Utilization of Rapid LC-MS for Screening and Quantitative Analysis of Pesticides in Food Matrix using an Exactive Plus Benchtop Orbitrap Platform

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Introduction
The demand for quick and simple analysis of large numbers of samples in agriculture analysis is growing year by year. Throughout the world pesticides are used to control pests that are harmful to crops, humans and animals. These substances can pose a significant health threat and therefore need to be accurately detected at the lowest levels requested by the governmental authorities typically at low part per billion (ppb) or low part per trillion (ppt) levels. Traditionally, triple stage quadrupole mass spectrometry is used for pesticide screening, but requires optimization of mass spectrometric conditions for each compound, and therefore time-consuming analysis. The Thermo Scientific Exactive Plus Orbitrap mass spectrometer provides high-resolution, accurate mass (HR/AM) to unequivocally identify compounds without the need for optimization. The results of this unique solution are improved sensitivity and precision. Mass spectrometric detection for screening experiments with HR/AM using only one chromatographic run. An Exactive™ Plus mass spectrometer with the proven power of the Thermo Scientific Orbitrap mass analyzer and Thermo Scientific fulfills these demands with higher confidence and precision.

Methods
Sample Preparation
Onion matrix were prepared for analysis by using a modified quick, easy, cheap, effective, rugged, and safe (QuEChERS) method, which is a sample preparation procedure using rapid extraction from the sample. The QuEChERS extracts were obtained from the California Department of Food and Agriculture (CDFA). For the QuEChERS extraction, 65 g of homogenized sample and 15 mL of acetonitrile were used. Then, 200 μL of final QuEChERS extract, 300 μL of acetonitrile, and 500 μL of water were transferred into an autosampler vial, spiked with 20 μL of the pesticides of interest. The extract was vortex mixed and centrifuged at 12,900 rpm for 5 minutes. The supernatant was transferred into the C-trap where all ion fragmentation (AIF) happens. All the fragmented ions are then detected in accurate mass. (Figure 1)

Hardware
The new Exactive Plus mass analyzer has the proven S-Lens configuration for ion focusing for more sensitivity. The mass analyzer is coupled with an UltiMate 3000 HPLC system which provides full scan and selected ion monitoring (SRM) capabilities.

Results
The new Exactive Plus mass analyzer was coupled with the UltiMate 3000 UHPLC system for MS/MS experiments. A set of standards were injected to calibrate the new Exactive Plus mass analyzer (Figure 2). In addition to the quadrupole, TraceFinder software has a very easy-to-use report page where you can see all the results at a glance. Figure 3 shows a simple high-density calibration report is shown below – allowing you to search for a particular compound by clicking on the binocular to open the search window. Figures 2 and 3 show a particular compound in the onion matrix and one compound in the neat matrix 0.10 ng/mL depending on starting concentration in mixture).

Conclusion
The Thermo Scientific Exactive Plus mass spectrometer powered by Orbitrap technology provides easy access to full quantitative and screening data in one package. The results show very high sensitivity using the Exactive Plus which will assist in detecting pesticides at ultra-low levels.

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Table 1. List of pesticides and associated retention times with actual vs. theoretical run with calculated mass errors.

Table 2. Tabulated results of LOQ's per compound, retention times and curve fit R2 values.

FIGURE 2. TraceFinder displaying trendline overlaid calibration curve plot of matrix, R^2, list of compounds, and chromatogram.

FIGURE 3. A simple high-density calibration report is shown below – allowing you to search for a particular compound by clicking on the binocular to open the search window.