Introduction

Challenges in multi-residue pesticide analysis include the diversity of pesticide compound classes found in food analyses, matrix complexity, low concentrations and varying ionization efficiency of some pesticides. In this work we evaluated the use of dilution as a means of increasing sensitivity and reducing matrix effects. Sample preparation involved extraction and quantitation at trace levels in black tea using UPLC-triple quadrupole mass spectrometry and dynamic MRM with fast pesticide switching. Black tea was selected as test matrix due to its high complexity. Increased sample sensitivity achieved using dual ion funnel technology allowed a 20-fold sample dilution while still achieving the maximum possible level (MRL) stipulated by the European Union.

Sample preparation

The extraction procedure was based on the 9620HS5 method. The final extract contained 25 mL of black tea sample per mL of acetonitrile (ACN), obtained by 1:10 dilution of the pesticide mixture at four different levels were prepared in ACN. These levels were spiked in the same extract of black tea to prepare the calibration curves in black tea in the range of 0.5 ppt to 50 ppb.

Matrix effects in non-diluted and 1:20 diluted black tea samples

Comparison of matrix effects in non-diluted and 1:20 diluted black tea samples was done using the enhancement factor (EF). EF is calculated as the ratio of signal in spiked matrix to that in pure solvents. Both matrices were in the same composition solution (ACN).

Experimental

Analyzed pesticides: 68 pesticides of different chemical classes including organophosphates, triazines, pyrimidines, phenylureas, carbamates, oxinyl carbamates, thiacarbamates, teminal, azolyl, and pyridyl herbicides were selected for the evaluation covering the full pesticide range and including pesticides classified as difficult to analyze due to their low proton affinities, thermal lability or susceptibility to matrix effects.

Effect of Dilution on Signal response and Matrix Effects

After 2:10 dilution, all pesticides were detected at a LLOQ at least 2:1 below the EU MRL and 50 from 68 pesticides were detected at a LLOQ at least 2:1 below the EU MRL. At LLOQ, all pesticides exhibited Area RSD [%] < 20% with most of the pesticides showing RSD [%] < 10%. At LLOQ, all pesticides were detected at a LLOQ at least 200 x below the EU MRL. The lowest EU MRL was 5 ppb. At LLOQ, all pesticides were detected at a LLOQ at least 200 x below the EU MRL. The lowest EU MRL was 5 ppb.

Conclusions

1. Taking full advantage of dual ion funnel technology, it is possible to use a 20:1 dilution to minimize matrix effects while still achieving a LLOQ below 5 ppb. All analyzed pesticides were detected at a LLOQ at least 2:1 below the EU MRL. When using sample dilution as an improved concentration method, a 2:10 dilution at LLOQ in black tea matrix resulted in a LC-MS system which leads to better chromatographic, increased chemical noise and lower matrix effects for all 68 pesticides.

2. A generic set of Agilent Jet Stream (AJS) settings was found that allowed reliable quantitation of multiple pesticides of different chemical classes in food and feed matrices at LLOQ without being detected at a LLOQ at least 2:1 below the EU MRL. At LLOQ, all pesticides were detected at a LLOQ at least 200 x below the EU MRL. A 20:1 dilution at LLOQ in black tea matrix resulted in a LC-MS system which leads to better chromatographic, increased chemical noise and lower matrix effects for all 68 pesticides.

3. Precision at LLOQ after 1:20 dilution was excellent with most of the pesticides exhibiting Area RSD [%] < 10%.