmable robotic stage has improved reproducibility

  - **Developed a variety of sample positioning devices:**
    - **Transmission DART (T-DART)**
      - Metal mesh used as sampling substrate
        - Prolonged analyte signal

    - **"3+D" Three Dimensional Scanner**
      - Improves sample throughput

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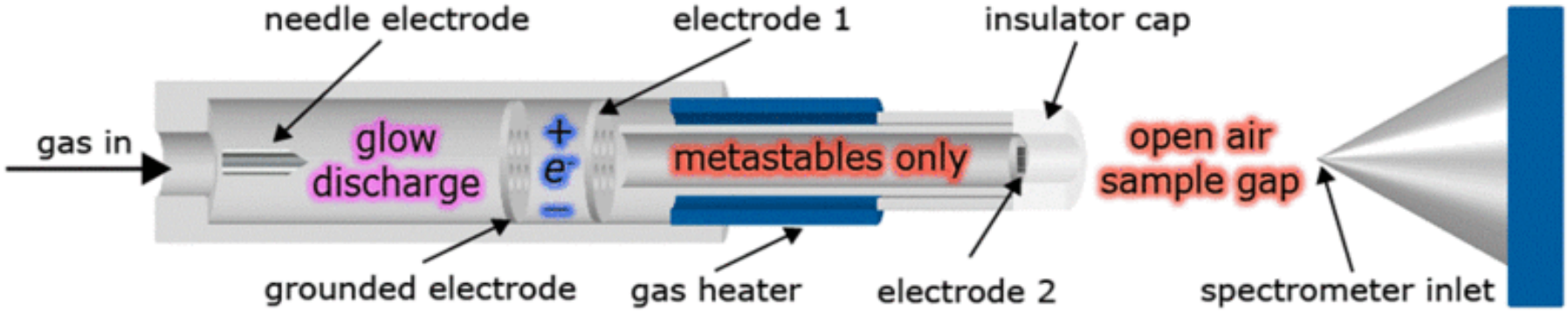
Direct Analysis in Real Time (DART)

- $M^* + S \rightarrow S^{+\bullet} + M + e^-$
- Where *M* is *excited* Helium ('positive' mode):
  - $\mathbf{He}(2^3s) + H_2O \rightarrow H_2O^{+\bullet} + \mathbf{He}(1^1s) + e^-$
  - $H_2O^{+\bullet} + H_2O \rightarrow H_3O^+ + OH^\bullet$
  - $H_3O^+ + nH_2O \rightarrow [(H_2O)_nH]^+$
  - $[(H_2O)_nH]^+ + \mathbf{S} \rightarrow \mathbf{S}H^+ + {}_nH_2O$



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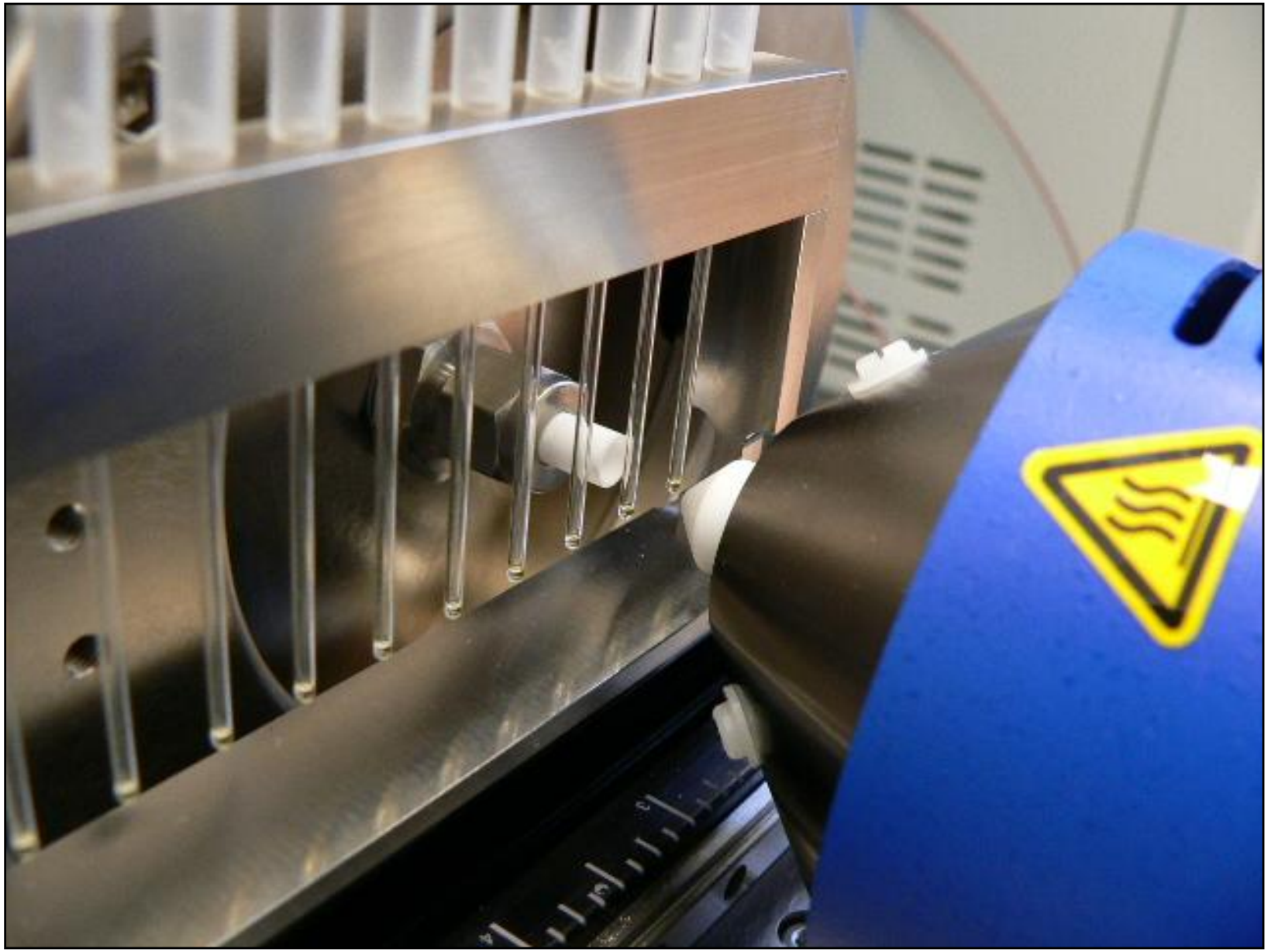
Cody et al. Anal. Chem. 2005; Image: JOEL USA, Inc.

Traditional DART Sampling

12 DIP-it Module



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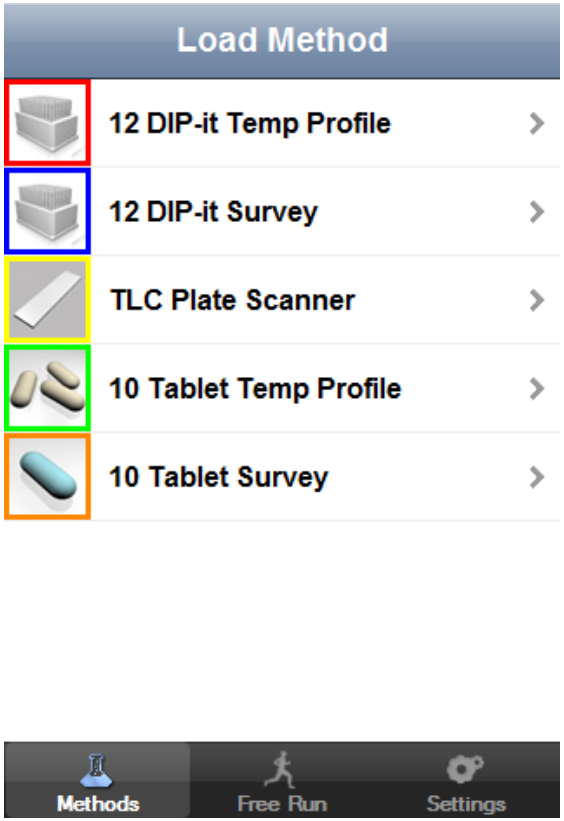
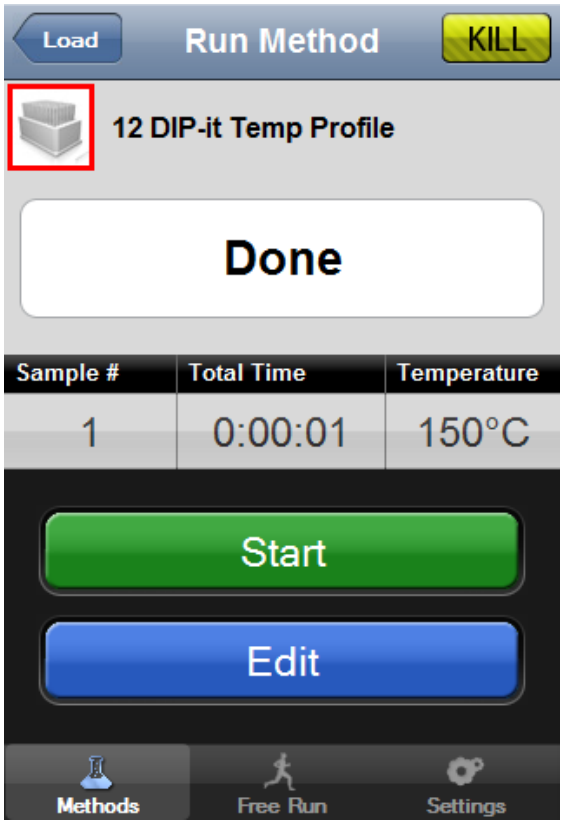
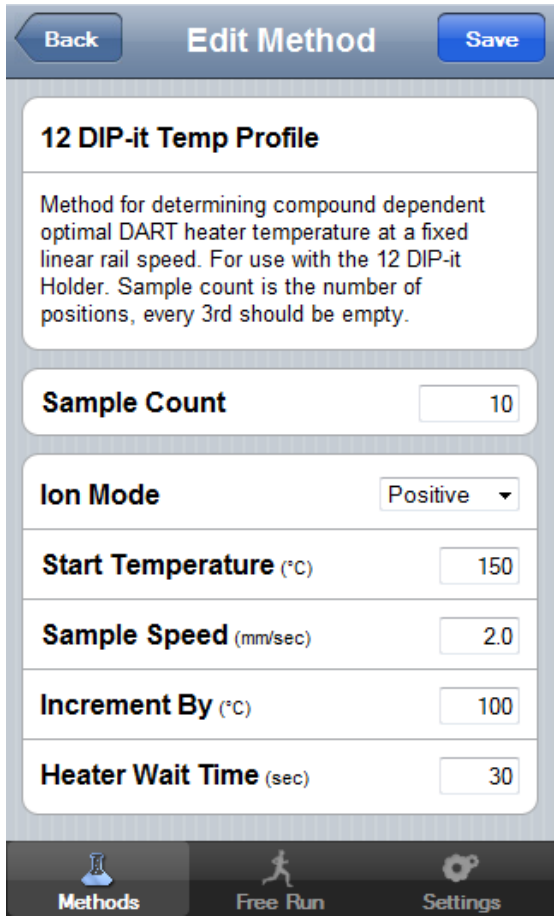
DART GUI: Automated Methods







