

**Evaluating Porous Materials
for Sampling Pesticides
from Surfaces using
Direct Analysis in Real Time
(DART)-Mass Spectrometry**

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Overview

- **Rapid screening of pesticides** present on the surface of fruits and vegetables has been facilitated by using a **Direct Analysis in Real Time (DART®)** open air surface desorption ionization source interfaced to a **Thermo Exactive** high resolution accurate mass mass spectrometer.
- Based on **EPA tolerance levels for pesticide residues** in food commodities set forth in the Electronic Code of Federal Regulations¹ we have spiked **cherry tomatoes, oranges, peaches and carrots** with pesticides at 10 and 100 times below the EPA tolerance levels. The surface of a store-bought orange was also sampled before washing to screen for pesticides.
- These experiments focus on the use of primarily **cotton** and also **polyester swab materials** to collect pesticides from the surface of produce to evaluate the efficiency of the swabs to capture and retain the analytes for analysis. These experiments follow on original pesticide screening experiments conducted by Edison *et al.*² of the FDA. They utilized polyurethane foam discs as both the collection and desorption substrate to detect pesticides in and on the surface of fruits as completed using “Transmission-Mode” DART-MS analysis.

1. Electronic Code of Federal Regulations. *Title 40, Part 180 – Tolerances and Exemptions for Pesticide Chemical Residues in Food*. Available: <http://ecfr.gpoaccess.gov>. Accessed on July 8, 2011.

2. Edison, S. E.; Lin, L. A.; Gamble, B. M.; Wong, J.; Zhang, K., *Surface swabbing technique for the rapid screening for pesticides using ambient pressure desorption ionization with high-resolution mass spectrometry*. *Rapid Comm. Mass Spec.*, 2011, **25(1): 127-139**.

Instrumentation

Thermo Exactive Settings

•Scan Parameters:

- Positive Ion Mode
- Resolution: “Enhanced” - 25,000 @ 4 Hz
- Fragmentation: None, HCD Gas Off
- Scan Settings: 1 μ -scan by 100 ms max inject time
- AGC Target: Ultimate Mass Accuracy ($5e^5$)

•Exactive Inlet Parameters:

- Capillary Temp: 200° C
- Capillary Voltage: 25 V
- Tube Lens Voltage: 120 V
- Skimmer Voltage: 26 V

•All of the following parameters were set to zero:

- Sheath Gas Flow, Aux Gas Flow, Sweep Gas Flow, Spray Voltage

DART-SVP Settings

•DART Source:

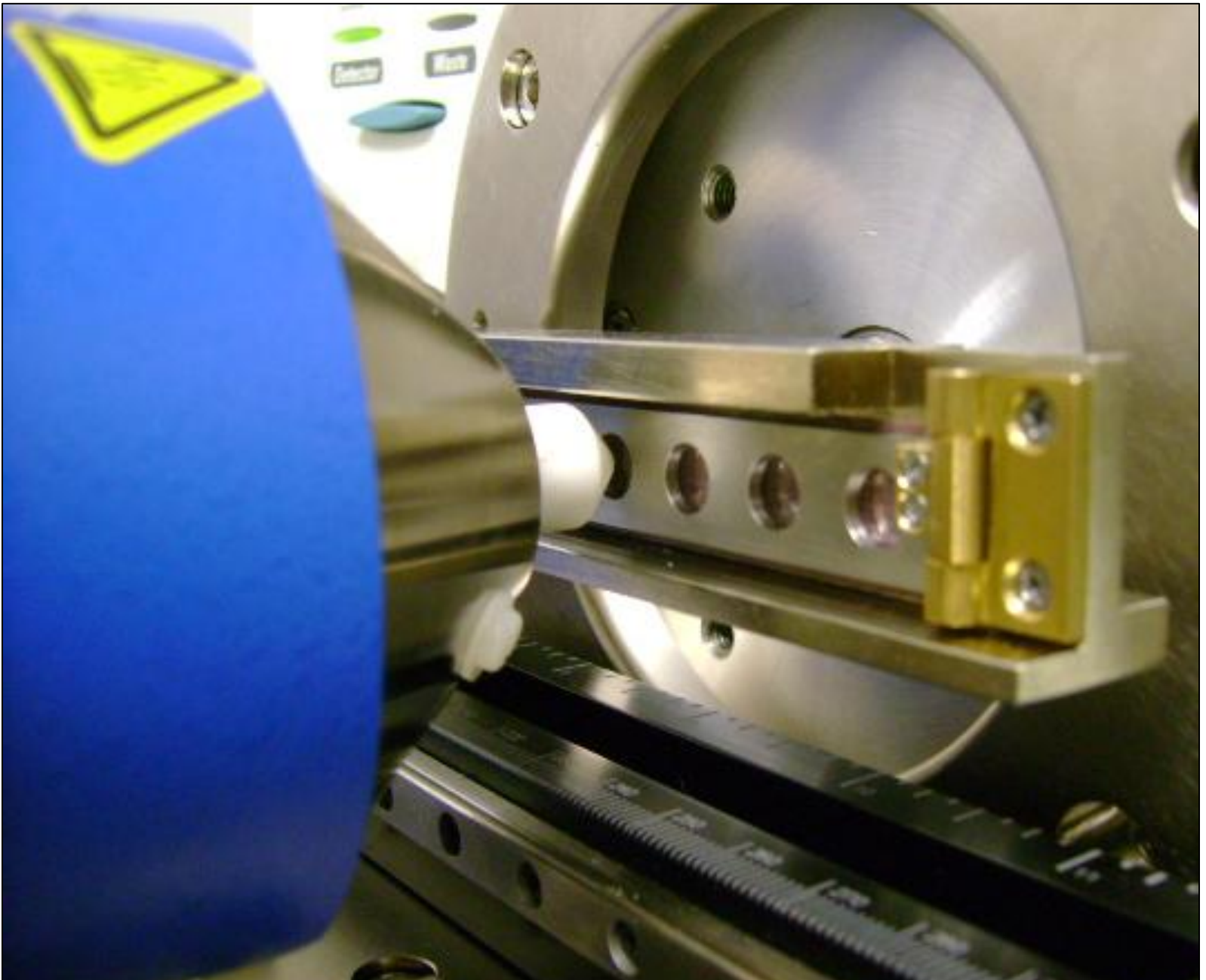
- Positive Ion Mode
- Heater Temperature:
 - 150° C - Dimethoate & Malathion
 - 250° C - Methamidophos

•Motorized Linear Rail:

- Sample Introduction Speed: 10 mm/s



Transmission DART



Stainless steel mesh screens:
Used as the sampling surface to generate **standard curve plots**



