

Pesticide Detection in Hop (*Humulus lupulus*) Extracts by GC-TOFMS

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Introduction

The enormous growth in the craft brewing sector coupled with the popularity of IPA-style beers has led to an increased demand for Hops (*Humulus lupulus*). It is anticipated that the demand for routine pesticide monitoring will likewise continue to rise. Due to their matrix complexity, hops have traditionally been a difficult commodity to monitor for pesticide use. In addition to normal matrix interferences from strongly pigmented samples, the vast array of flavor and fragrance components within the samples are often orders of magnitude larger than pesticides you wish to monitor. In this study, gas chromatography was combined with time-of-flight mass spectrometry (TOFMS) to detect commonly monitored pesticides in whole leaf hops.



System Settings and Sample Prep

Each sample type was extracted using the QuEChERS technique as described in other sources (<http://www.restek.com/pdfs/FFBR1183D-UNV.pdf>). In place of the standard dispersive solid phase extraction (dSPE) cleanup step an SPE cartridge cleanup procedure was employed. The SPE cartridge improves matrix cleanup while allowing acceptable recovery of pesticides. The resulting extracts for each sample were combined into common pools.

A standard curve was created for each sample type by combining 180 µL of matrix extract (190 µL for sample blanks), 10 µL of internal standard spike, and 10 µL of pesticide mix. The samples were injected into a gas chromatograph (GC) coupled to LECO's Pegasus® BT time-of-flight mass spectrometer (TOFMS).

Table 1. GC-TOFMS Data Acquisition Parameters.

Gas Chromatograph	Agilent 7890 with MMI and 7693 Autosampler
Injection	1 µL, Splitless 80 °C (0.5 min) to 300 °C at 720 °C/min
Carrier Gas	He @ 1.8 mL/min, Constant Flow
Column	Rxi-5MS, 30 m x 0.25 mm ID x 0.25 µm df (Restek)
Temperature Program	90 °C (1.2 min), 10 °C/min to 340 °C, 0.5 min hold
Mass Spectrometer	LECO Pegasus BT
Ion Source Temperature	225 °C
Ionization Mode	El
Mass Range (m/z)	45-520
Acquisition Rate	10 spectra/s



Figure 1: Pegasus BT GC-TOFMS.

GC-TOFMS Results

Once the data were acquired they were analyzed in ChromaTOF® brand software using a combination of targeted and untargeted peak find with retention index and mass spectral matching to NIST17 libraries.

