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Automated MS Optimization of a Modified Triple Quadrupole Mass Spectrometer Enabled Improved Multi-Residue Pesticide Analysis in Fruit and Vegetables

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Introduction

Multi-residue pesticide analysis in food presents several challenges due to the diversity of pesticide compound classes, matrix complexity, thermal lability and varying ionization efficiencies. Increased instrument sensitivity coupled with software tools that enable automated optimization of MS parameters is therefore essential and a continuous demand in the food safety testing arena.

In this work we evaluate a modified ion funnel Triple-Quadrupole Mass Spectrometer in combination with Source and iFunnel Optimizer Software to improve sensitivity, reproducibility, throughput and ruggedness in the analysis of a comprehensive set of 250 pesticides in tomato, orange and black tea. Data presented show the software capabilities and quantitative performance results. In a complex matrix like black tea, dilution is often performed to minimize the matrix effects and allow quantitation based on a solvent calibration. The highly sensitive MS coupled with automated MS parameter optimization enabled a 100-fold dilution of the black tea samples while most of the pesticides can be detected at or below the European Union maximum residue limit (EU MRL).

Experimental

Matrix Preparation
Organic tomato, orange and black tea matrices were prepared based on QuEChERS EN protocol using Agilent BondElut QuEChERS kits (P/N 5982-6650; 5982-5356CH).

Agilent 1290 Infinity UHPLC
Column: Agilent Rapid Resolution High Definition (RRHD) Zorbax Eclipse Plus C18, 2.1 x 100 mm, 1.8 µm
Mobile phase:
A: water + 5 mM ammonium formate + 0.1% formic acid
B: methanol + 5 mM ammonium formate + 0.1% formic acid
Flow rate: 0.6 mL/min; Injection Volume: 2 µL
Gradient: 0 min 5% B, 0.2 min 5% B, 2.2 min 50% B, 10.5 min 100% B, 13 min 100% B, 13.1 min 5% B, post-time 3 min

Modified Agilent 6490A Triple Quadrupole MS
Drying Gas Temp: 120ºC; Drying Gas Flow: 15 L/min
Sheath Gas Temp: 375ºC; Sheath Gas Flow: 12 L/min
Nebulizer Pressure: 35 psi
Capillary Voltage: 3500 V positive; 3000 V negative
Nozzle Voltage: 300 V positive; 500 V negative
Funnel RF voltages: Low pressure funnel RF: 60 V (+), 90 V (-); High pressure funnel RF: 150 V (+), 110 V (-)

Dynamic MRM Acquisition:
Cycle Time: 600 ms
Maximum Concurrent MRMs: 80
Minimum Dwell Time: 5.38 ms

Optimizer Software

The Source and iFunnel Optimizer Software enables the automatic creation of methods and worklists as well as Quantitation batches for optimization of all Agilent Jet Stream parameters and iFunnel RF voltages.

Figure 1 shows a screen capture of the optimizer tool. The user interface includes 3 sections:

1. **Project setting:** The user needs to load a "base" method, which will be used as the template method for optimization.
2. **Parameter selection:** The parameters can be selected in the table together with ranges, step size and wait times for equilibration of temperatures.
3. **Worklist setting:** Allows the selection of a sample name and sample position for the optimization process.

After setting up the project, parameters and worklist, all optimization methods and worklists are generated under the project folder name. All the worklists are submitted to the Study Manager application and are ready to run.
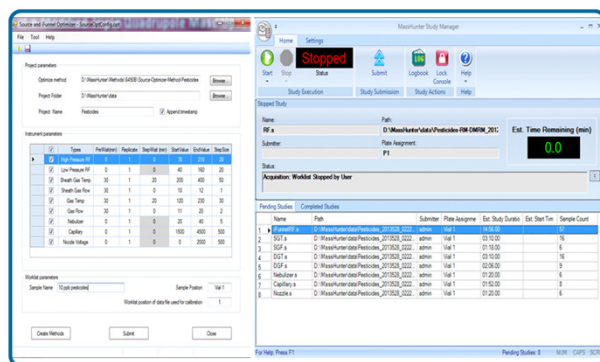

Figure 1: Source and iFunnel Optimizer SW user interface and MassHunter Study Manager showing pending studies.