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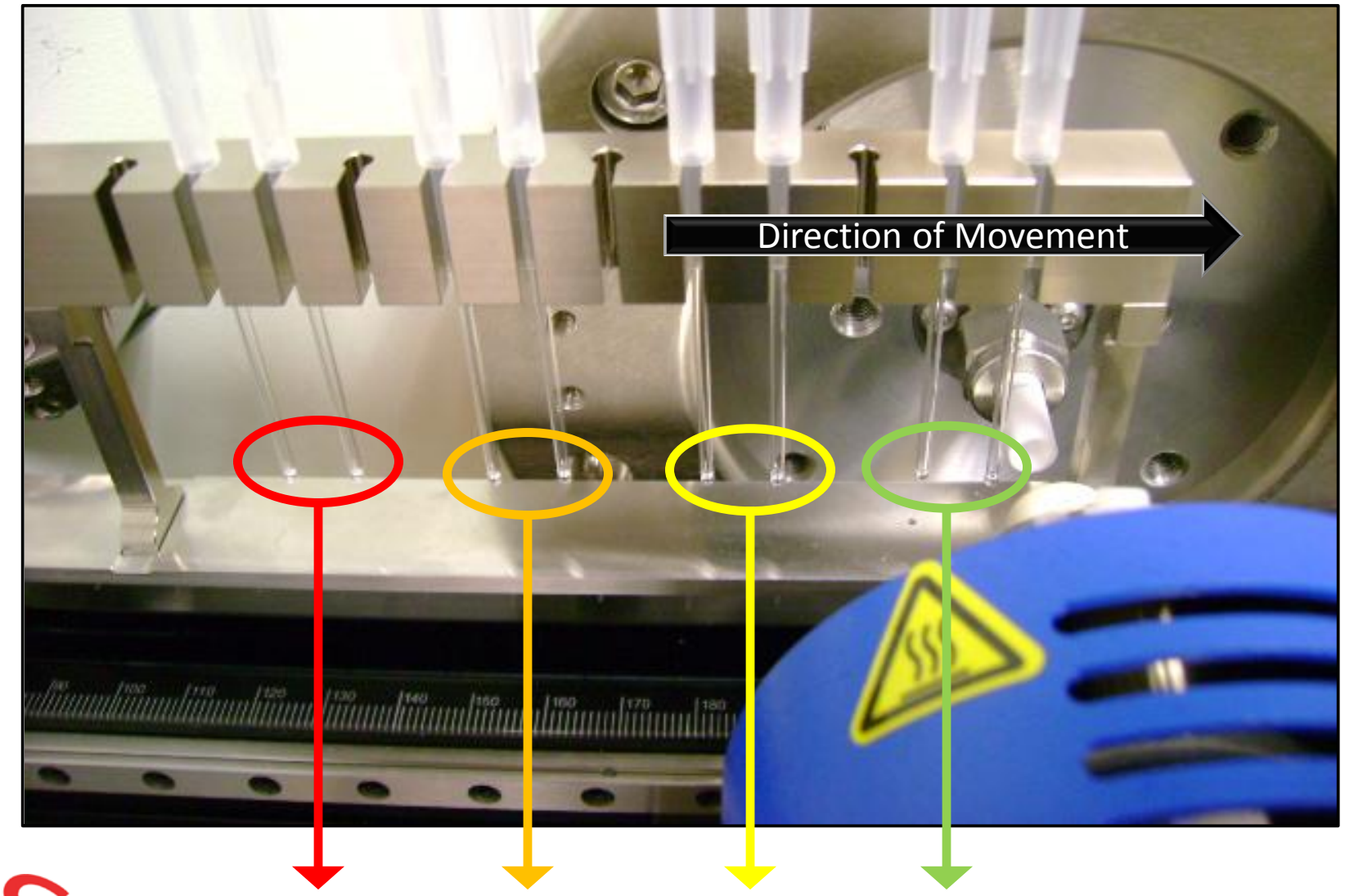
Thermal Profiling Experiment:
Single Dimension Automated Set-up with DIP-it Tips



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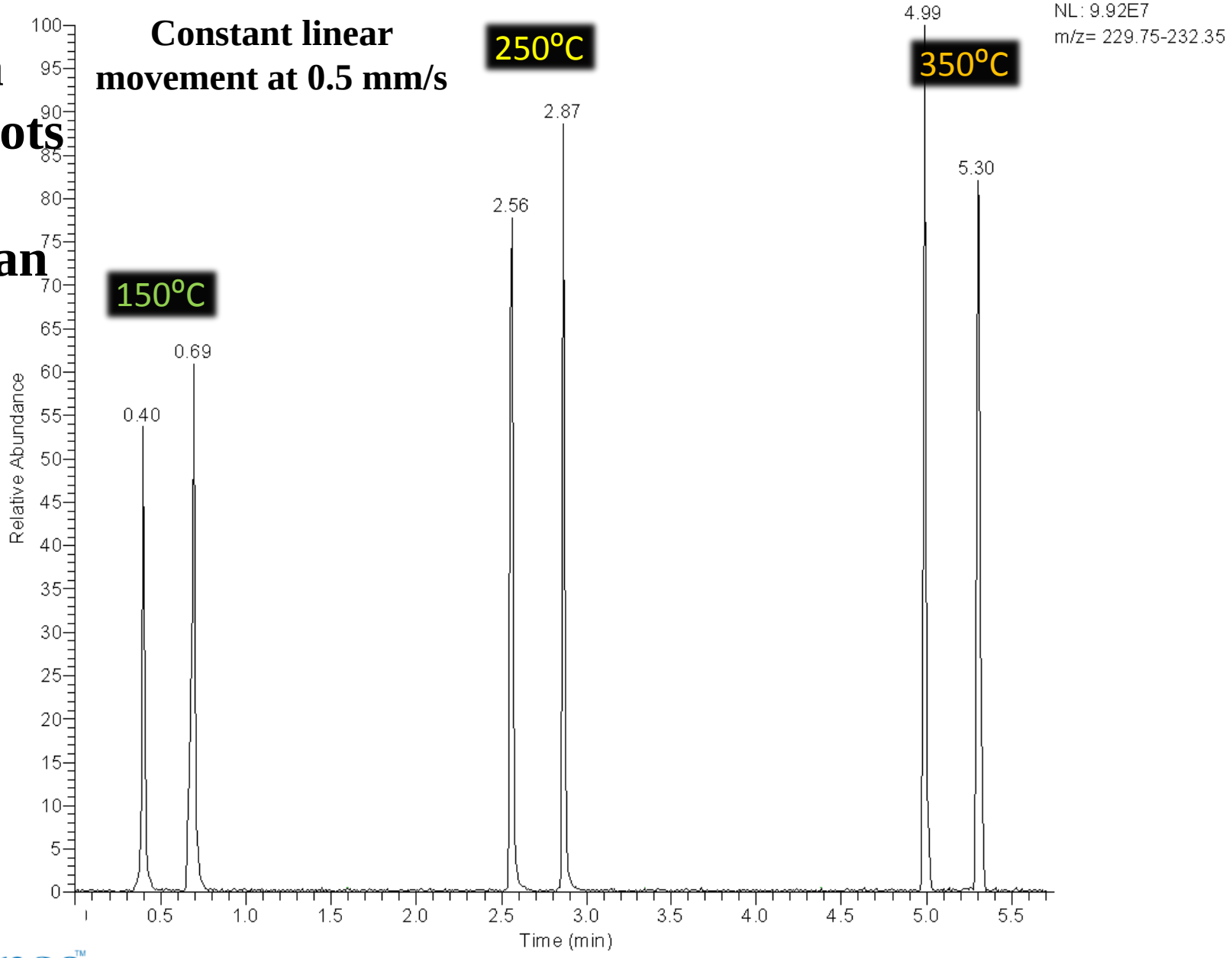
Temp Ramp DIP-it Tips - Dimethoate (Neat)

10 ppm
2 uL spots

Full Scan



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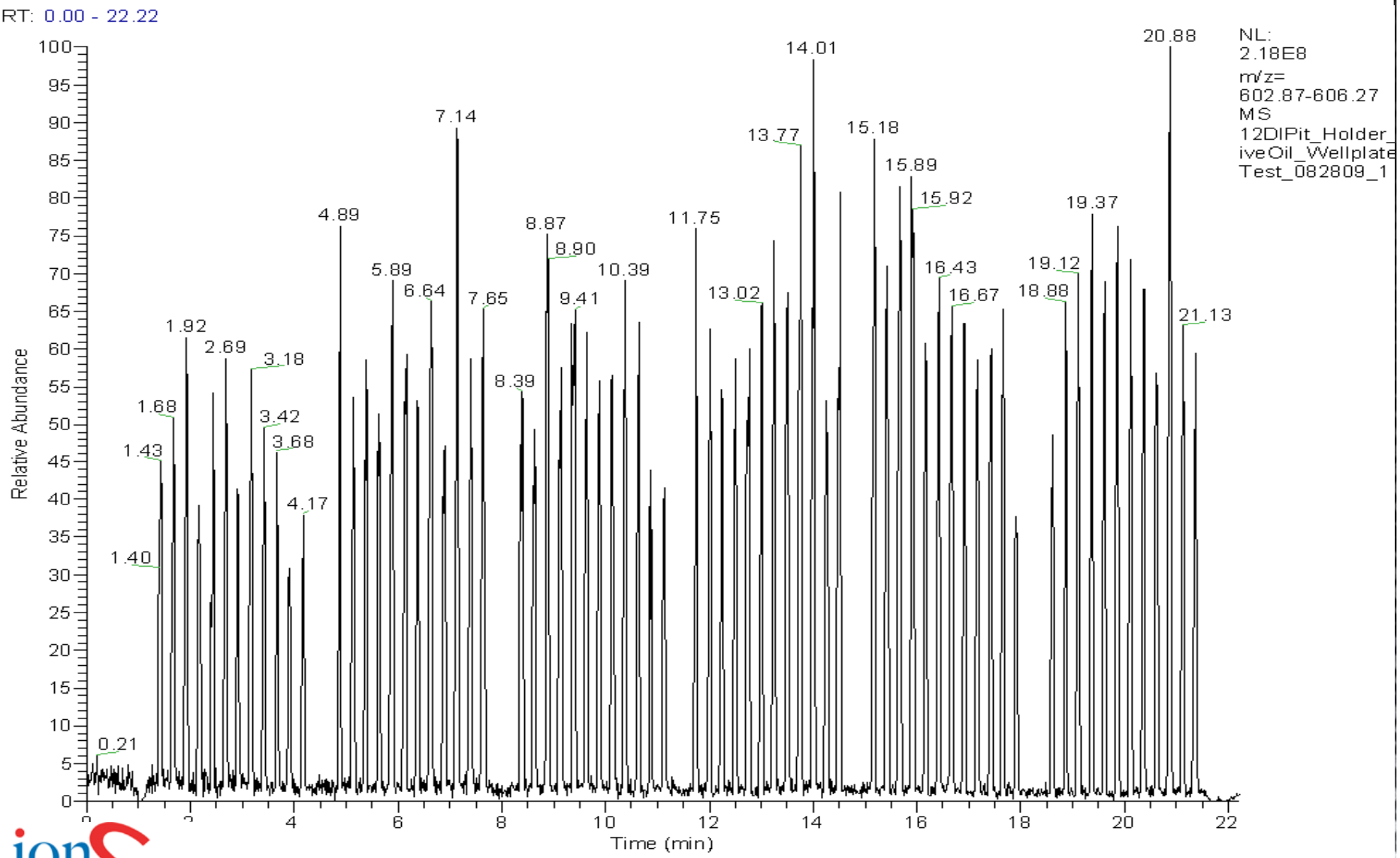
Typical Chromatogram for DART-MS Analysis using DIP-it Tips with 2 uL Sample Spots