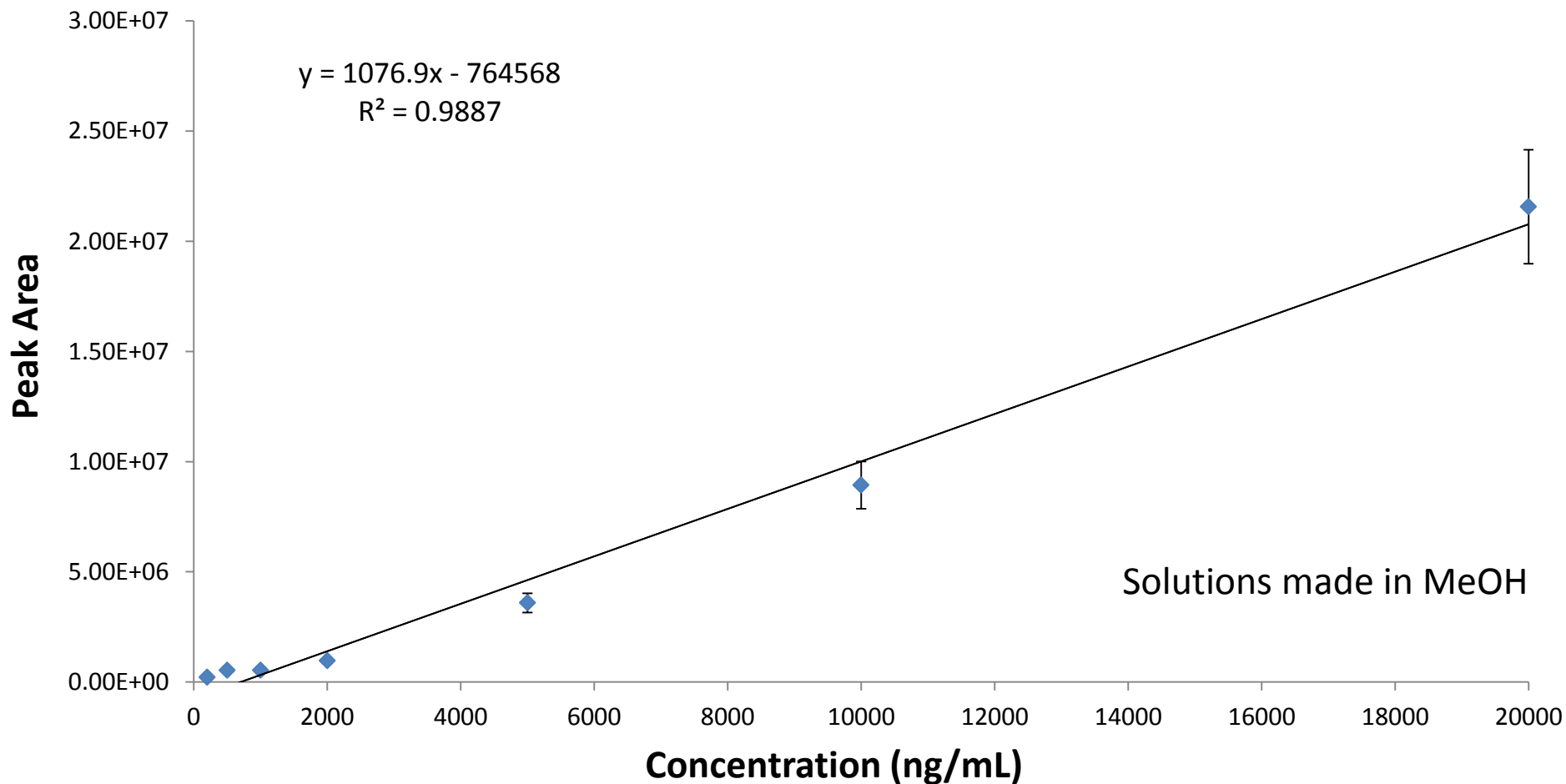
5 μL of liquid sample pipetted onto stainless steel mesh screen and allowed to **completely dry** before analysis



Transmission-Mode DART

Standard Curve - Methamidophos

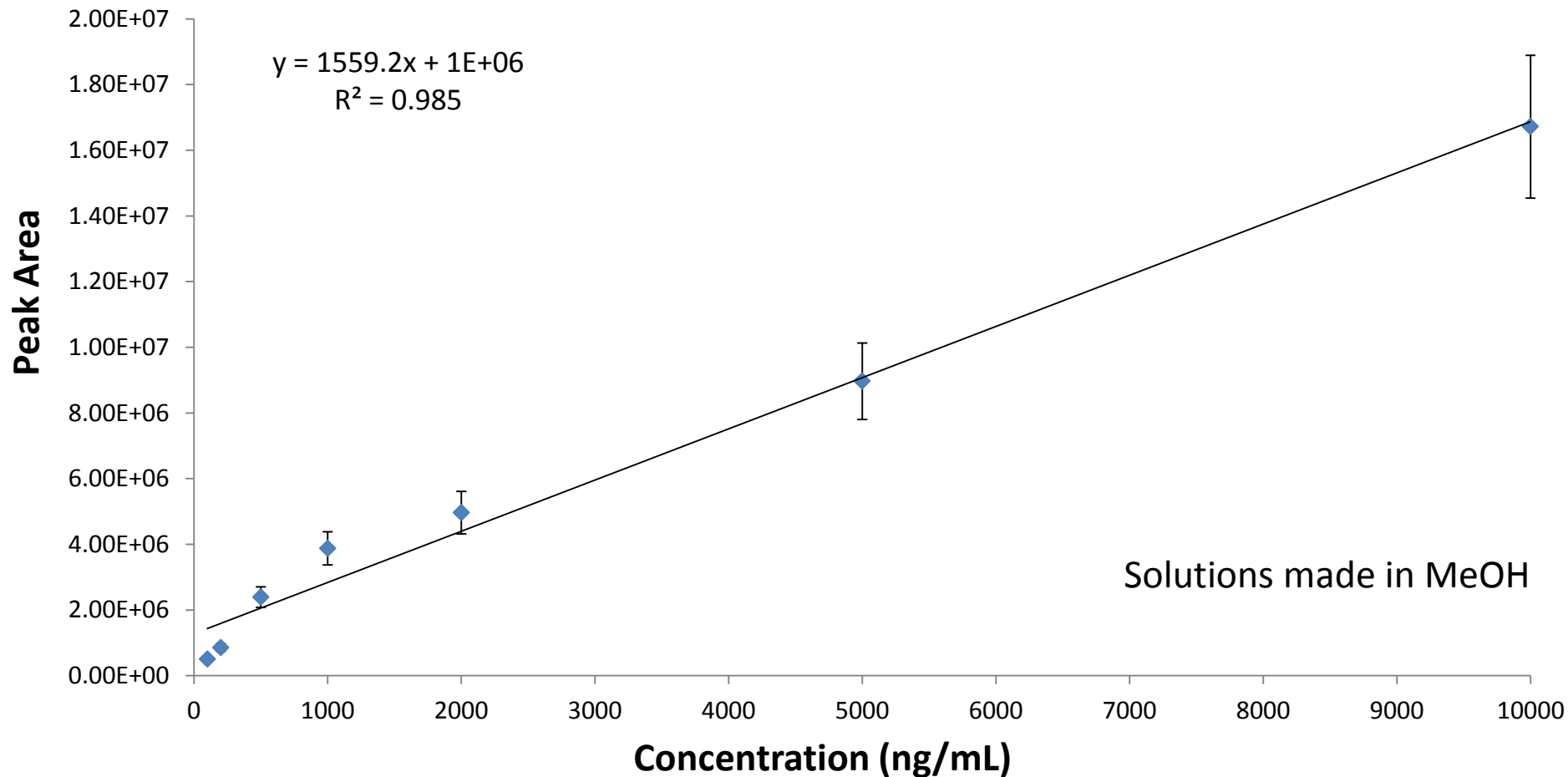
200 – 20,000 ng/mL



Transmission-Mode DART

Standard Curve - Dimethoate

100 – 10,000 ng/mL



Commodity & Spiked Level(s)	EPA Tolerance Levels ¹		
	Methamidophos C ₂ H ₈ NO ₂ PS	Dimethoate C ₅ H ₁₂ NO ₃ PS ₂	Malathion C ₁₀ H ₁₉ O ₆ PS ₂
Tomato 200 ng/g	2,000 ng/g	-	-
Orange 20 ng/g	-	2,000 ng/g	-
200 ng/g	-	-	-
Carrot 80 ng/g	-	-	8,000 ng/g
800 ng/g	-	-	8,000 ng/g
Peach 80 ng/g	-	-	8,000 ng/g
800 ng/g	-	-	8,000 ng/g

Pesticide Spiking Solutions

Methamidophos

- A stock solution was prepared at 1 mg/mL from the pure solid with 1:1 MeOH:H₂O.
 - A serial dilution was performed using only MeOH yielding the following solutions:
 - 100, 200, 500, 1000, 2,000, 5,000, 10,000, 20,000, 100,000 ng/mL
 - The 20,000 ng/mL was used as the spiking solution for the 200 ng/g spiking.

Dimethoate

- A stock solution was prepared at 1 mg/mL from the pure solid with 1:1 MeOH:H₂O.
 - A serial dilution was performed using only MeOH yielding the following solutions:
 - 100, 200, 500, 1000, 2,000, 5,000, 10,000, 20,000, 100,000 ng/mL
 - The 2,000 ng/mL and 20,000 ng/mL was used as the spiking solutions for the 20 ng/g and 200 ng/g respective spiking levels.