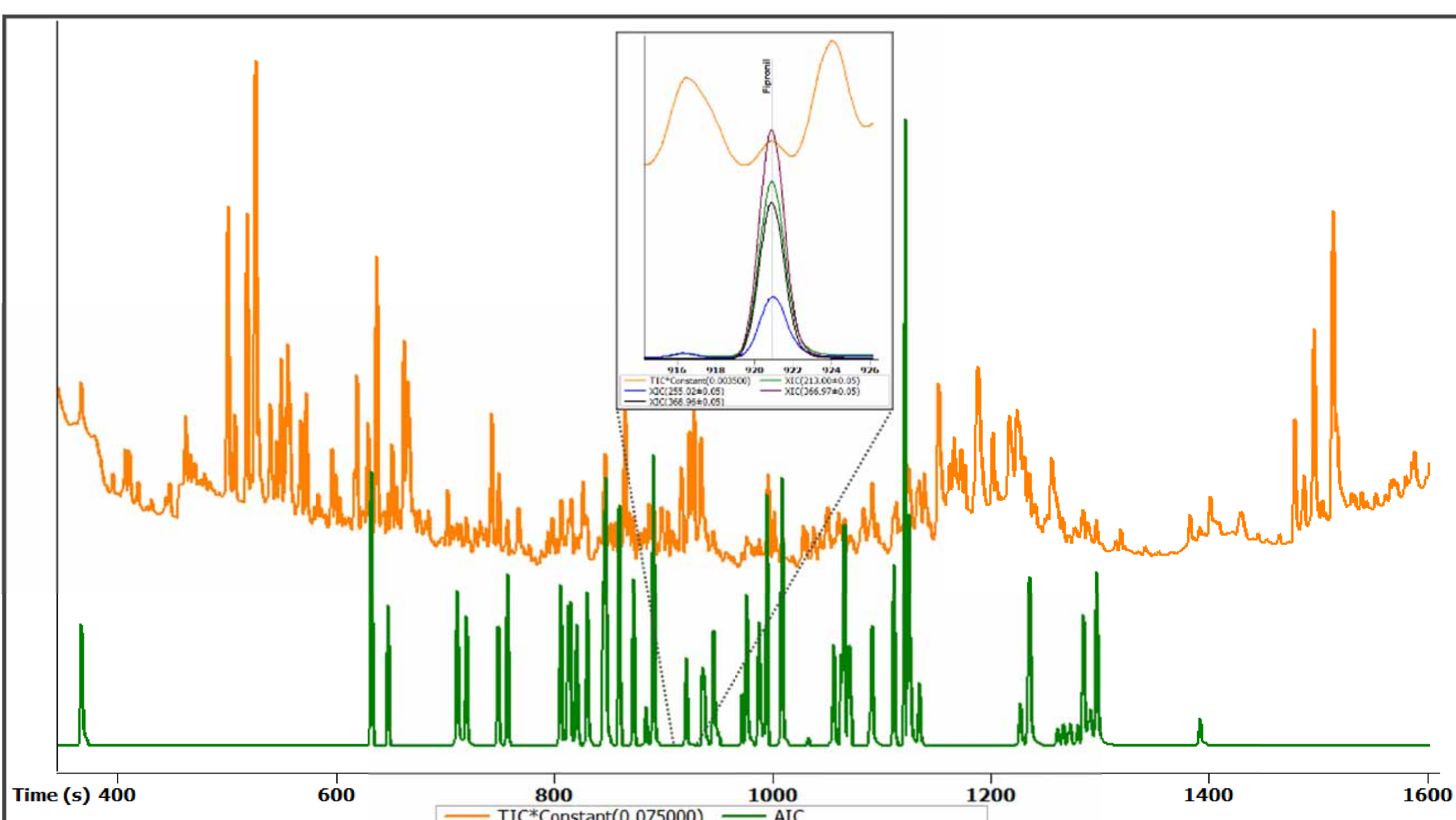


Figure 2. Overlay of the Total Ion Chromatogram (TIC) scaled down to 7.5% of actual and Analytical Ion Chromatogram (AIC). The AIC shows the localized, summed signal of the pesticides. In this example the concentration of the pesticides are 500 ppb. The insert shows a scaled TIC trace and the eXtracted Ion signal (XIC) of Fipronil's most abundant ions.