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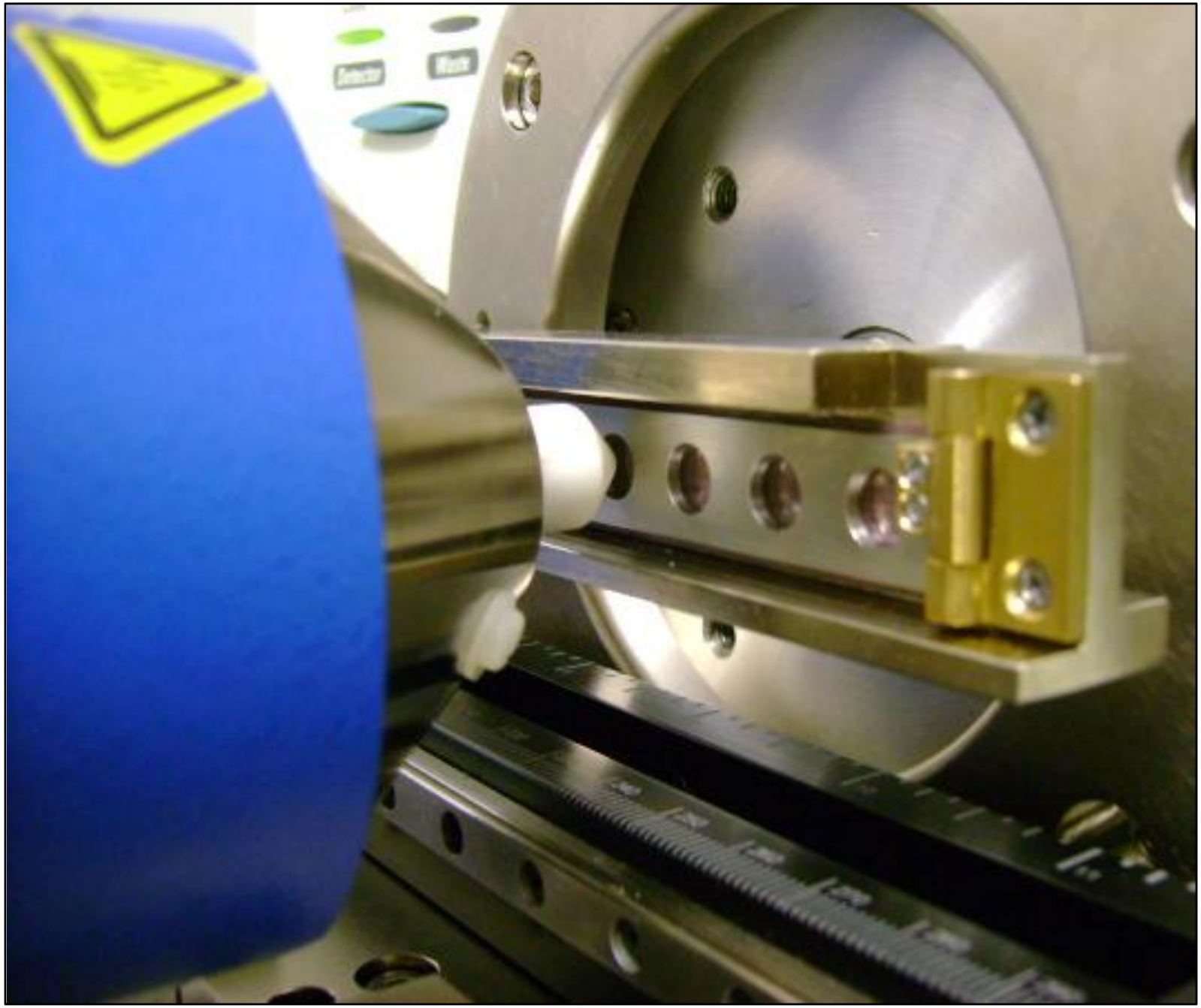
Transmission DART



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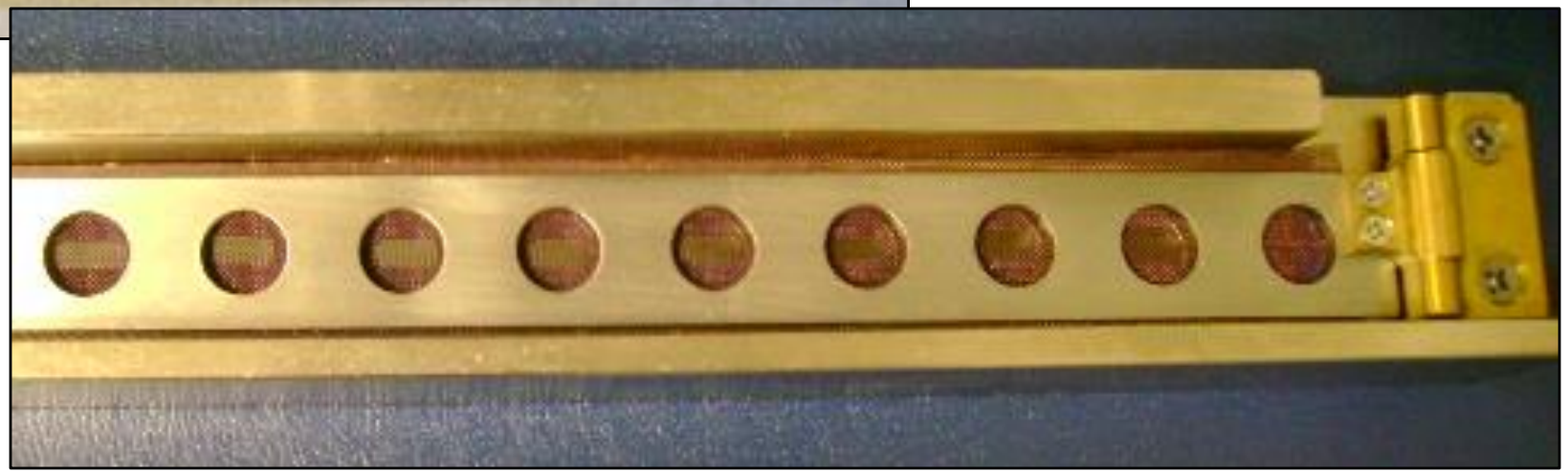
Stainless steel mesh screens with 0.004 inch strand diameter

10 uL of liquid sample pipetted onto stainless steel mesh screen and allowed to completely dry



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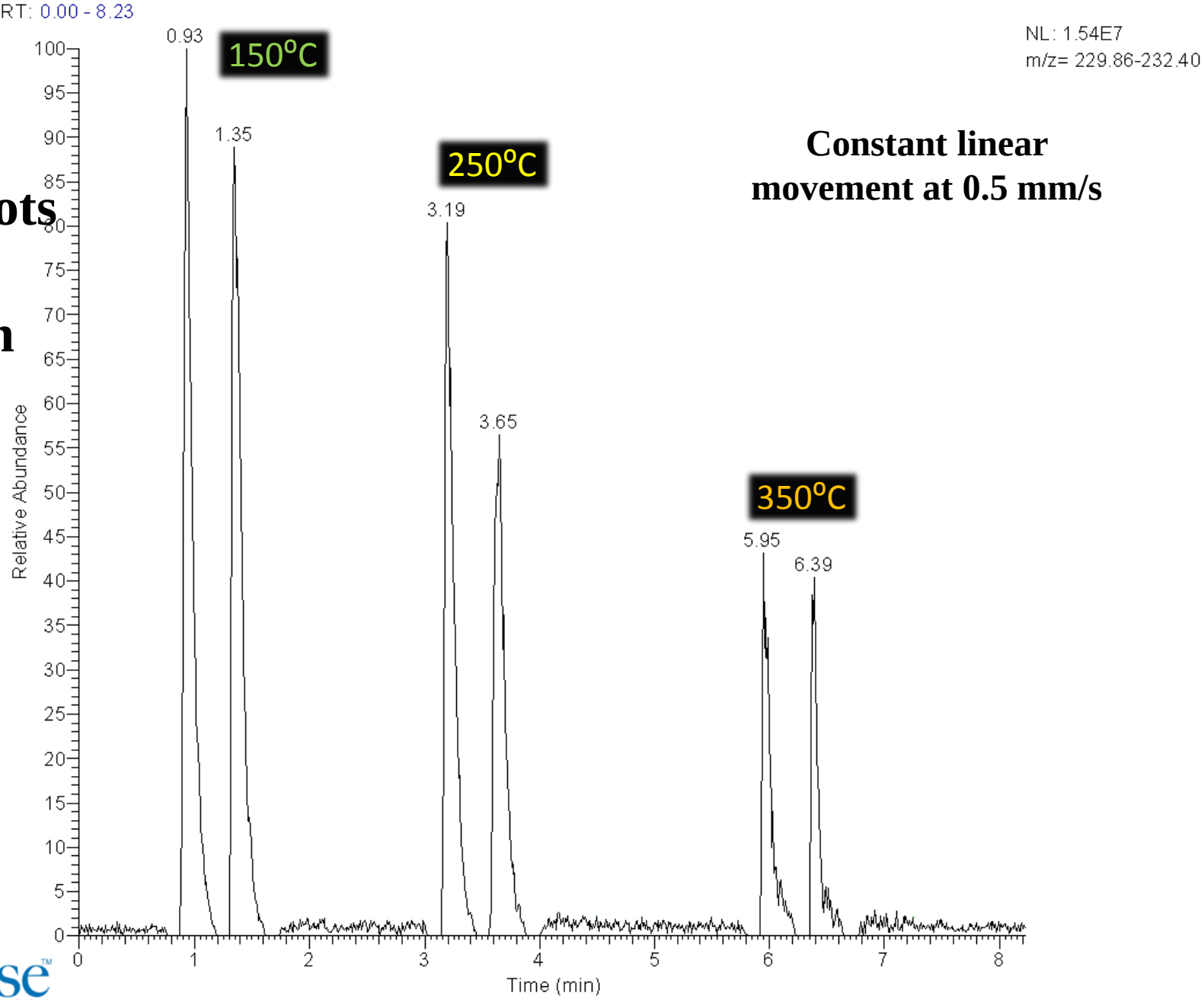
Temp Ramp Metal Mesh - Dimethoate (Neat)

10 ppm
10 uL spots

Full Scan



Constant linear movement at 0.5 mm/s

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Transmission Mode DART for MS/MS Tuning:
Method for Automated Sample Introduction

- **Transmission DART** experiment module secured on linear rail.
- **"Start" Method…**
  - DART source automatically heats to desired **"Run" temperature**.
  - Once the desired heater temperature is reached:
    - The linear rail automatically positions the first sample in the DART ionization area.
    - Each sample was held for **10 seconds** in the DART ionization region.
    - At the end of the sample analyses the source cools down and is set to **"Off"** or goes into **"Standby"** and maintains the "Run" heater temperature.