Malathion Solution from Concentrate

Malathion Soln. Prep

- Malathion was the only pesticide of the three examined that did not come from a pure solid to prepare the standard solutions.

- Malathion is present at 50% in the “Spectracide Malathion Insect Spray” concentrate.

- A stock solution of malathion was prepared at 10 mg/mL in MeOH from the concentrate and then diluted down with MeOH to 100 $\mu\text{g/mL}$ and 10 $\mu\text{g/mL}$ spiking solutions.



Protocol: Spiking to Swabbing



Weight

- Each piece of produce was weighed to determine the pesticide dosing volume based on the determined spiking levels.

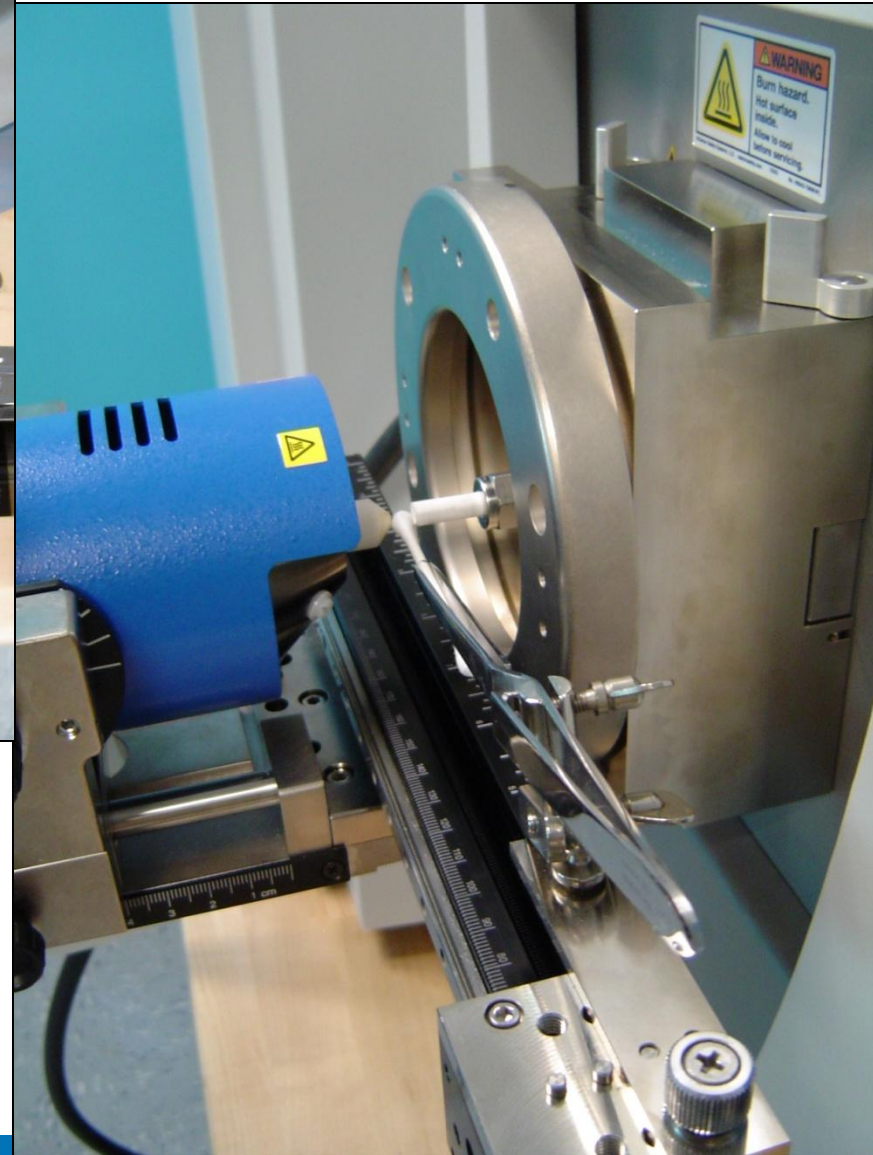
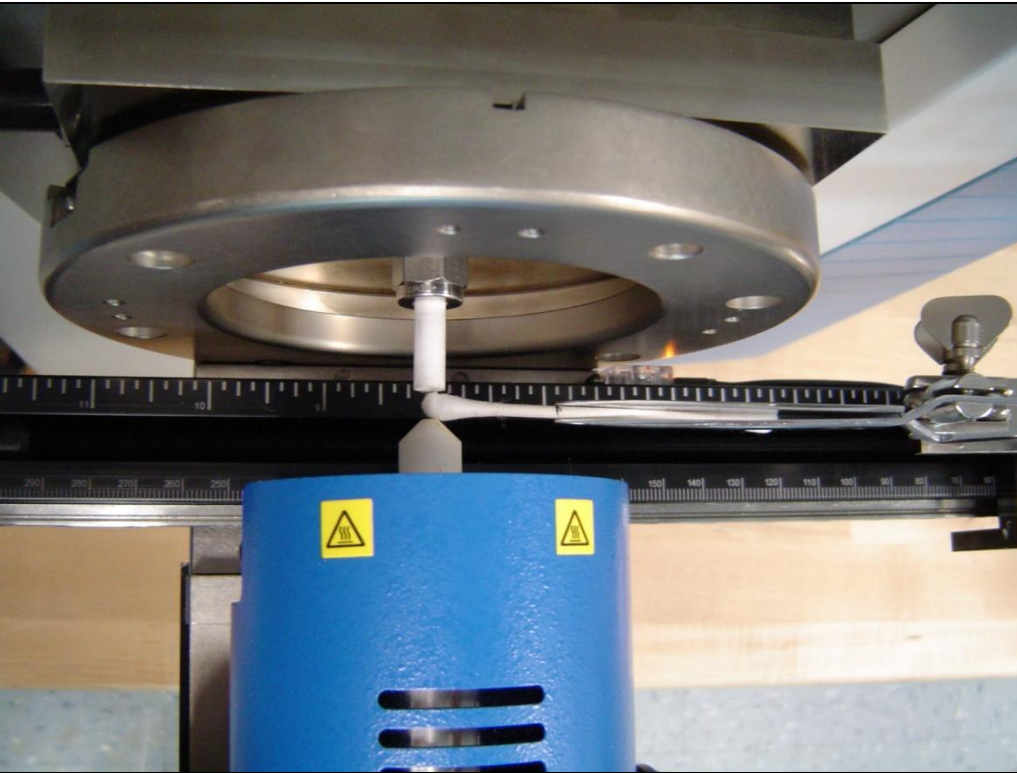
Dosing the Produce Surface

Application of Solution

- After the produce was weighed the mass determined how much pesticide should be applied to the surface at the determined spiking levels.
- The pesticide solution was aspirated into a micro-pipette tip and then dispensed directly onto the surface of the washed produce trying to cover the entire surface of the piece of produce evenly with the liquid volume.
- The dosed produce was allowed to dry for 5 – 10 minutes before being swabbed for direct DART-MS analysis.