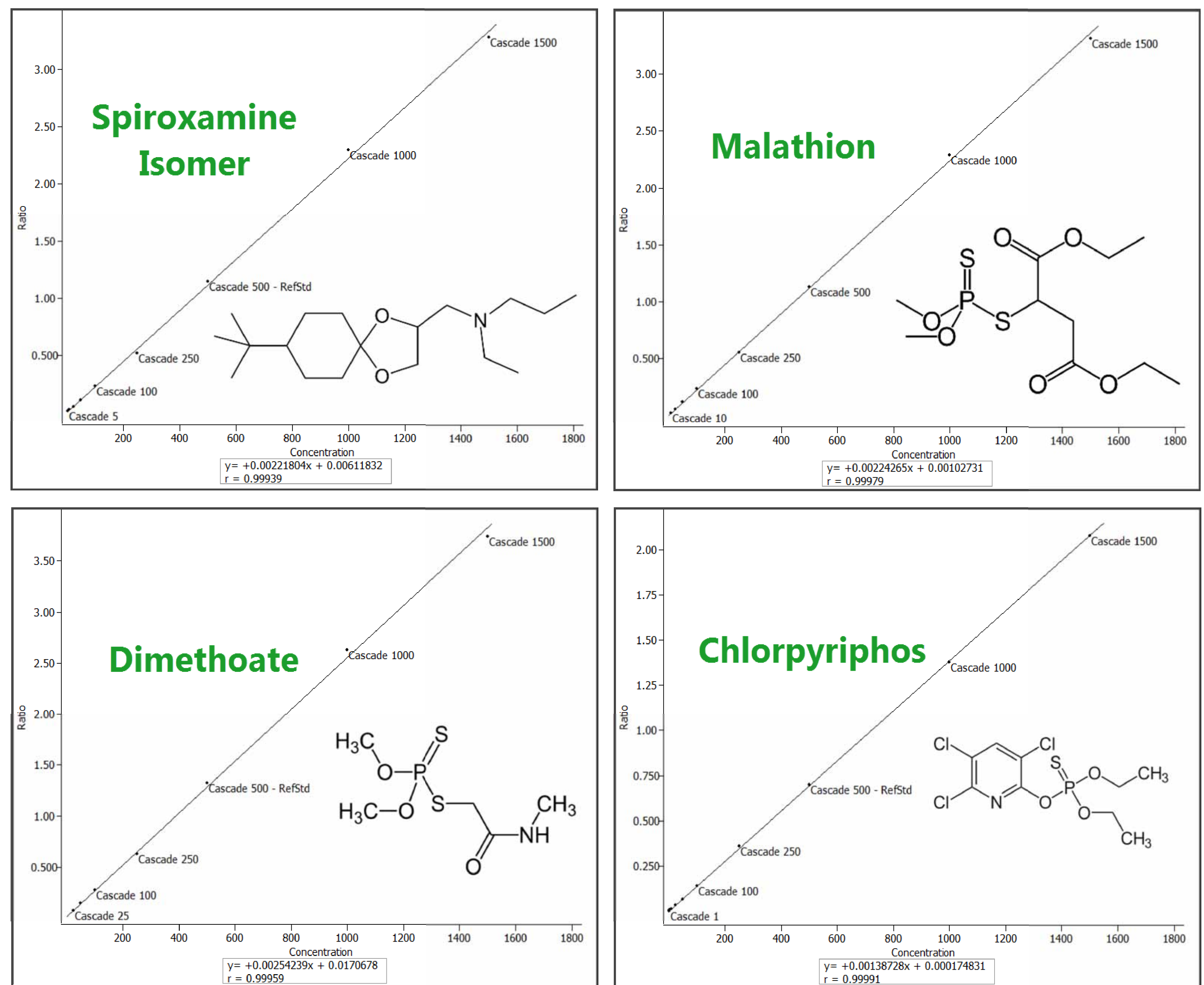


Figure 3. Example quantitation curves generated within ChromaTOF. All analyte responses were normalized with an internal standard. Concentrations shown in the curves are the concentration (pg/µL) of the pesticide mix spiked into the hop matrix. Table 3 shows the analyte concentration adjusted for the sample weight.

Table 2. Minimum reporting levels per analyte. MRL was determined as the lowest level standard with a calculated concentration within 20% of the spiked amount. All values calculated based on a 1st order linear fit curve.

Analyte	RT (sec)	Cascade Hop R ²	Cascade Hop MRL ng/g	Ethiopian Hops R ²	Ethiopian Hops MRL ng/g
Dichlorphos	367	0.9930	0.25	0.9989	0.1
Propoxur	632	0.9982	0.02	0.9978	0.25
Ethoprophos	648	0.9982	0.1	0.9985	0.25
Dimethoate	711	0.9992	0.25	0.9980	0.25
Carbofuran	719	0.9984	0.1	0.9975	0.25
Diazinone	757	0.9981	0.05	0.9997	0.25
Spiroxamine 1	813	0.9988	0.05	0.9985	0.1
Methyl parathion	815	0.9990	0.1	0.9977	0.25
Carbaryl	821	0.9995	0.02	0.9965	0.25
Metalaxyl	830	0.9994	0.05	0.9989	0.25
Spiroxamine 2	845	0.9988	0.1	0.9989	0.25
Malathion	859	0.9996	0.1	0.9979	0.25
Chlorpyrifos	873	0.9998	0.01	0.9988	0.25
MGK-264	891	0.9936	0.1	0.9982	0.05
Fipronil	921	0.9986	0.01	0.9990	0.25
Paclobutrazol	946	0.9972	0.25	0.9989	0.25
Fludioxonil	977	0.9989	0.05	0.9989	0.25
Kresoxim-methyl	995	0.9979	0.1	0.9987	0.25
Chlorfenapyr	1009	0.9953	0.25	0.9991	0.05
Propiconazole 1	1063	0.9981	0.25	0.9973	0.1
Trifloxystrobin	1066	0.9987	0.1	0.9973	0.02
Propiconazole 2	1070	0.9967	0.25	0.9988	0.25
Piperonyl butoxide	1091	0.9981	0.05	0.9985	0.1
Spiromesifen	1111	0.9873	0.5	0.9922	0.1
Phosmet	1121	0.9971	0.1	0.9972	0.25
Bifenthrin	1125	0.9989	0.1	0.9994	0.02
Bifenazate	1127	0.9929	0.5	0.9972	0.5
Etoazole	1134	0.9994	0.25	0.9994	0.25
Pyridaben	1235	0.9987	0.1	0.9984	0.25
Boscalid	1285	0.9998	0.25	0.9994	0.05
Etofenprox	1297	0.9993	0.25	0.9989	0.25
Azoxystrobin	1392	0.9991	0.1	0.9986	0.25

Summary

- The Pegasus BT's exceptional sensitivity combined with ChromaTOF's industry leading deconvolution with Target Analyte Find allows for excellent quantification of pesticides in challenging matrices.
- Time-of-flight data acquisition allows the user to collect and store a wide mass range without sacrificing sensitivity. Data can be reevaluated later for peak information not targeted in the initial analysis.