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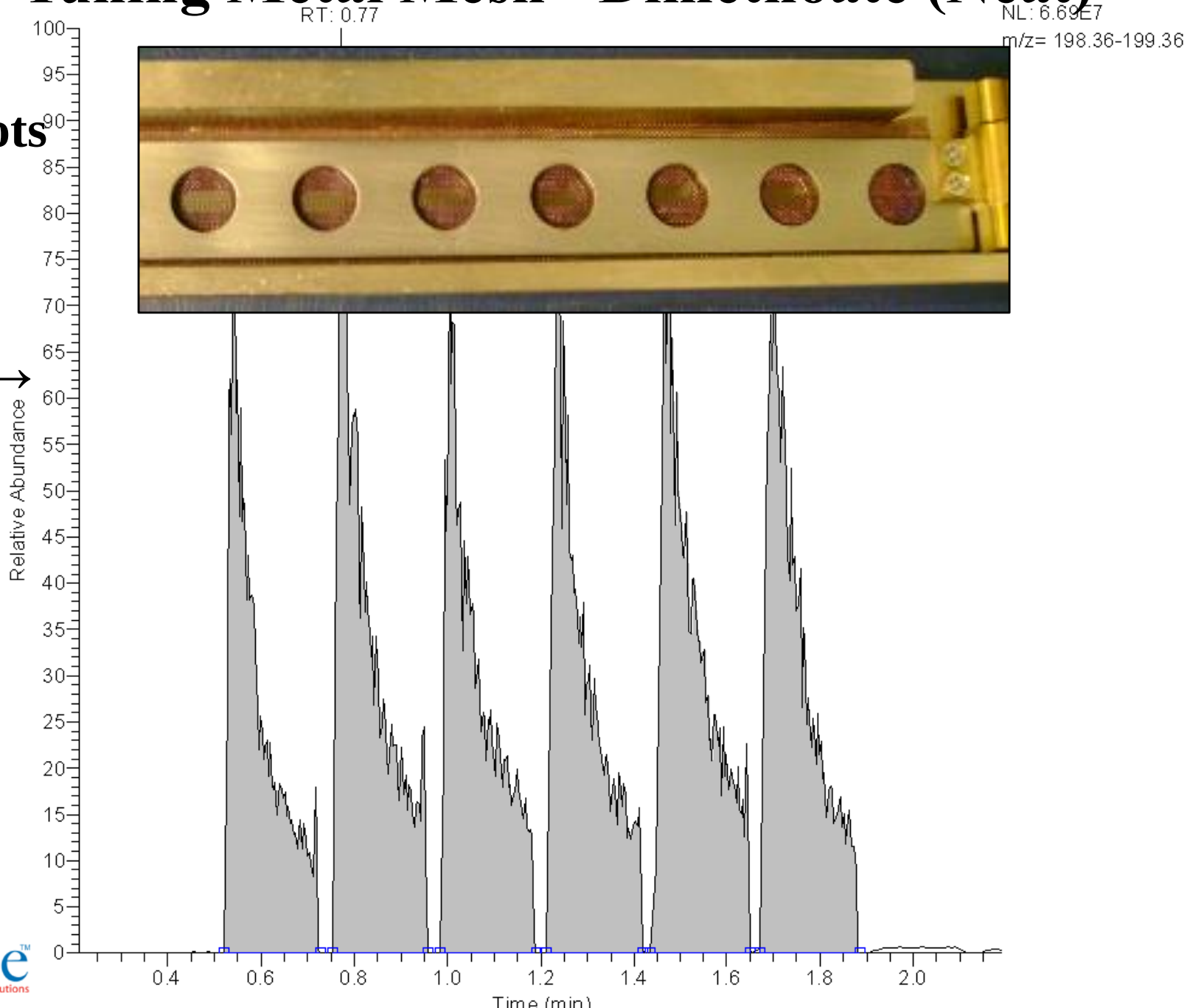
MS/MS Tuning Metal Mesh - Dimethoate (Neat)

10 ppm
10 uL spots
DART
150 º C

m/z 230 →
m/z 199



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Dimethoate Spiked into Apple Juice:

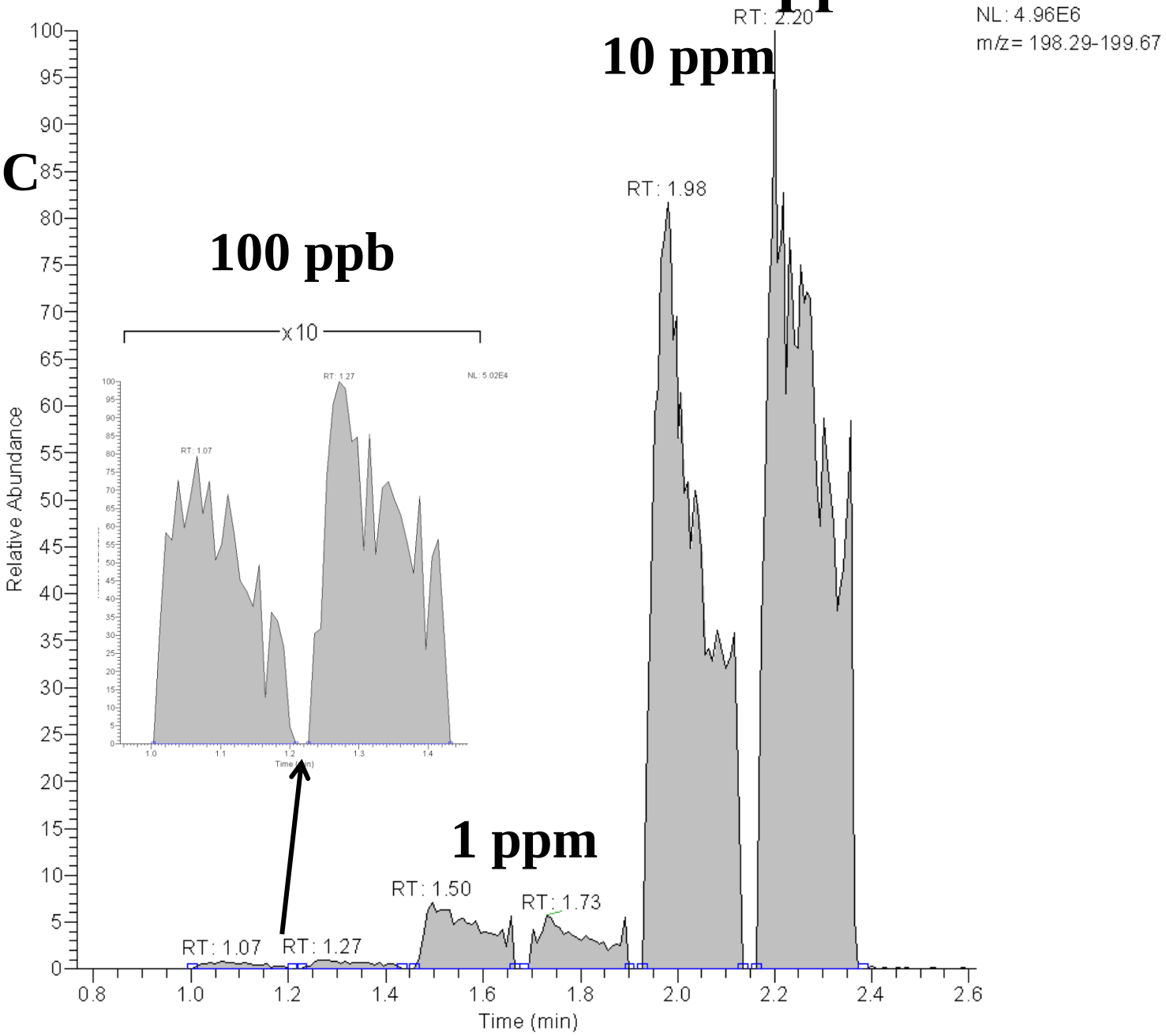
Samples prepared in Apple Juice at:

