Screening and Quantitation of Pesticides in Jonagold Apples by Comprehensive Two-Dimensional Gas Chromatography-Time-of-Flight Mass Spectrometry (GCxGC-TOFMS)

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1. Introduction

Screening and quantitation of pesticide residues in fruits and vegetables is of utmost importance for public health and safety concerns. These commodities can contain hundreds to thousands of analytes, making them extremely difficult for the screening and accurate quantitation of pesticide residues. Many current methodologies incorporate the use of complex, time consuming sample cleanup techniques to eliminate much of the matrix interference prior to analysis by GC-MS. As sample loads increase, analysts are forced to find ways to increase the speed of sample preparation and analysis while maintaining high quality of the analytical results.

This application note shows the successful use of comprehensive two-dimensional gas chromatography with time-of-flight mass spectrometry (GCxGC-TOFMS) for effective screening and quantitation of pesticides in apples. Jonagold apples from Southwest Michigan were analyzed for potential pesticide residues following preparation by a QuEChERS (quick, easy, cheap, effective, rugged, and safe) extraction approach.

2. Samples

The skins of Jonagold apples were prepared utilizing the QuEChERS extraction approach and dispersive solid phase cleanup with PSA +C18. The extracts were analyzed by GCxGC-TOFMS and the mass spectra obtained were searched against a pesticide reference library to facilitate rapid screening. Calibration curves were prepared for the pesticide residues that were detected in the Jonagold apples so that a quantitative determination could be made. Pesticide residue levels detected in both washed and unwashed apples were compared.

3. Experimental Conditions

A LECO Pegasus® 4D GCxGC-TOFMS system equipped with a cryogen-free (CF) modulator was used for these analyses. System conditions are shown below.

GC:
Agilent 6890 w/LECO dual-stage, quad-jet thermal CF modulator and secondary oven

Column 1:
Rxi-5 Sil MS, 15 m x 0.25 mm x 0.25 µm

Primary Oven:
90°C hold 1 min, 5°C/min to 300°C, hold 10 min

*Column 2:
Rtx-200, 1.25 m x 0.18 mm x 0.18 µm

Secondary Oven:
+25°C offset from main oven

Injection:
1 µL, splitless at 250°C

Carrier Gas:
Helium at 1.5 ml/min

Modulator Temperature Offset: 25°C

Modulation Period:
5 s with a 1.2 s hot pulse time

Chiller Temperature: -80°C

MS:	LECO Pegasus 4D
Acquisition Delay:	240s
Saved Mass Range:	45-550 m/z
Acquisition Rate:	100 spectra/s
Source Temperature:	225°C

**The columns used for these analyses were connected using the NLISIS Meltfit One (see Fig. 1). The system remained leak free for the entirety of these experiments.*

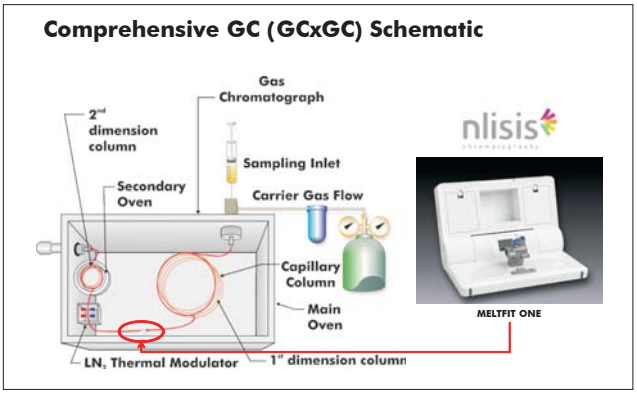

Figure 1. Comprehensive GCxGC Schematic showing location of MeltFit Connector.