Finally, quantitation batches are automatically created in the MassHunter Quantitative analysis software showing optimization results. An example of the results obtained in MassHunter Quant is given in Figure 2 for the optimization of nozzle voltage for the pesticide fipronil.

Figure 2: Selected example of Quantitation batch generated for nozzle voltage for the pesticide fipronil.

1:100 Dilution Enabled by Improved Sensitivity

Sample dilution is an effective means to reduce matrix effects in multi-residue pesticide analysis. The modified triple quadrupole MS provided enhanced sensitivity and allowed extensive dilution of the extracts. Figures 3-5 show the number of detected pesticides in the different matrices. The number of detected pesticides is consistent even at the 1:100 dilution level. Most of the pesticides were detected in the 1:100 diluted samples at the EU MRL, which is 10 μg/kg for most compounds in several different commodities including tomato, orange, and black tea.
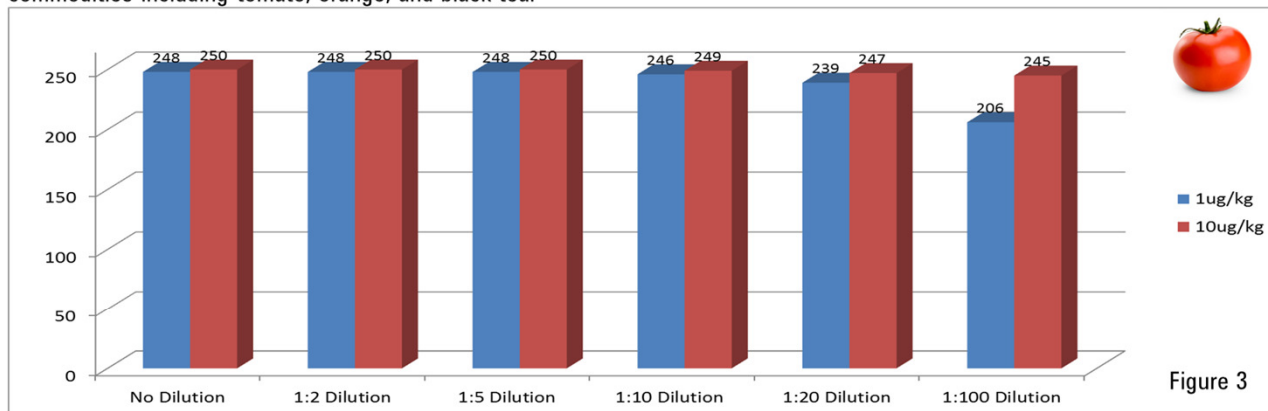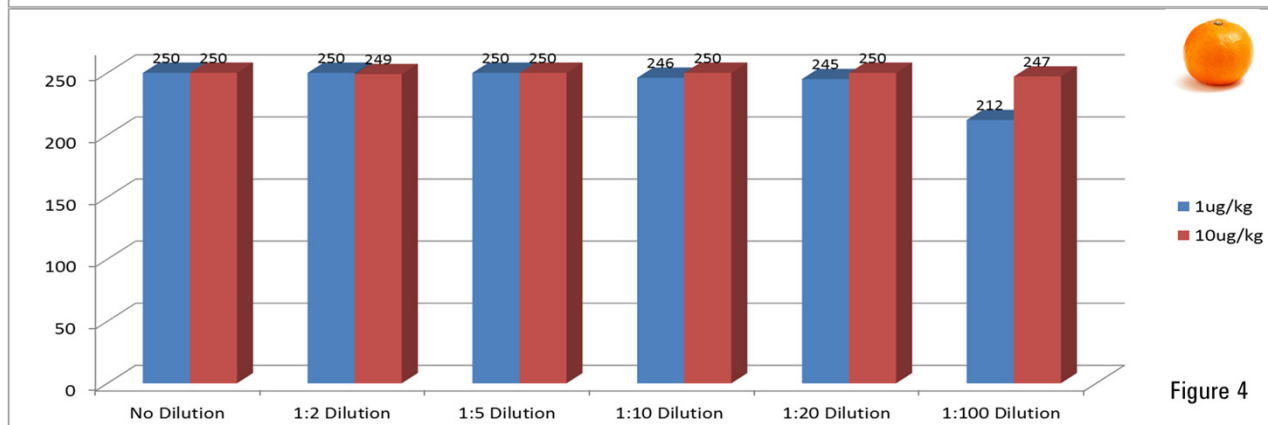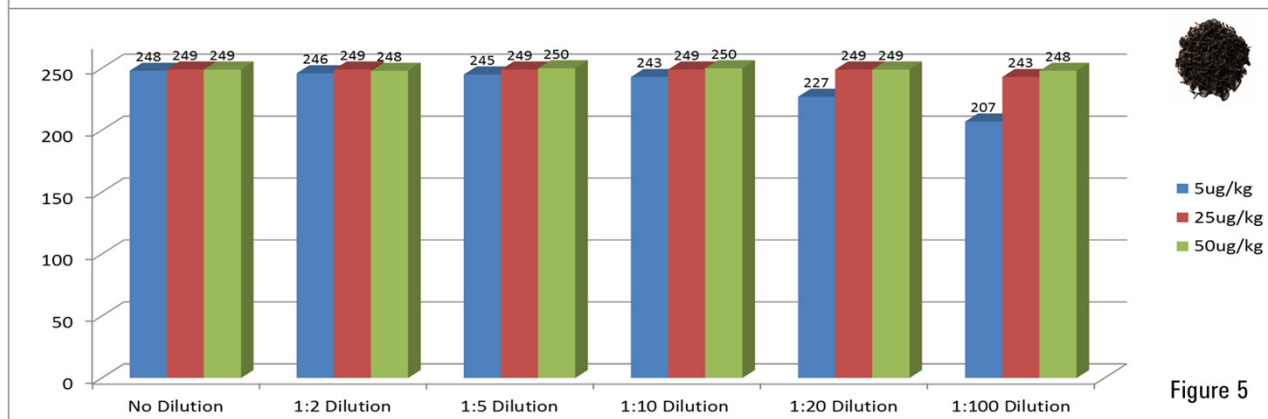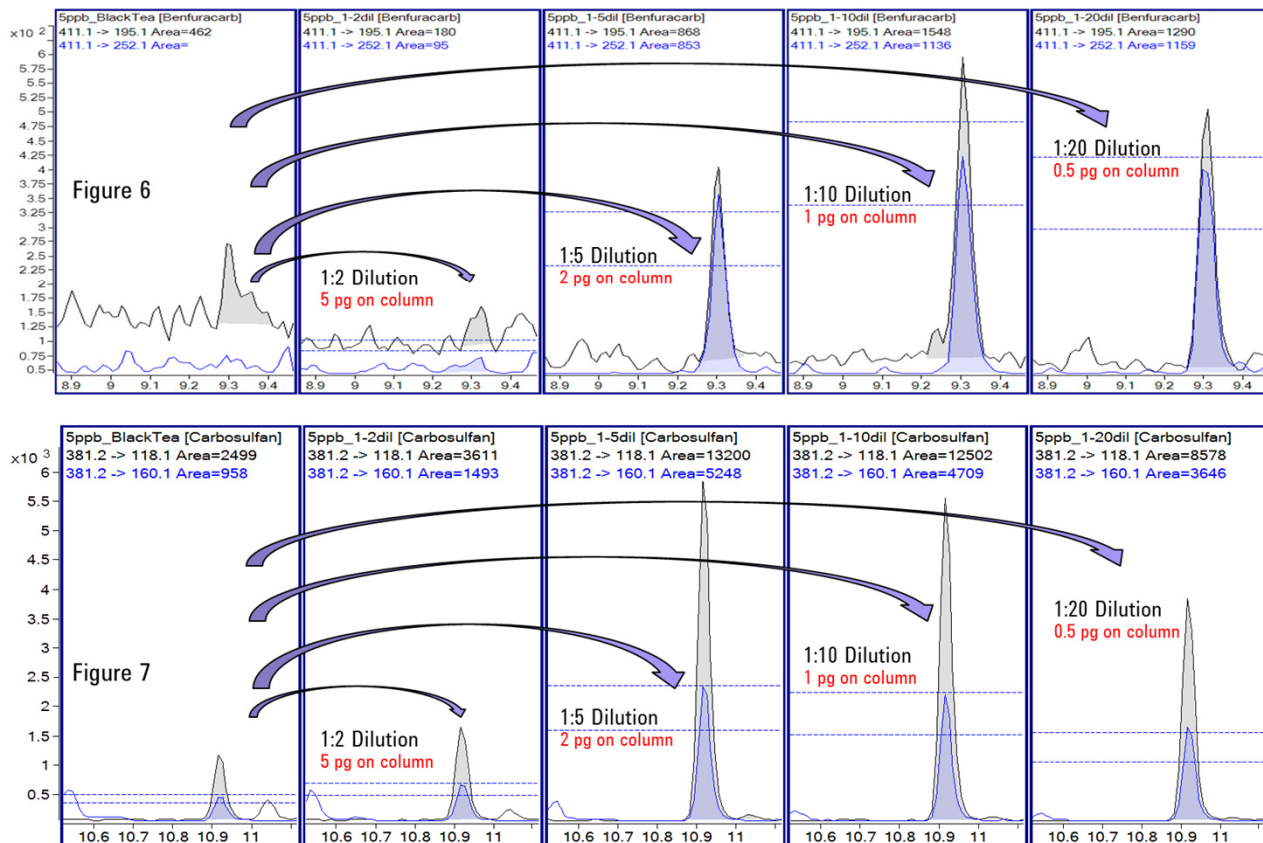