- **10 ppm**
- **1 ppm**
- **100 ppb**

SRM: Metal Mesh - Dimethoate in Apple Juice

10 uL spots
DART 150º C

SRM:
m/z 230 → m/z 199
23 eV



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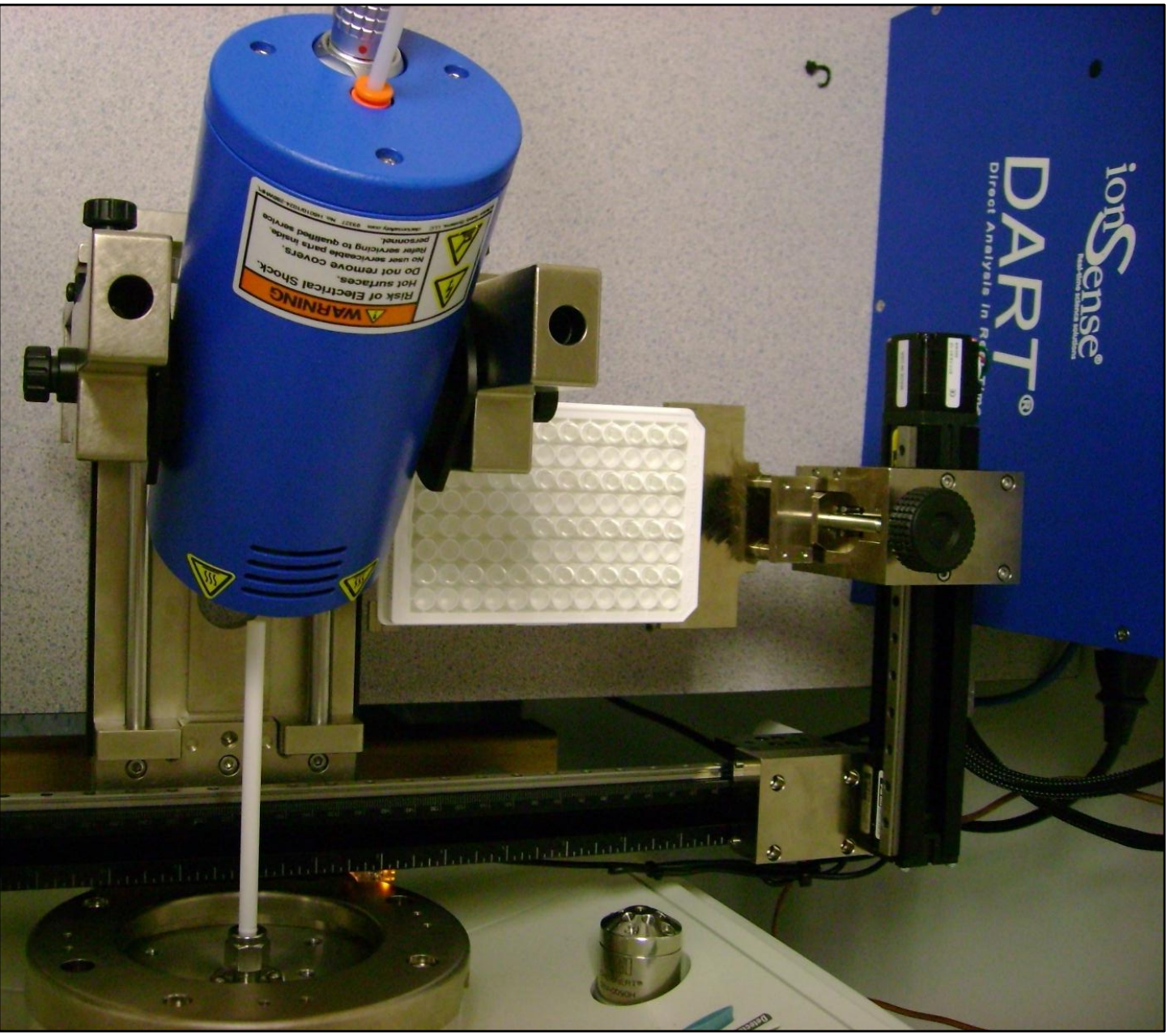
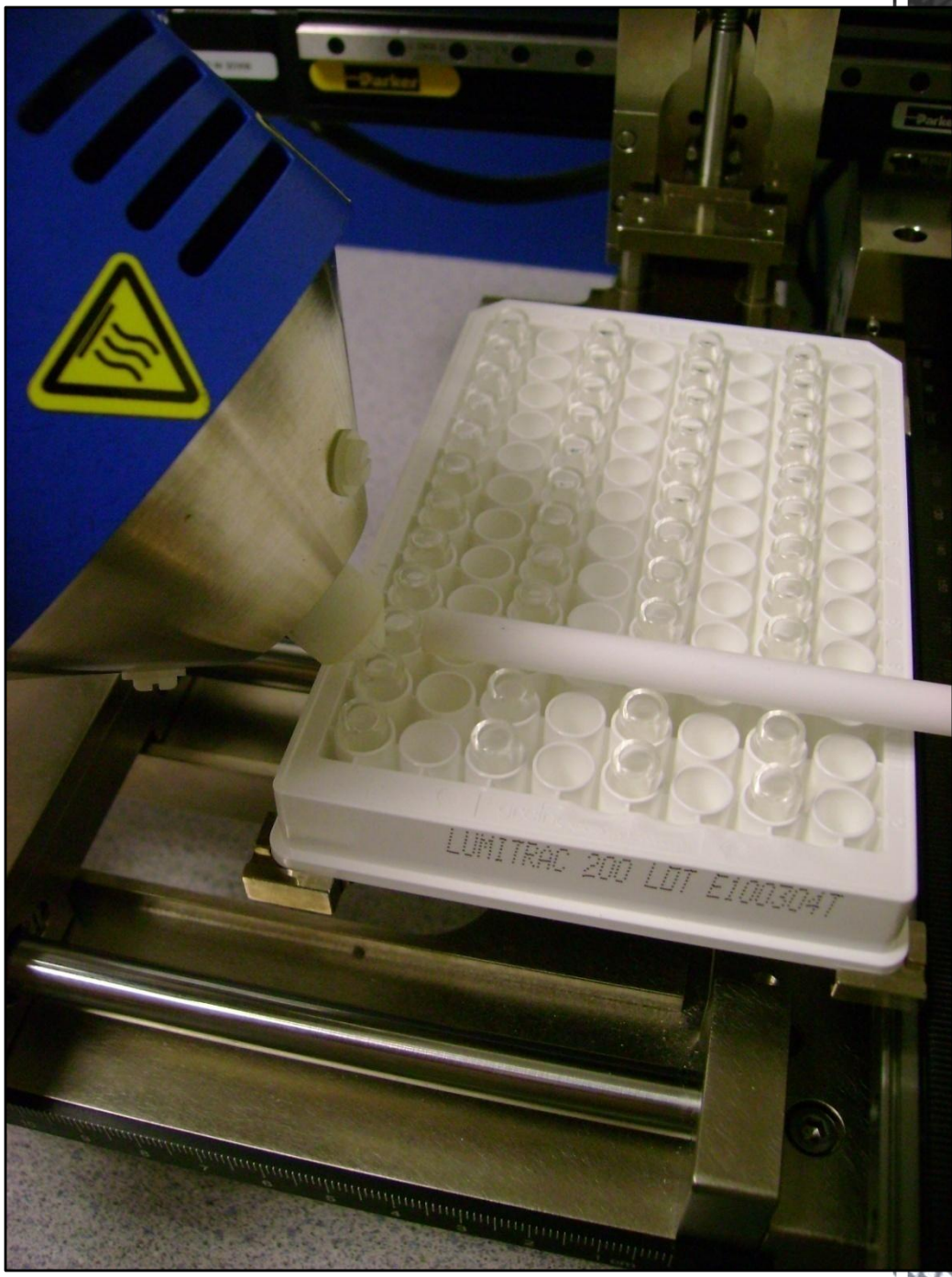
3+D Scanner



Glass inserts with 6 mm diameter

Samples (5 uL) were pipetted directly onto the top surface of the glass and allowed to dry before DART analysis



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3+D Scanner DART:
Method for Automated Sample Introduction

- Load 96-well titer plate onto the tray holder.
- **"Start" Method…**
  - DART source automatically heats to desired **"Run" temperature**.
  - Once the desired heater temperature is reached:
    - The linear rail automatically positions the first sample in the DART ionization area.
    - Each sample was held for **5 seconds** in the DART ionization region.
    - The method currently samples up to **48 samples** in **14 minutes**.

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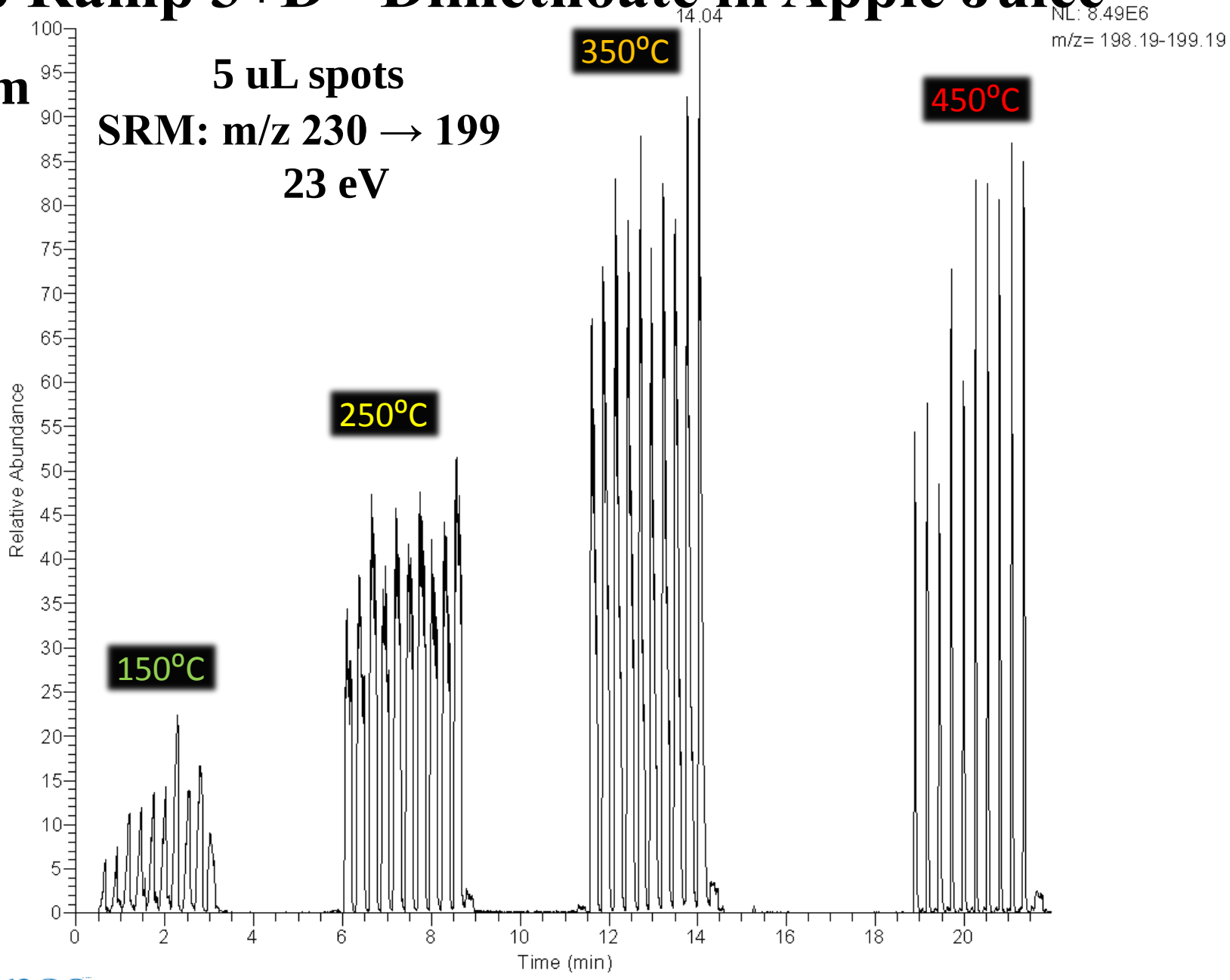
Temp Ramp 3+D - Dimethoate in Apple Juice