Set-up - Desorbing Directly from Swabs



Swabbing Protocol

• Moistened Swab:

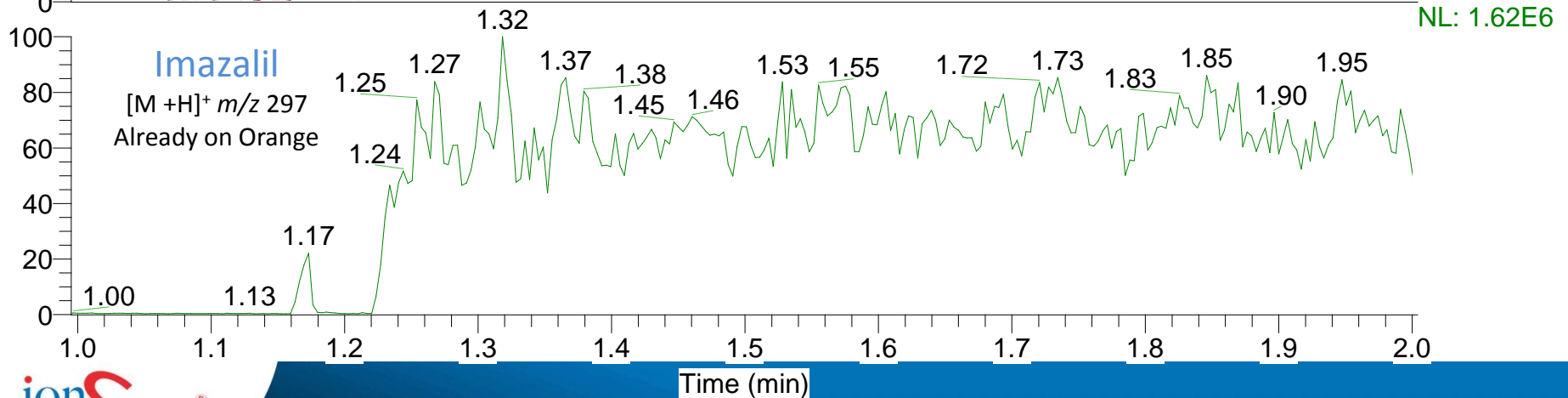
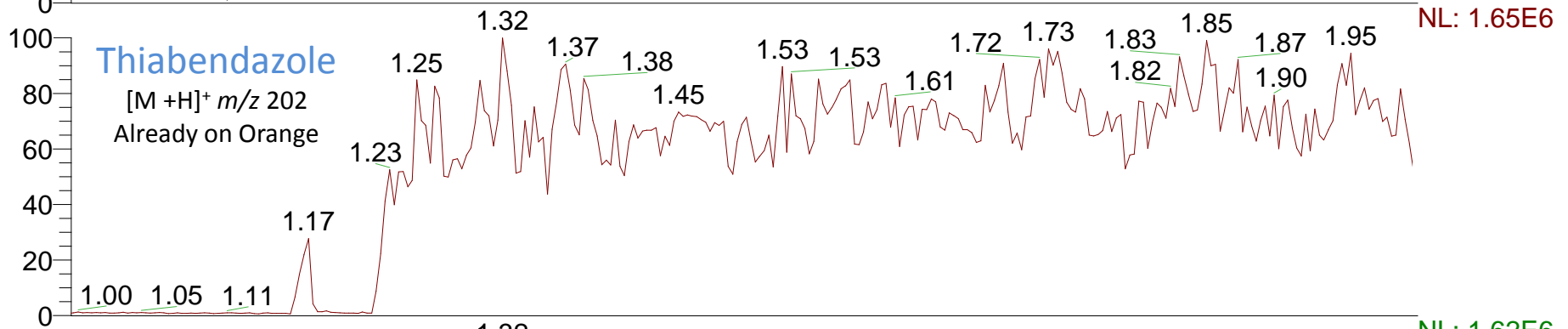
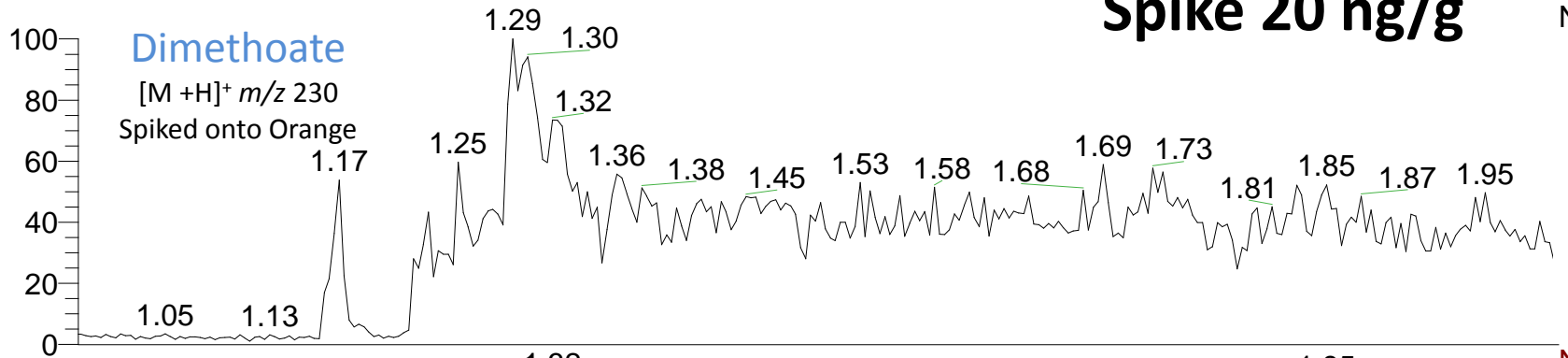
- Each swab was **pre-moistened** with a squirt of **MeOH** from a squeeze bottle.
 - Any **excess solvent** was **shaken off** the swab
- The entire surface of each piece of produce was swabbed.

