Evaluation of matrix effects by molecular mapping using liquid chromatography electrospray high resolution mass spectrometry

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INTRODUCTION

The presence of matrix effects is one of the major concerns in food analysis. Its presence affects the analyte signal and can lead to errors in the quantification and the detection of the analytes. In this work, the relation between matrix suppression and co-extracted matrix components has been investigated. Twenty-three different commodities were extracted by various extraction Multi-residue Methods –MRM-, mapping their natural compounds by retention time and accurate mass. Mapping them allow to evaluate the benefit in using one specific method or what can be the main natural compounds that can interact with the target analytes.

EXPERIMENTAL SECTION: SAMPLE TREATMENT AND LC-TOF-MS ANALYSIS

SAMPLE TREATMENT

Extraction of blank matrices

Citrate buffered QuEChERS (1)
Blank extract
Spiked with 140 pesticides 100 µg/L

LC-QTOF-MS

Chromatography Agilent 1200 HPLC system
Column: XDB-C18 Agilent. 50mm x 4.6 mm (1.8 µm)
Mobile phase:
ACN [A] [5% water, 0.1% formic acid] and MiLiQ Water (B) [0.1% formic acid]
10% (A) isocratic t=1 min, then to 100% (A) in 10 min and maintained for 6 min. Flow rate of 0.6 mL/min.

RESULTS

Mapping of Co-extracted matrix compounds-Pesticides

“Difficult” matrices

Correlation of signal suppression and co-extracted compounds

An increase of signal suppression is noted when the signal area of matrix components at the same retention time window increases

Dilution to overcome matrix effects

A sample dilution decreases the number of competing molecules and thus the analyte signal increases and matrix effects improved for the majority of pesticides.

Evaluation of Multi-Residue Extraction Methods

QuEChERS vs QuEChERS+SPE with ZrO2 in Parsley matrix

QuEChERS vs QuEChERS+CaCl2 in Green tea matrix

CONCLUSION

Molecular mapping of matrix components by molecular weight and retention time is a very effective approach for assessing matrix difficulty, risk of matrix suppression effects and evaluation of sample preparation methods. The number and distribution of co-extracted compounds, vary much depending on vegetable matrix even those included in the same commodity group according to EU SANTE/11945/2015 guidance document. “Difficult” matrices providing a high number and concentration of natural components have associated a high suppression. Dilution of the extracts was shown as an effective method to reduce the interfering compounds and to diminish the signal suppression for the majority of the pesticides in all commodities. In tea and parsley matrices the use of CaCl2 and ZrO2 respectively. In the clean-up step, showed to be much more efficient removing interfering compounds than the original QuEChERS clean-up.

Screening Software

Agilent MassHunter “Molecular Feature Extraction”