10 ppm

5 uL spots

SRM: m/z 230 → 199

23 eV



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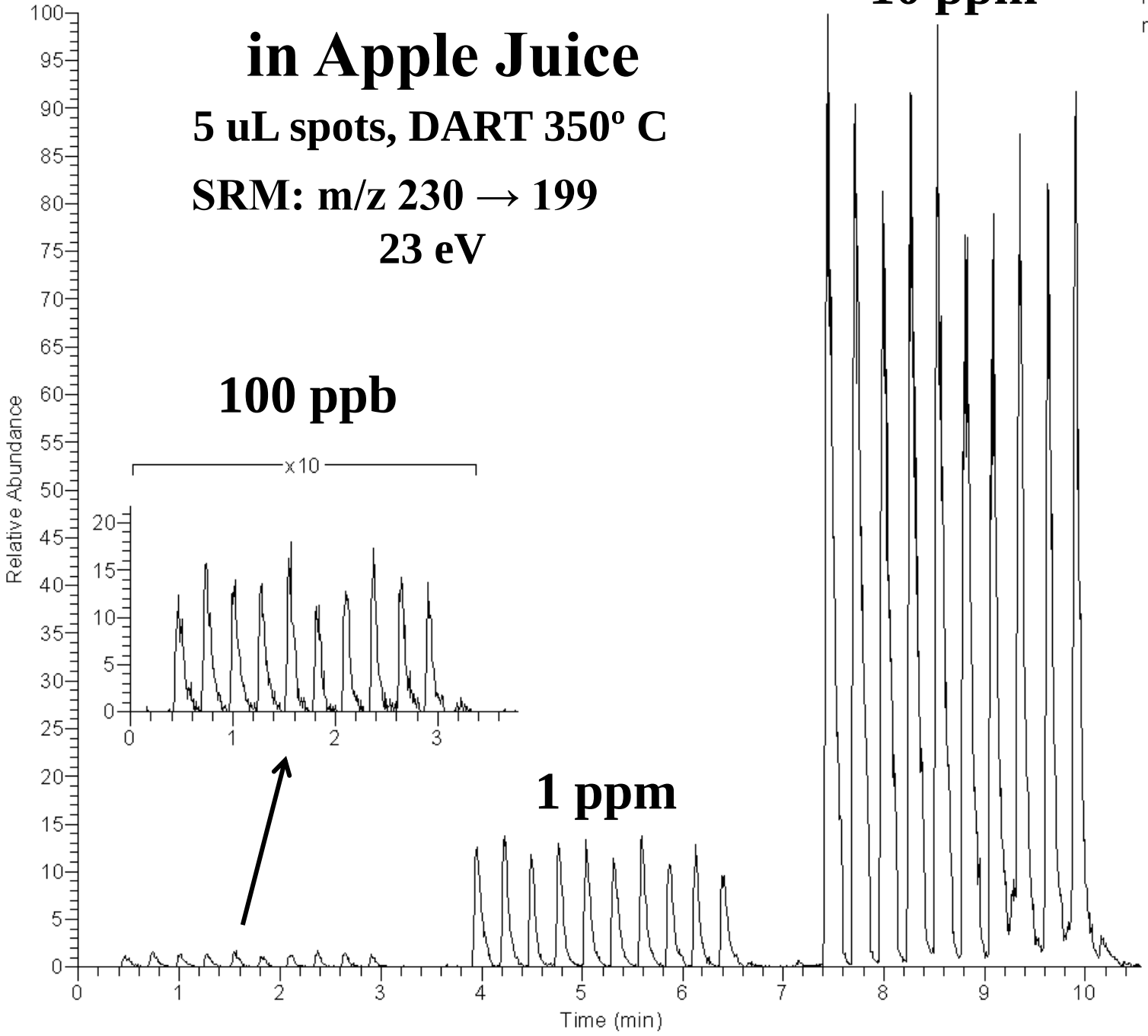
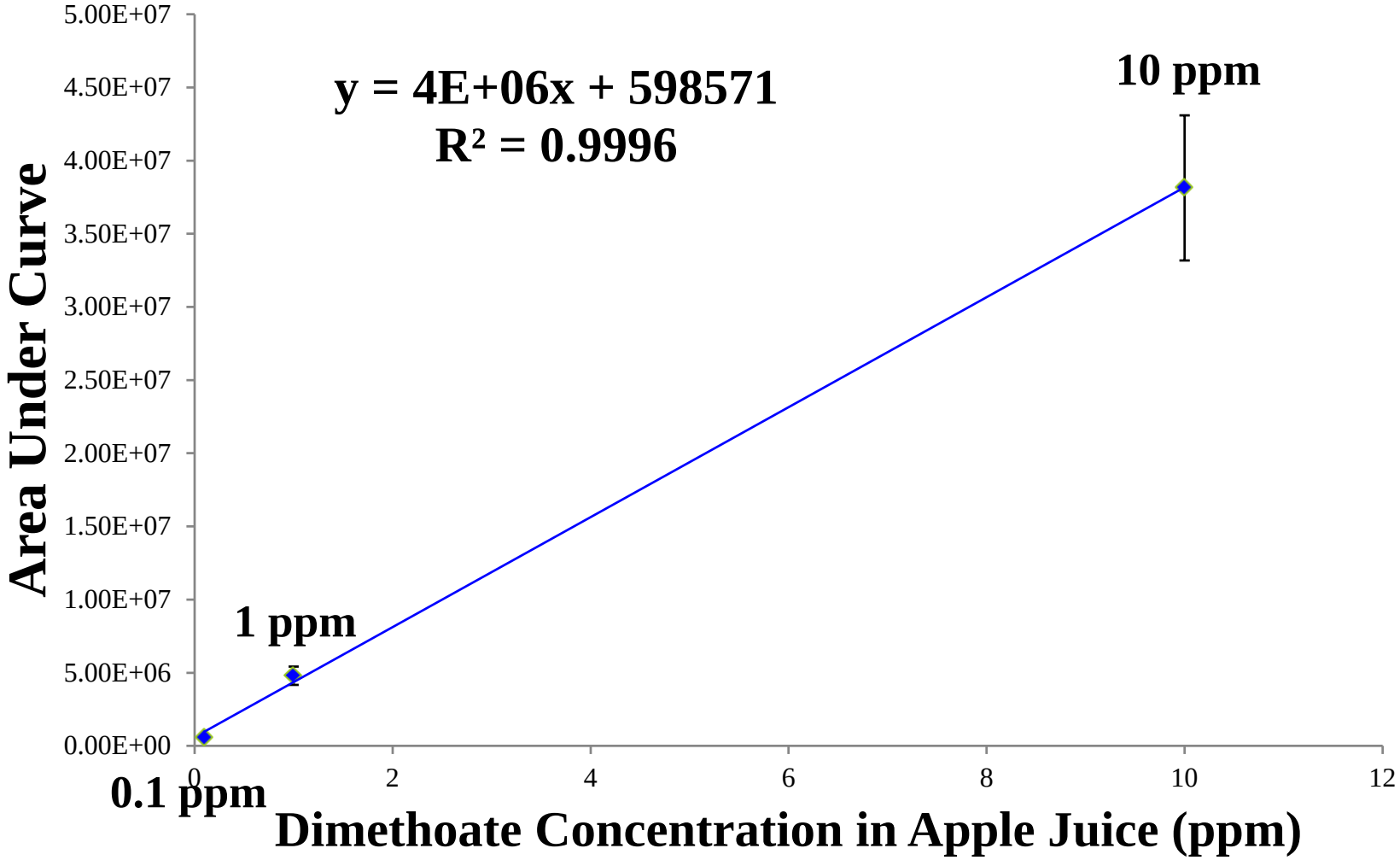
3+D Scanner - Dimethoate in Apple Juice

5 uL spots, DART 350º C

SRM: m/z 230 → 199
23 eV



DART-MS/MS Detection of Dimethoate Direct from Apple Juice



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3+D Scanner DART:
Analyzing a Pesticide Mixture

- **Pesticide Mix 2**
  - Provided by the US FDA
    - **Contained 140 pesticides**
      - Most of the pesticide standards were obtained from the U.S. EPA Pesticide Repository (Ft. Meade, MD), whereas others were obtained through Fluka/Sigma Aldrich (St. Louis, MO), Wako Chemicals USA (Richmond, VA), Honeywell Riedel-de Haën (Seelze, Germany), and EQ Laboratories, (Atlanta, GA).

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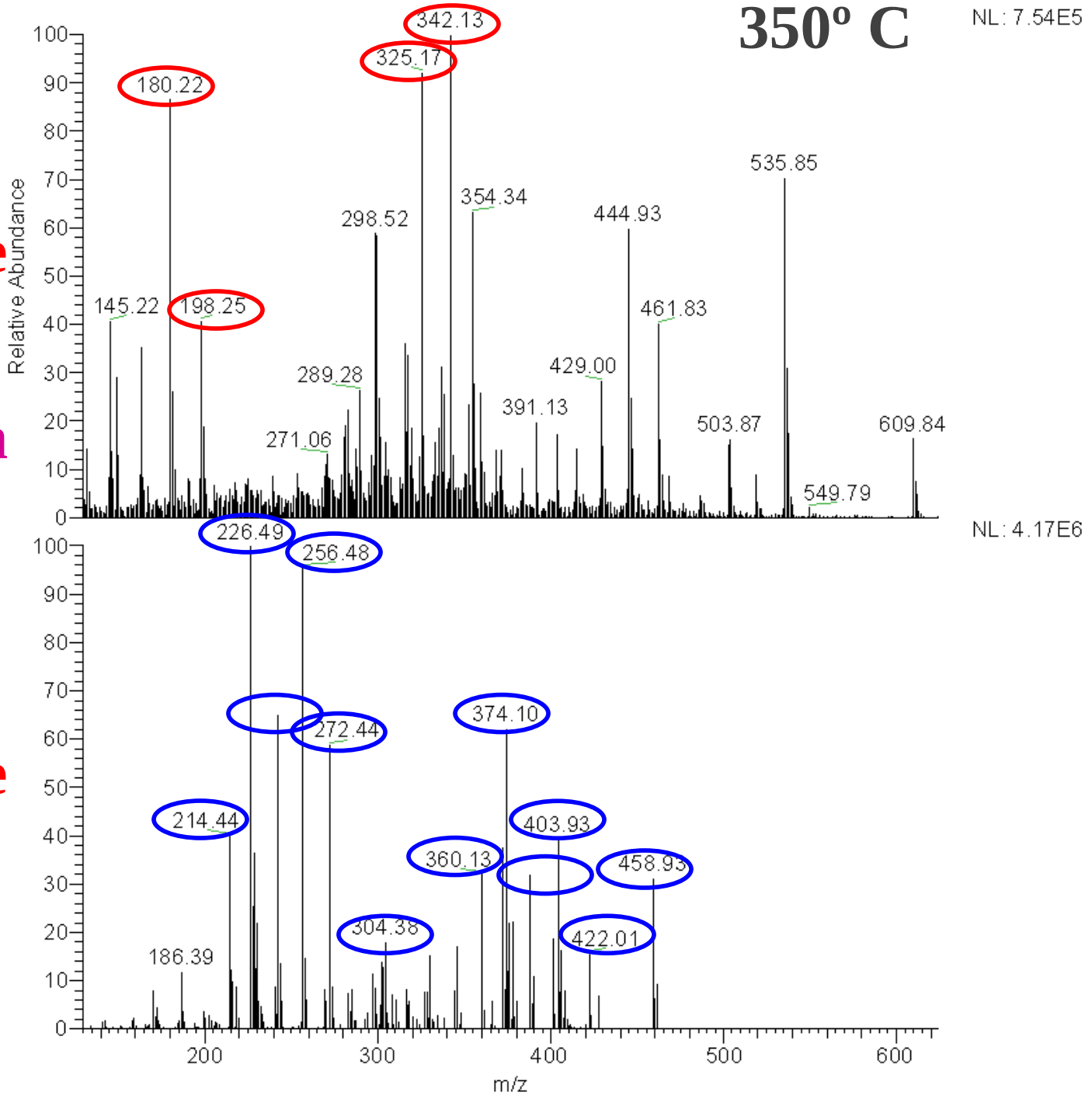
DART Spectra