Orange Peel - Cotton Swab - Dimethoate

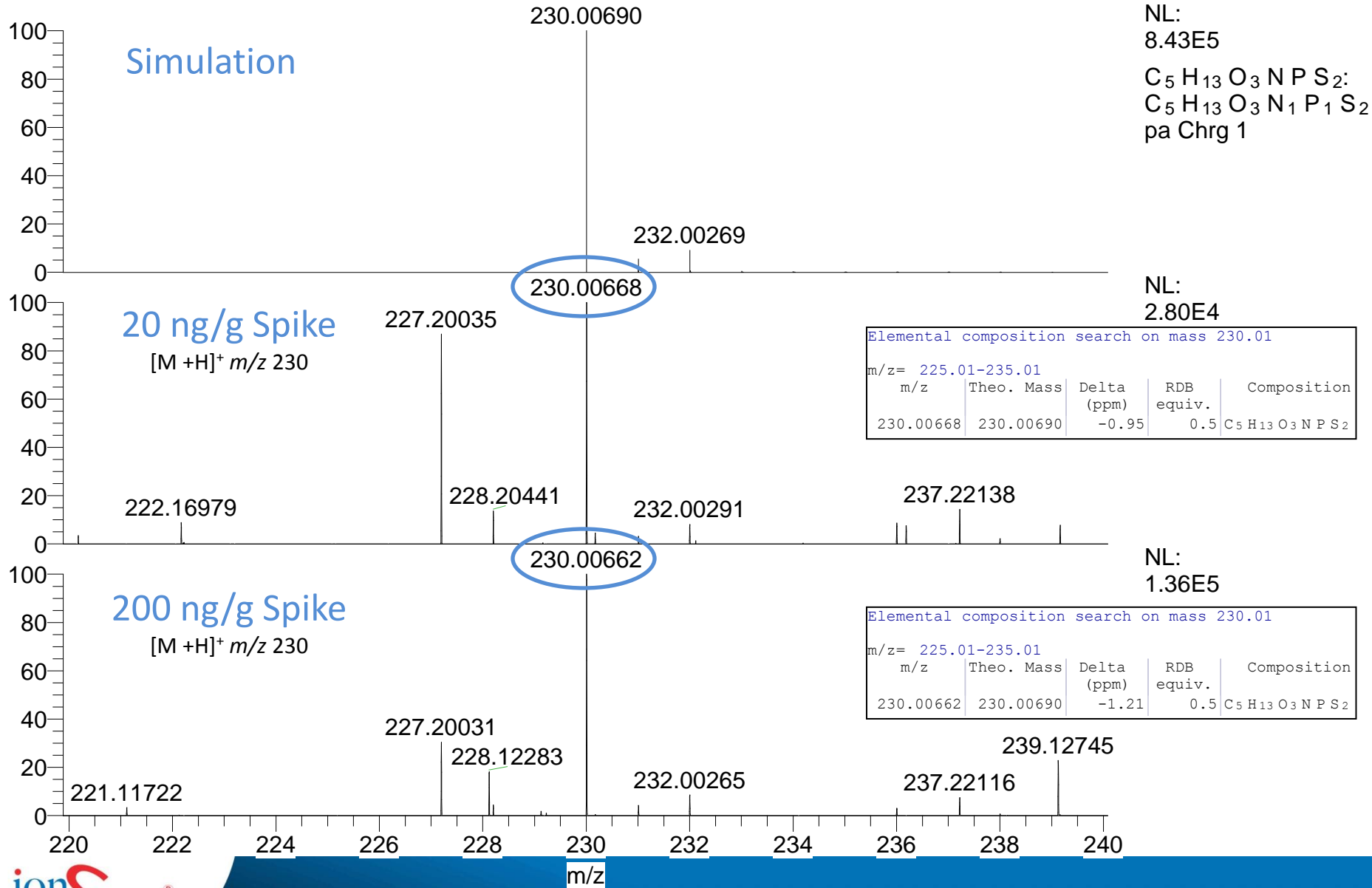
RT: 1.00 - 2.00

Spike 20 ng/g

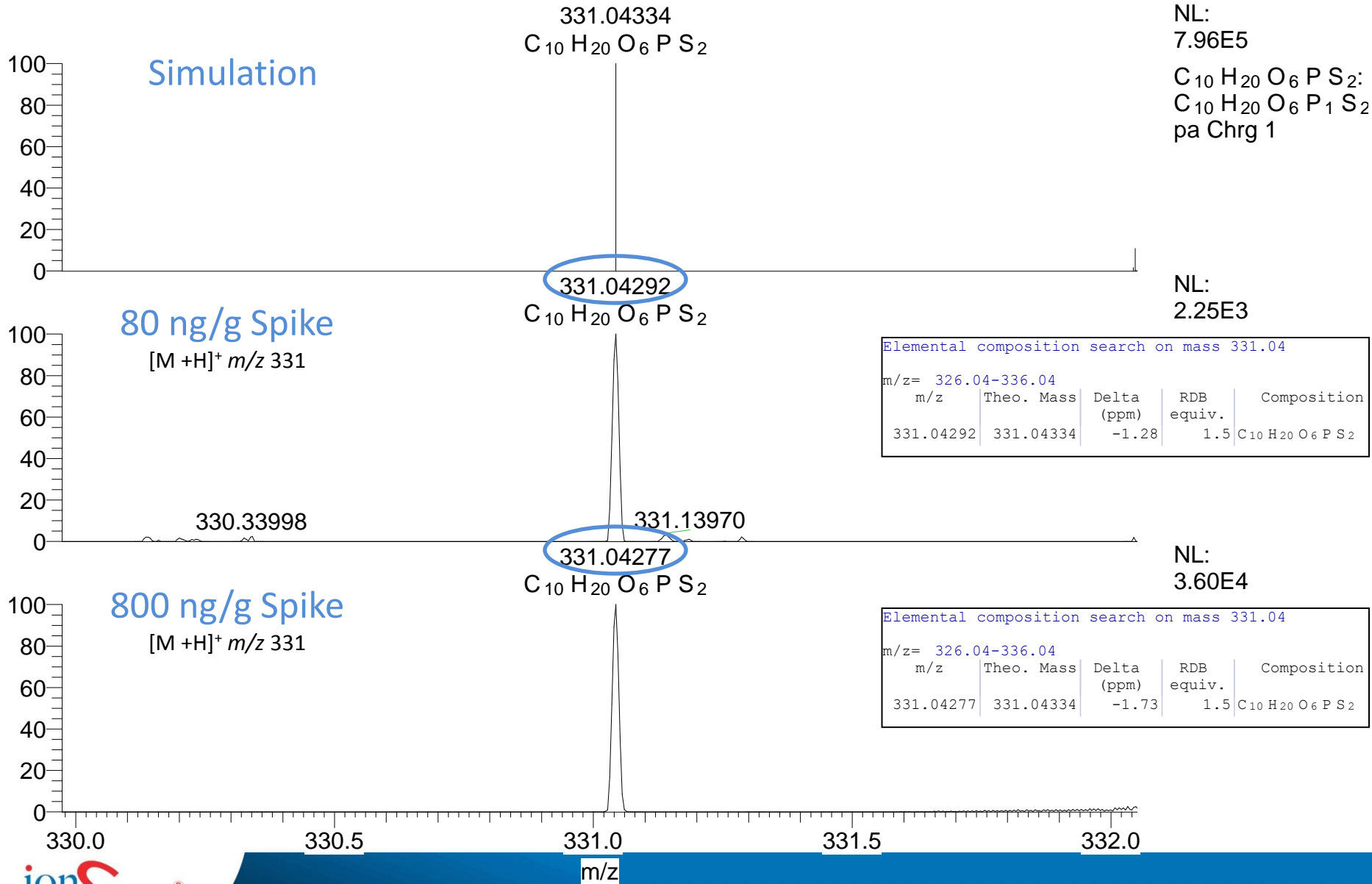
NL: 8.89E4



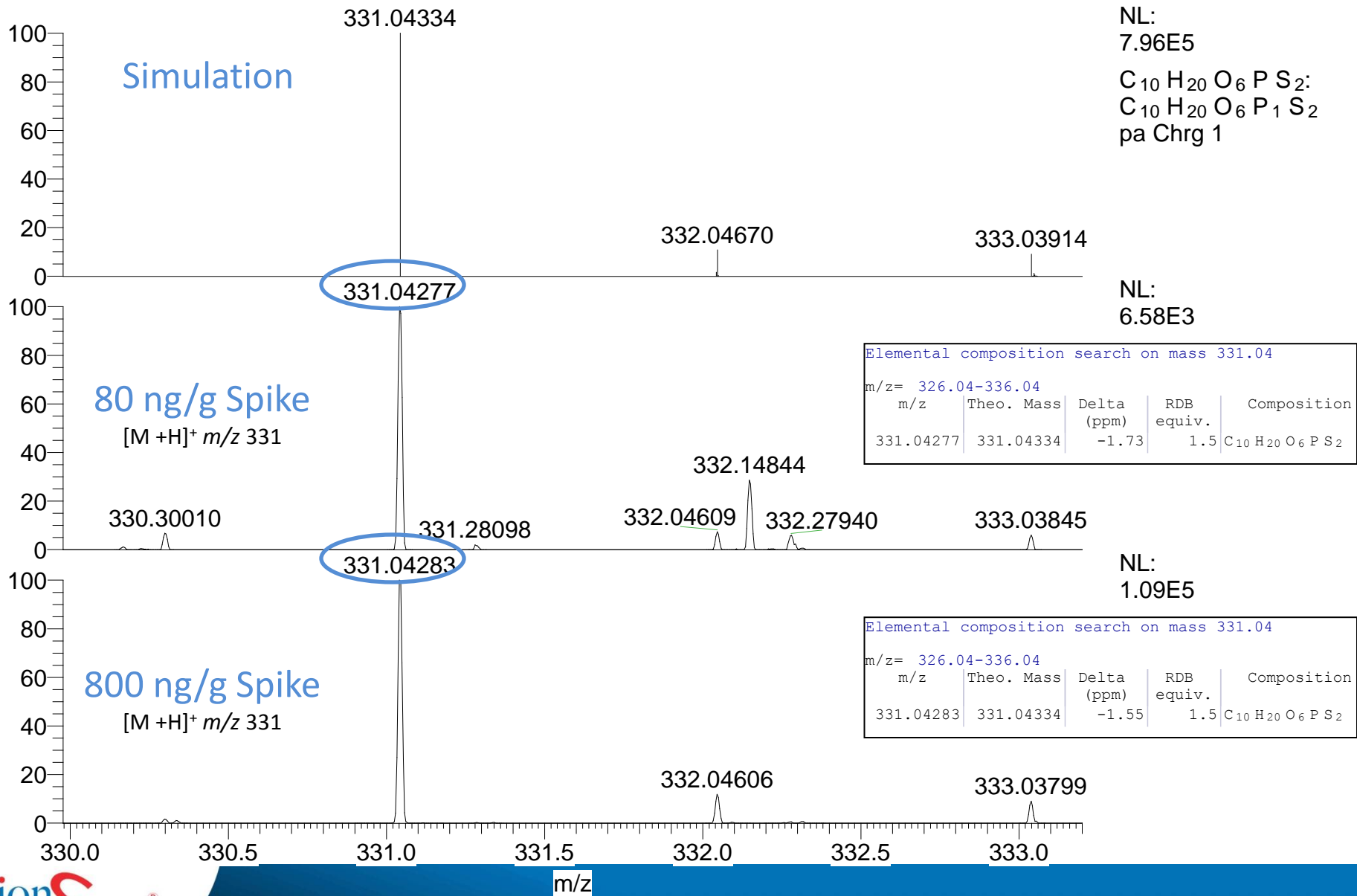