Figure 3

Figure 4

Figure 5

Figures 3-5: Number of detected pesticides from a total of 250 pesticides in tomato (Figure 3) orange (Figure 4), and black tea (Figure 5) at different spike-in concentrations and different dilution of the samples up to 100-fold dilution of the extracts at the EU MRL spike-in concentrations.

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Positive Impact of Sample Dilution on Matrix Effects and Detectability

Sample dilution is sometimes essential for pesticide detection, especially in the analysis of complex matrices such as black tea. Figures 6 and 7 demonstrate the advantage of black tea extract dilution for the detection of benfuracarb and carbosulfan, respectively. A spiked tea extract corresponding to 25 μg/kg was diluted with acetonitrile prior to injection. The figures show that the signal does not decrease on the same order as the dilution. Benfuracarb can only be detected when the extract is diluted 5 fold or more. Carbosulfan shows much better signal to noise when the matrix is diluted 5-20 fold.

Figures 6 and 7: Positive impact of sample dilution on detectability of benfuracarb (Fig 6) and carbosulfan (Fig 7) at 25 μg/kg.

Conclusions

The source optimizer software allows automatic creation of methods, worklists and quantitation batches with the goal of determining an optimal and generic set of MS parameters. Using the source and iFunnel Optimizer software significantly reduces the amount of operator time required, and ultimately selects a set of MS parameters that enable the reliable detection of most pesticides from different chemical classes at or below the European Union Maximum Residue Limit (EU MRL) even after 1:100 dilution.

Sample dilution offers an effective way of reducing or eliminating matrix effects, which can affect method performance. However, this requires a highly sensitive mass spectrometer capable of detecting analytes at sub-picogram levels on column. The results obtained using a modified triple quadrupole mass spectrometer show that most of the 250 pesticides can be detected at 100-fold dilution of the samples in different matrices at or below the EU MRLs.

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