Apple Juice Blank

Positive Ion Mode

Pesticide Mix 2 in Apple Juice 1.2 ppm



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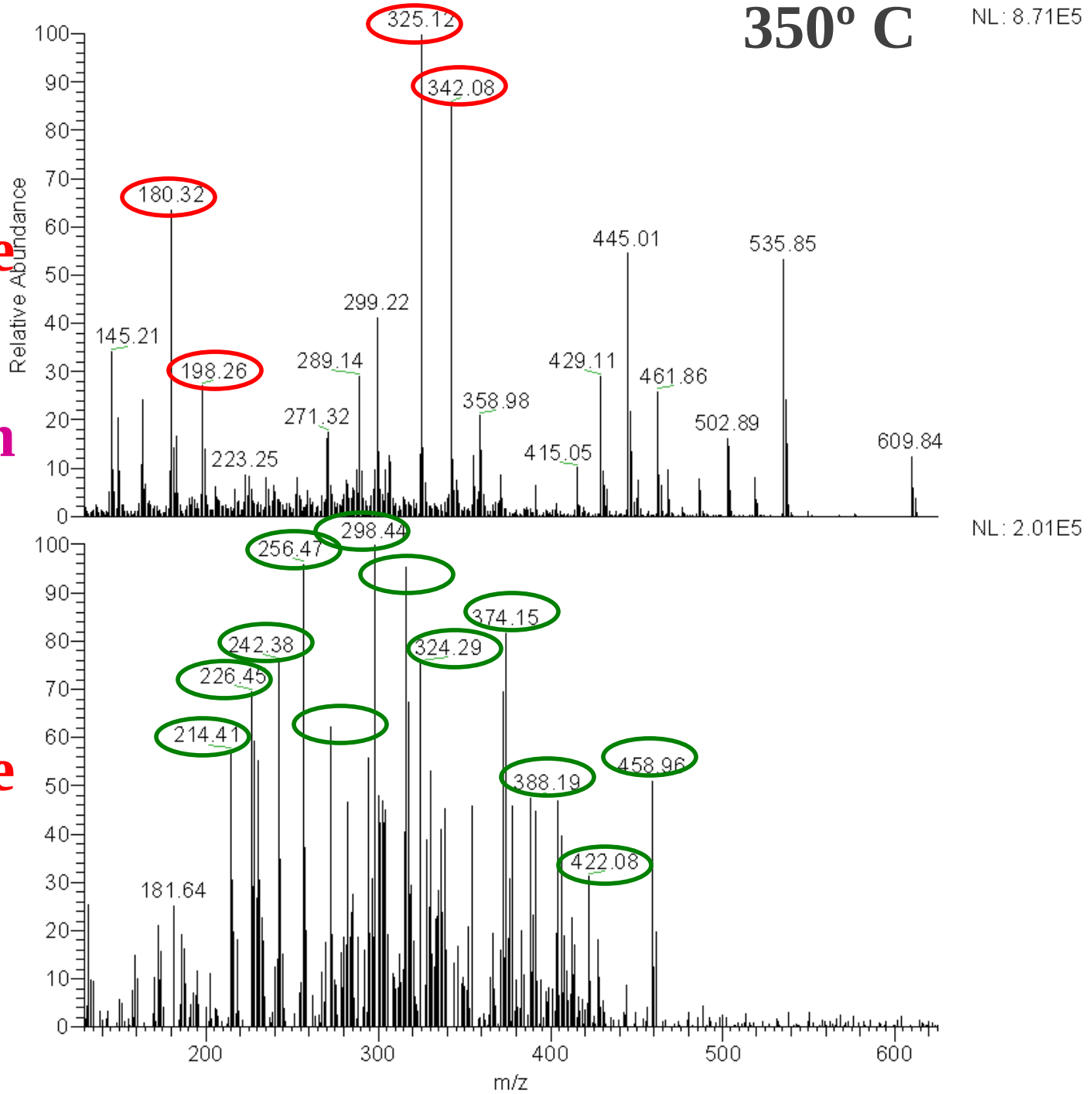
DART Spectra

Apple Juice Blank

Positive Ion Mode

Pesticide Mix 2 in Apple Juice 120 ppb



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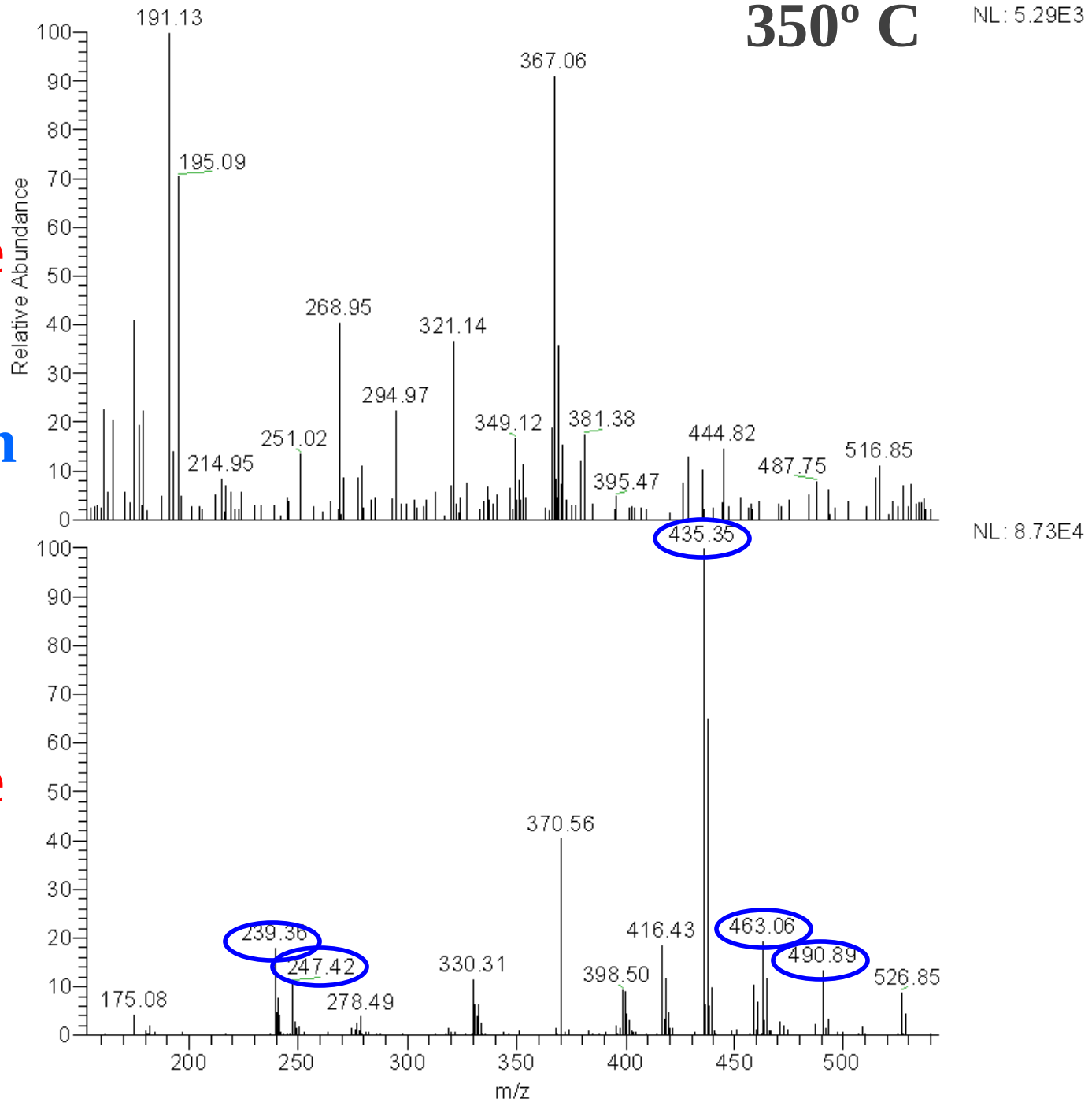
DART Spectra

Apple Juice Blank

Negative Ion Mode

Pesticide Mix 2 in Apple Juice 1.2 ppm



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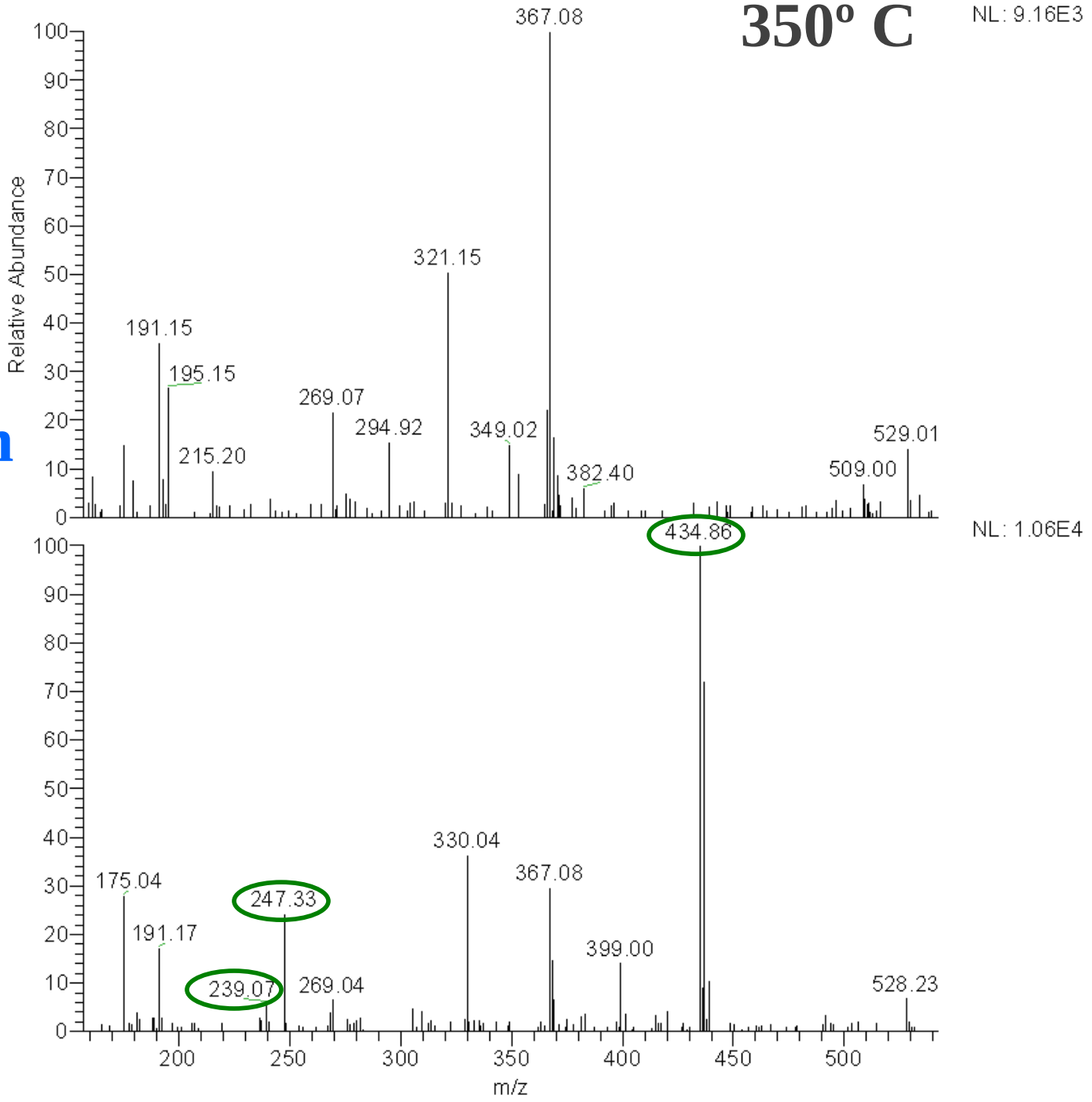
DART Spectra