Orange Peel - Cotton Swab - Dimethoate



Baby Carrot - Cotton Swab - Malathion



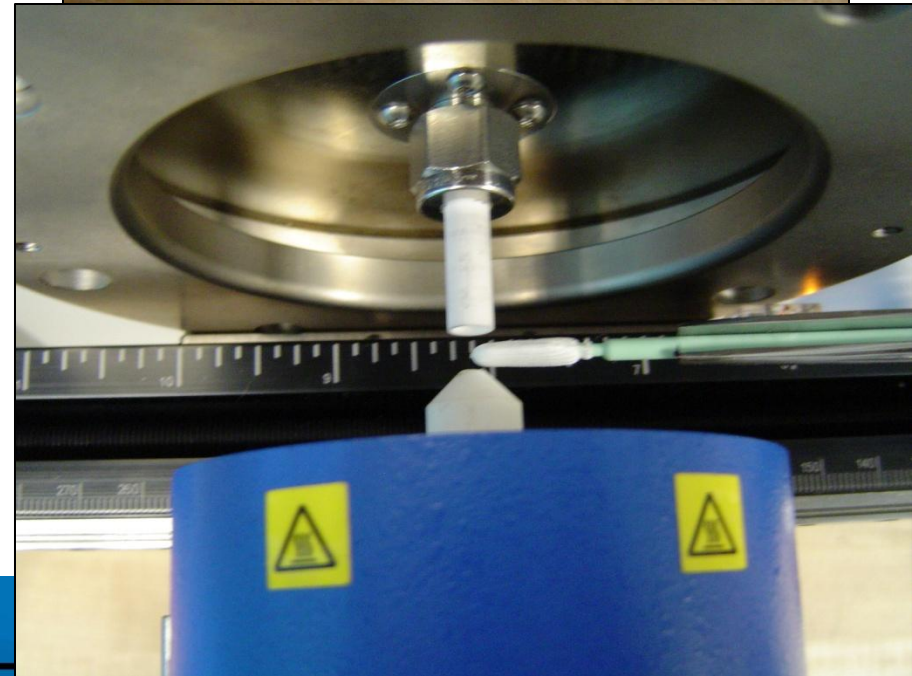
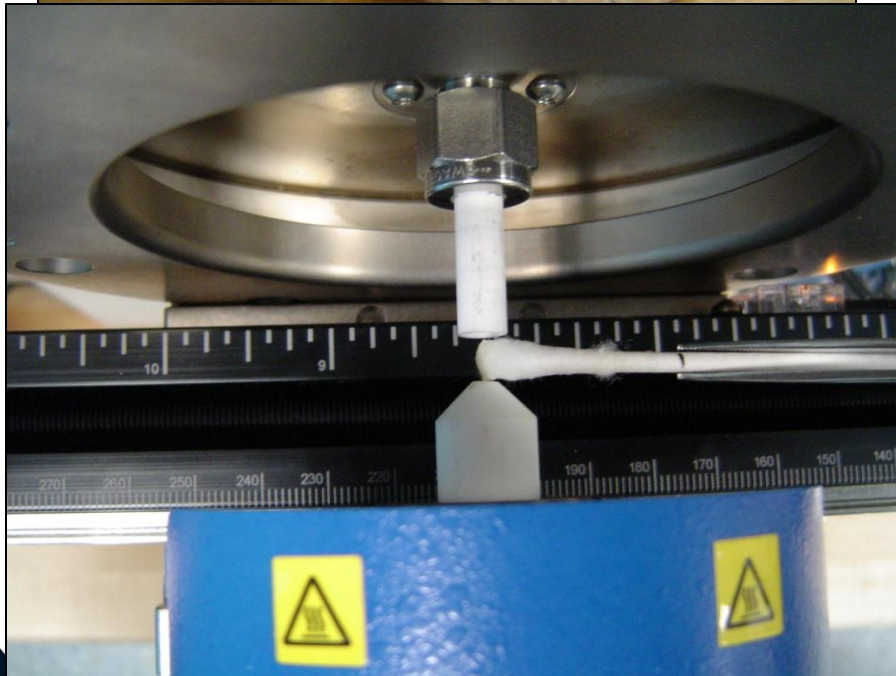
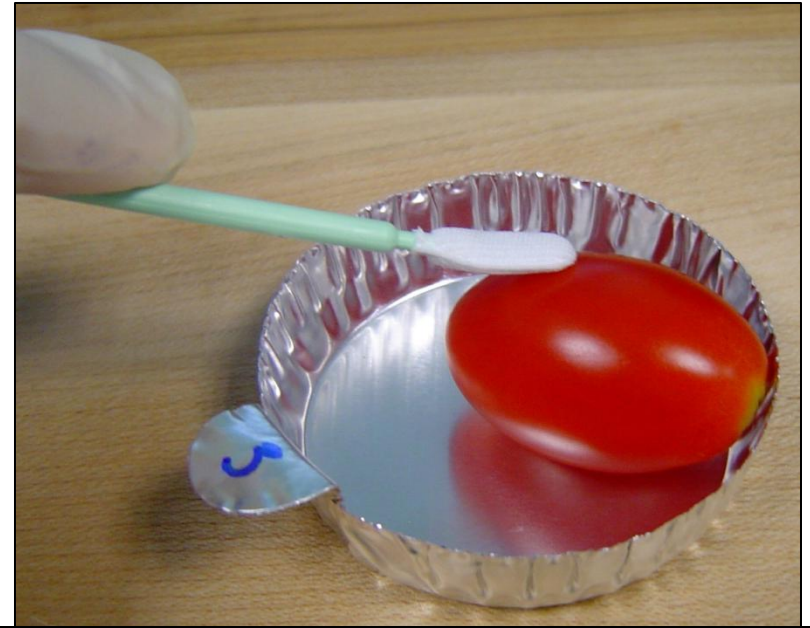
Peach - Cotton Swab - Malathion