4. Results

Both Phosmet (insecticide) and Chlorpropham (growth regulator) were detected in the extracts of Jonagold apples. Figure 2 shows the total ion contour plot with pesticide residues identified. Figure 3 highlights the chromatographic separation on the "y" axis of the GCxGC contour plot. If this were a one-dimensional separation, Phosmet would have coeluted with the other analytes which are aligned vertically on the contour plot. The interfering compounds are sugars and fatty acids from the apple matrix.

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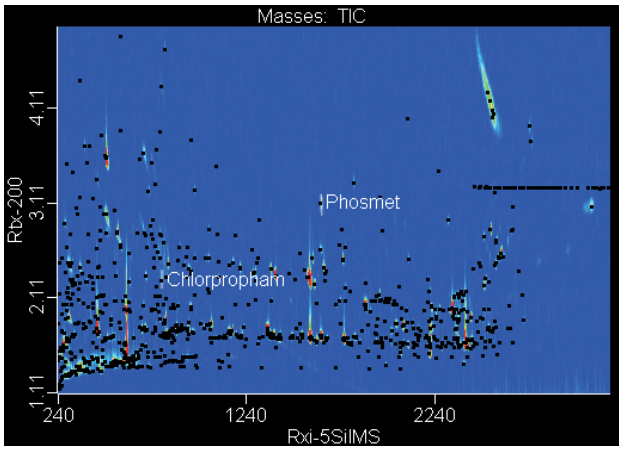

Figure 2. Total ion contour plot showing GCxGC-TOFMS analysis of the extract from an unwashed Jonagold apple. The black dots represent over 1000 analytes which were detected in the apple extract. The pesticide residues identified are labeled in white font.

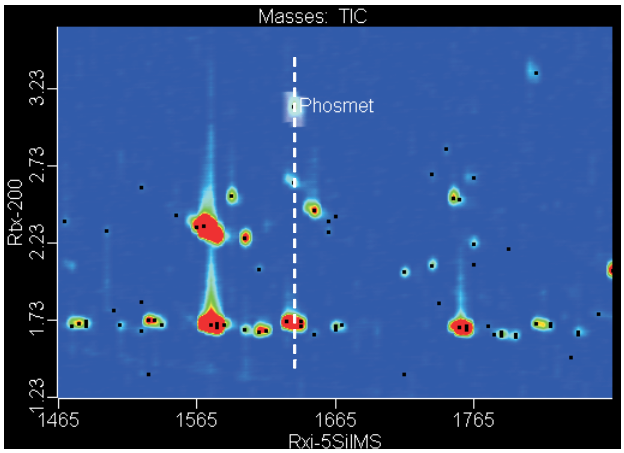

Figure 3. Contour plot displaying chromatographic peaks that are in vertical alignment. These are analytes that have been separated in the second dimension, but would have been chromatographically unresolved if this were a one-dimensional separation.

Quantitative determinations were carried out by preparing calibration curves with pure standards of the pesticide residues. Triphenyl phosphate was used as an internal standard. Standards were analyzed at concentrations ranging from 60 to 600 ng/mL (ppb). The calibration curves for phosmet and chlorpropham exhibited r^2 values of 0.997 and 0.999, respectively. The results for the quantitative determination of phosmet and chlorpropham in washed vs. unwashed Jonagold apples are shown in Table I.

Table I. Pesticide residue levels in unwashed vs. washed Jonagold Apples

Analyte	Unwashed	Washed
Chlorpropham	0.1	n.d.
Phosmet	18	13

Results in ng/g

5. Conclusions

This application shows the utility of GCxGC-TOFMS when combined with a rapid QuEChERS extraction approach. Compounds such as sugars and fatty acids, which can be left behind even after sample clean up, often lead to chromatographic interferences in one-dimensional chromatography. In this example, the enhanced peak capacity of the GCxGC separation is critical to removing the interferences which can ultimately lead to quantitation bias.

In addition to the increase in chromatographic resolution, the use of a Time-of-Flight Mass Spectrometer provides the ability to acquire full mass range spectra without sacrificing speed or sensitivity. This is beneficial for detecting not only target pesticides, but also new and emerging contaminants.

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