Apple Juice Blank

Negative Ion Mode

Pesticide Mix 2 in Apple Juice 120 ppb



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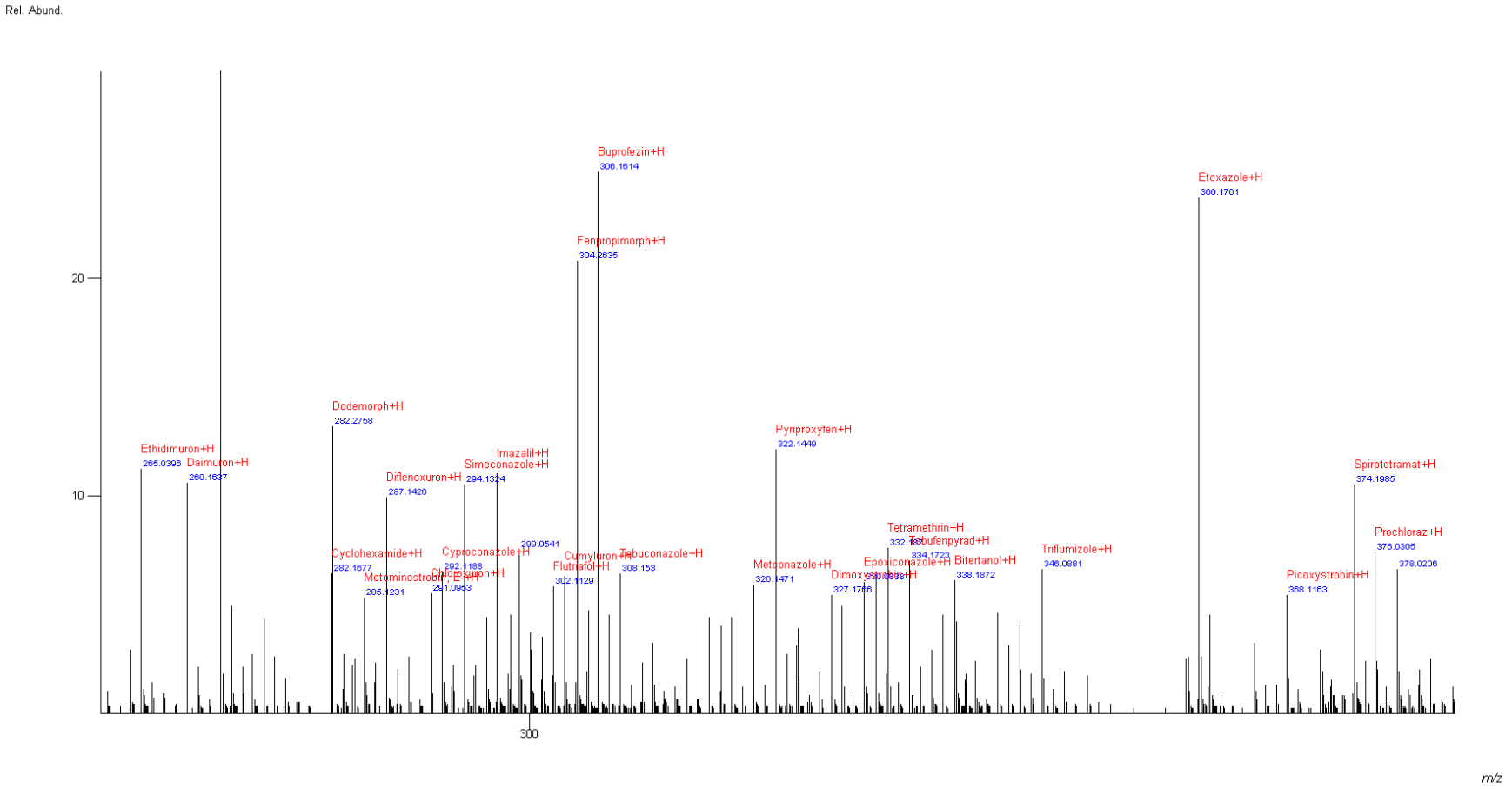
High Resolution Analysis of Pesticide Mix:
AccuTOF-DART 250º C
Positive Ion Mode



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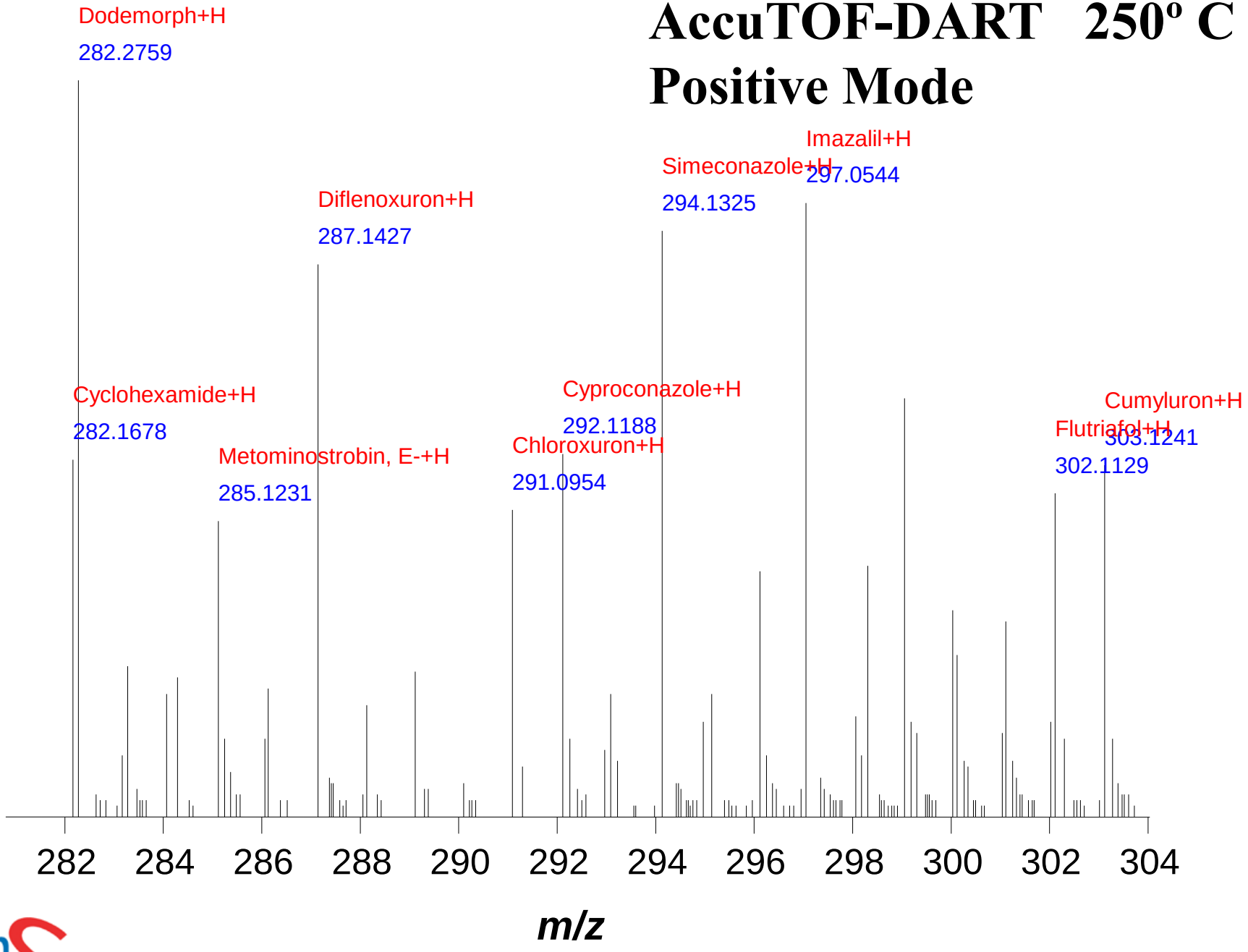
AccuTOF-DART 250º C Positive Mode



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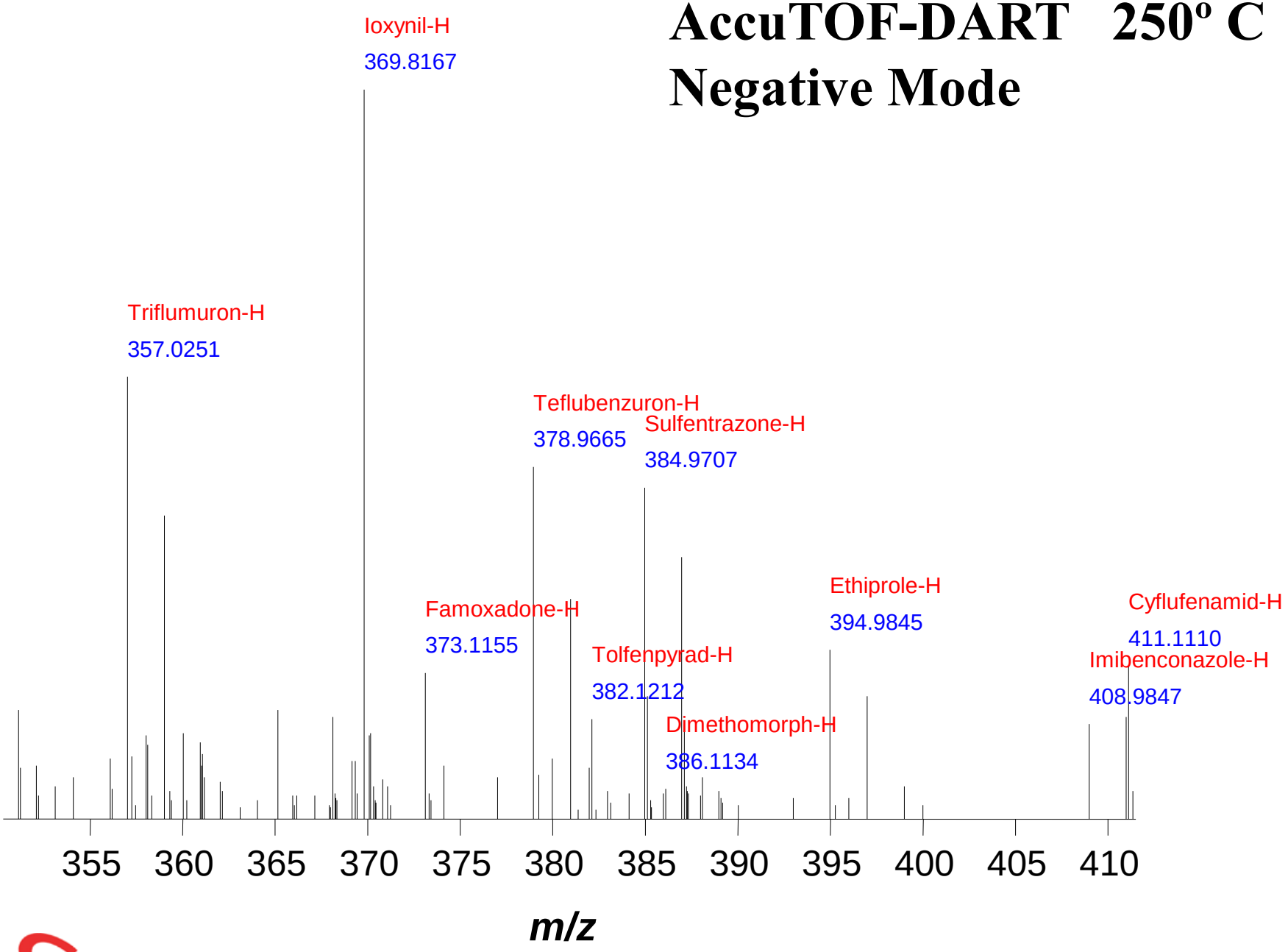
AccuTOF-DART 250° C
Negative Mode



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Conclusions

- **Both "Transmission" DART stainless steel screens and "3+D" glass inserts offer:**
  - **Application of larger sample volumes**
  - **Improve limits of detection by sample concentration**
- **Stainless screens provide longer lasting signal for MS/MS signal optimization**
- **Glass inserts set in 96-well titer plate permits the use of robotic liquid handling devices streamlining sample application and helping to reduce experimental error**
- **High resolution MS is ideal with DART ionization for rapid screening and identification of mixtures**

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Acknowledgements

- **Dr. Sara Edison from FDA Cincinnati for providing the Pesticide Mix 2**

- **Dr. Robert "Chip" Cody of JEOL USA for his expertise and assistance with obtaining the AccuTOF-DART data**

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