Cotton Swab



Polyester Swab

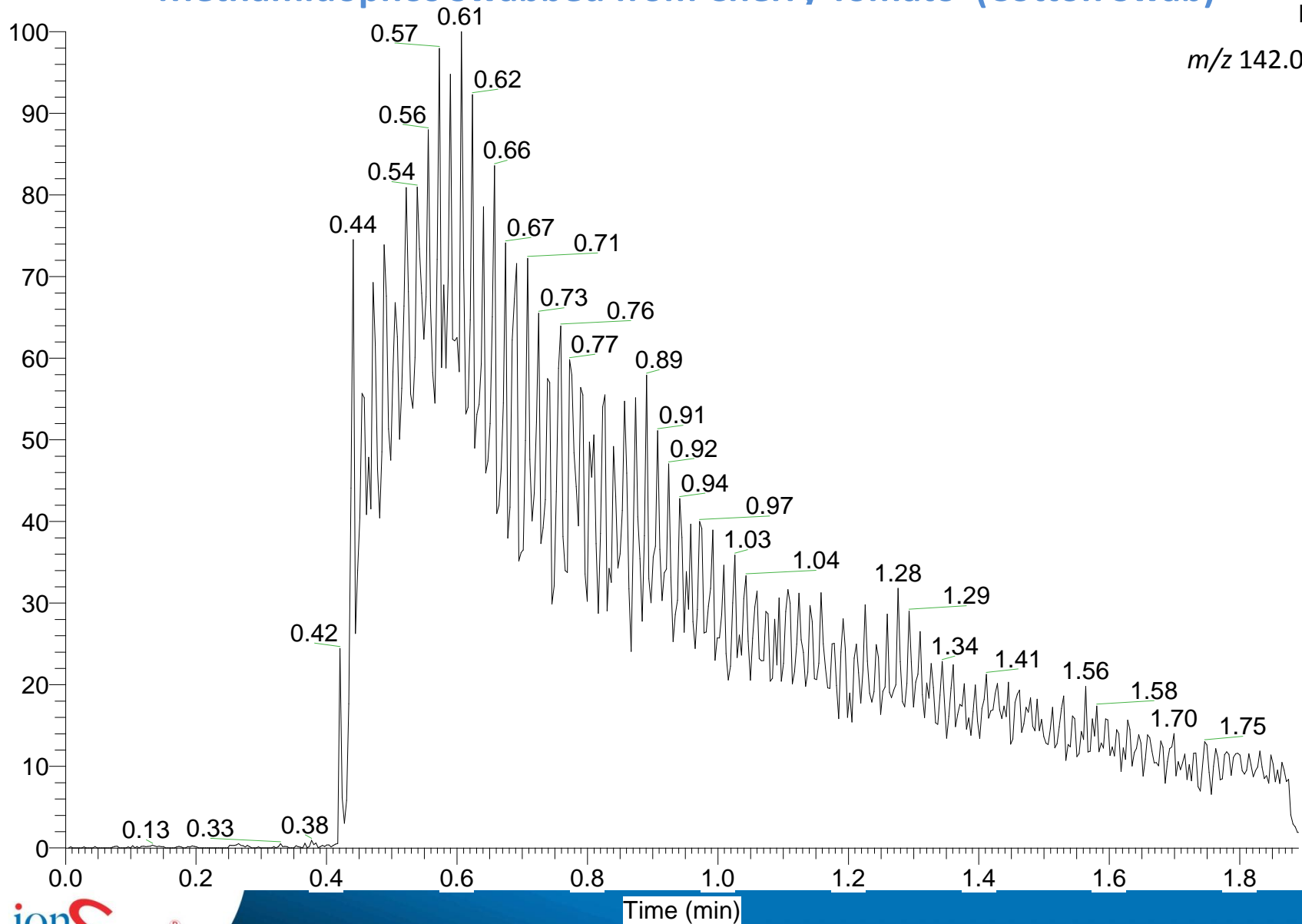


Example Chromatogram for Automated Swab Introduction

RT: 0.00 - 1.89 Methamidophos Swabbed from Cherry Tomato (Cotton Swab)

NL: 2.04E6

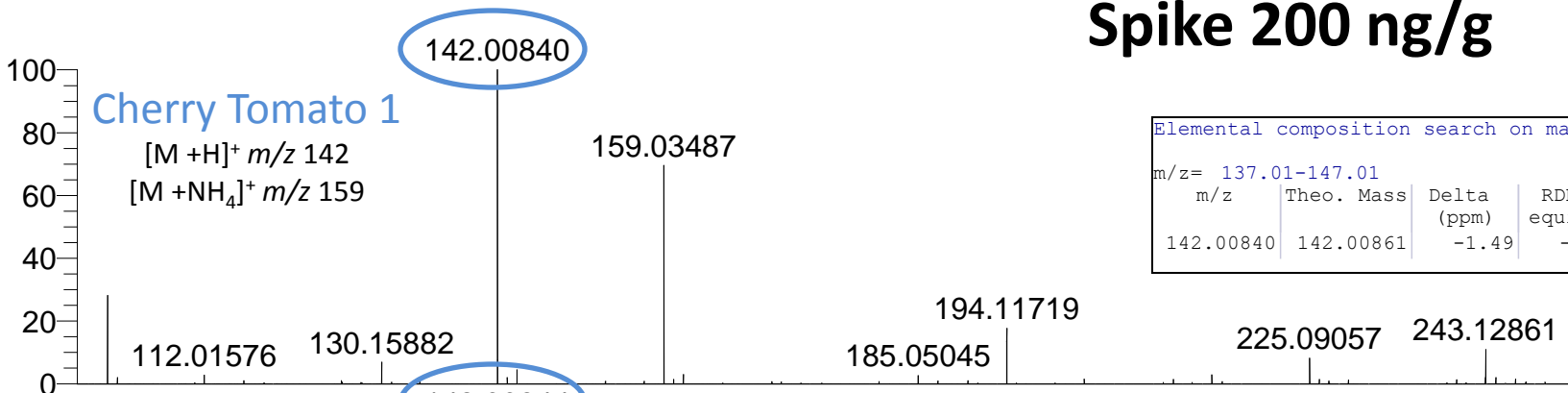
m/z 142.00 - 142.02



Tomato - Cotton Swab - Methamidophos

Spike 200 ng/g

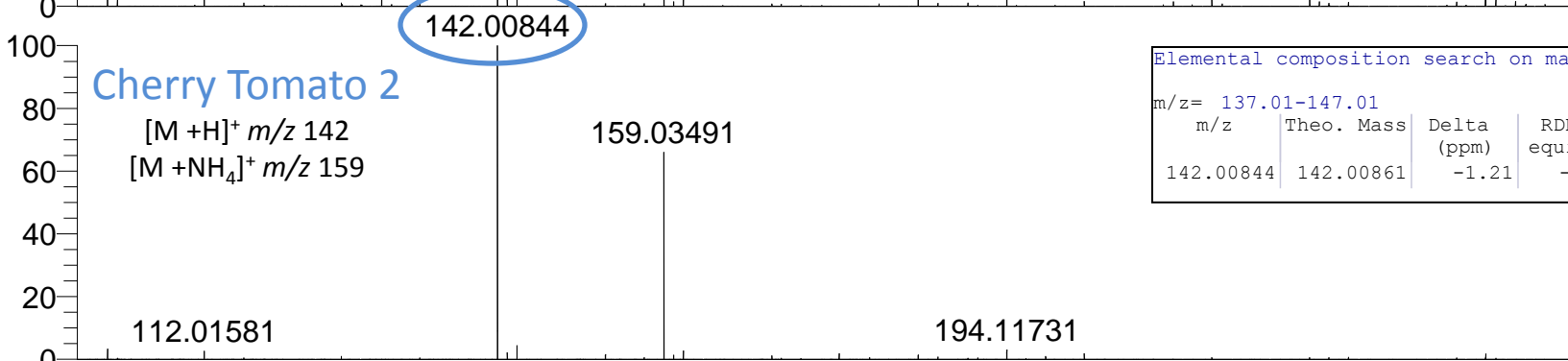
NL: 4.69E5



Elemental composition search on mass 142.01

m/z= 137.01-147.01

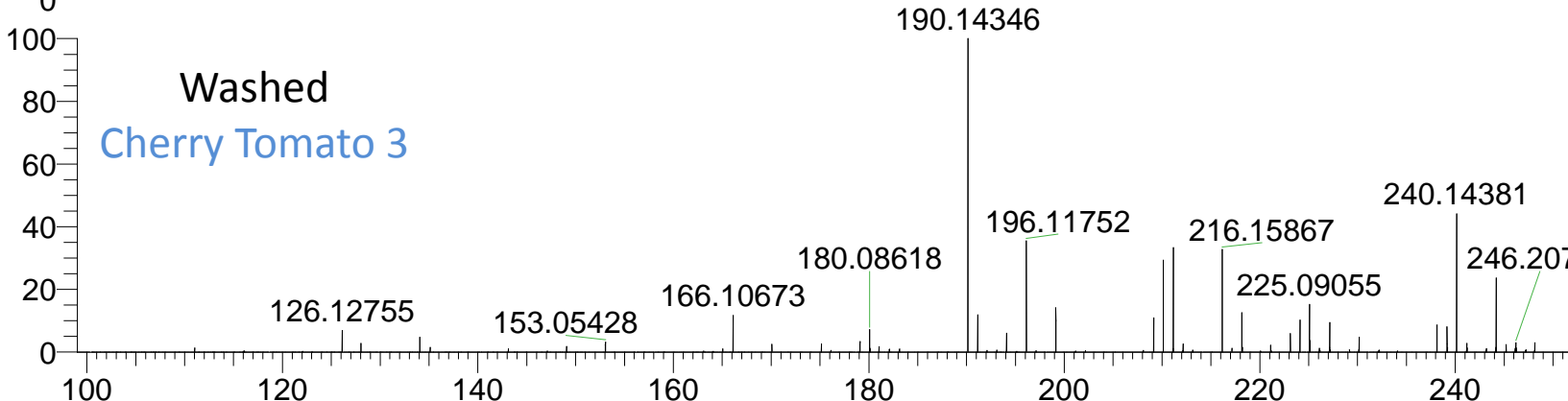
m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
142.00840	142.00861	-1.49	-0.5	C ₂ H ₉ O ₂ NPS



Elemental composition search on mass 142.01

m/z= 137.01-147.01

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
142.00844	142.00861	-1.21	-0.5	C ₂ H ₉ O ₂ NPS

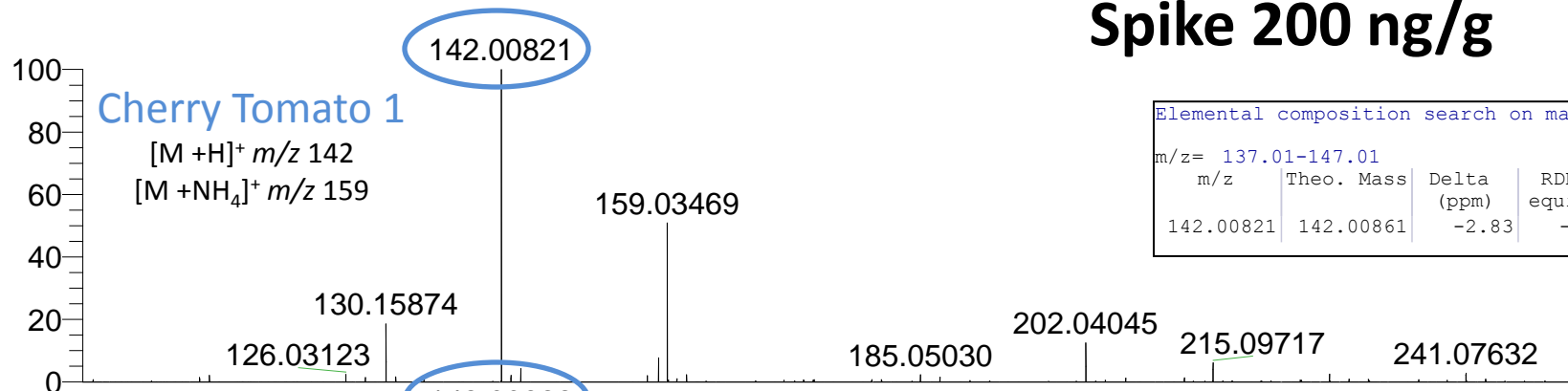


NL: 3.92E4

Tomato - Polyester Swab - Methamidophos

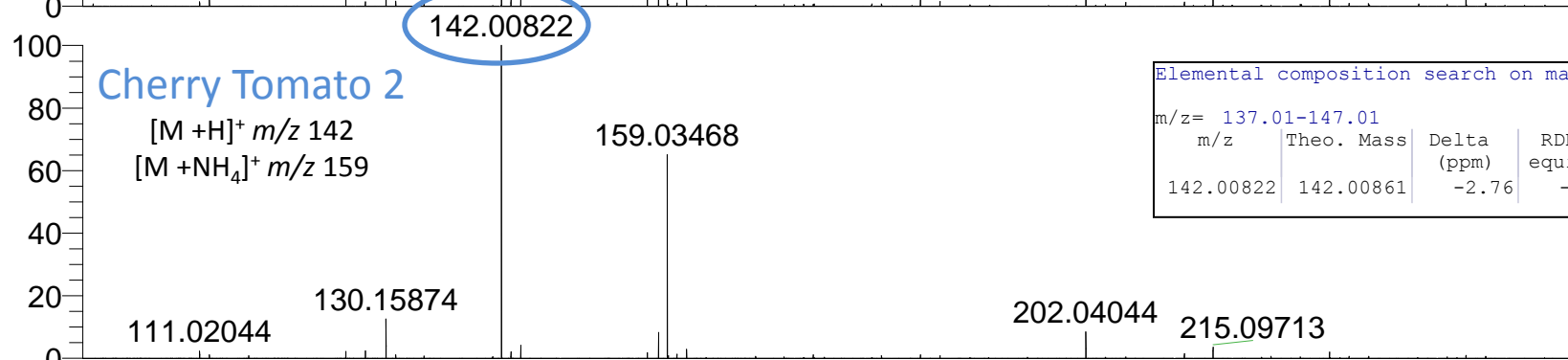
Spike 200 ng/g

NL: 3.66E6



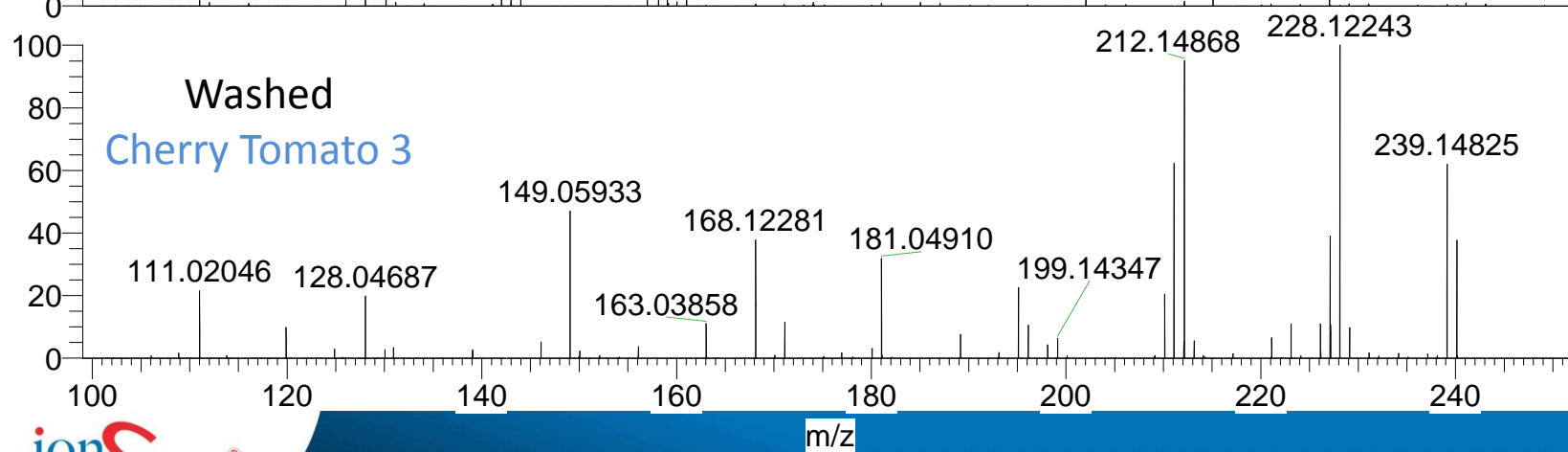
Elemental composition search on mass 142.01

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
142.00821	142.00861	-2.83	-0.5	C ₂ H ₉ O ₂ NPS



Elemental composition search on mass 142.01

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
142.00822	142.00861	-2.76	-0.5	C ₂ H ₉ O ₂ NPS



NL: 3.42E4

Summary

- Using this swabbing approach we have been able to detect the pesticides of interest 10 – 100 times below the EPA tolerances with excellent mass accuracy (< 2 ppm).
- The comparison of cotton vs. polyester swabs showed comparable results.
 - The cotton swab was less durable than the polyester swab, therefore a woven swab like the polyester swab would be more suitable for rough surfaces.
- Using a heater ramp to ramp the temperature of the helium gas in the DART is a way to attain some thermal separation of a mixture of pesticides as shown by Edison *et al.*²

Acknowledgements

The authors would like to kindly thank Maciej Bromirski at Thermo Scientific for coordinating the collaborative efforts for the loan of an Exactive MS.