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Evaluation of simultaneous MS and MS² workflows of LC/Q-Orbitrap for analysis of pesticides in fruits and vegetables

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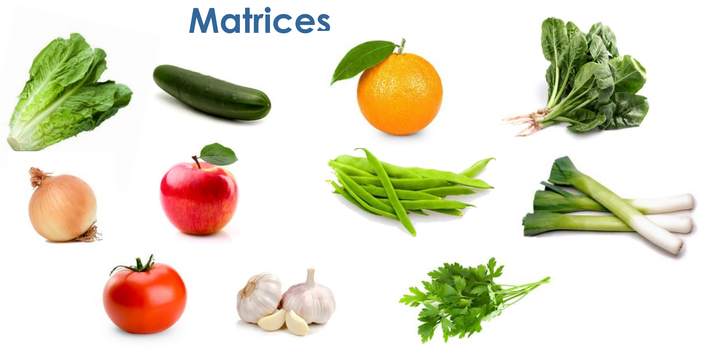
INTRODUCTION

During last decade high resolution accurate mass spectrometers have improved qualitative (resolution, mass accuracy) as well as quantitative (sensitivity, linear range) aspects. HARMS instruments are well known for their high selectivity in full MS mode. Nevertheless even spectrometers which have very high resolution may produce false positive results. Isotopic pattern and alternative adducts not always can correctly discard false positives. A solution to reduce number of false positive results is application of simultaneous full MS and MS².

The objective of this work was to compare three workflows of simultaneous MS and MS²: All Ion Fragmentation (no precursor ion selection, ions from entire mass range fragmented at the same time), variable Data Independent Acquisition (no precursor ion selection, mass range divided into smaller segments before fragmentation) and data dependent MS² (selection of precursor ion). Acatonitrile extracts (blanks and spiked with 166 pesticides) of 11 fruits and vegetables were used for the evaluation. Blank extracts were used to evaluate potential false positives (considering retention time window of 0.2 min) whereas spiked extracts (at 0.01 mg/kg and 0.1 mg/kg) to evaluate the false negatives. Samples were analysed with Q Exactive Focus working with resolution of 70,000 (at m/z 200) in full scan MS and 17,500 or 35,000 in MS² mode.

EXPERIMENTAL

Matrices



Chromatography

Mobil phase:
- A: 98% H_2O 2% MeOH 5mM $HCOONH_4$ 0.1% HCOOH
- B: 98% MeOH 2% H_2O 5mM $HCOONH_4$ 0.1% HCOOH

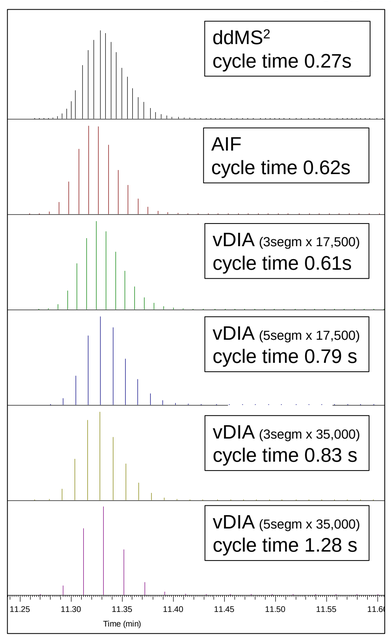
Flow: 0.35 mL/min
Gradient time: 14 min + 3 min reequilibration
Column: Accucore™ aQ C18, 100 mm x 2.1 mm x 2.6 µm
Column temperature: 30°C
Ijnection volume: 10 µL

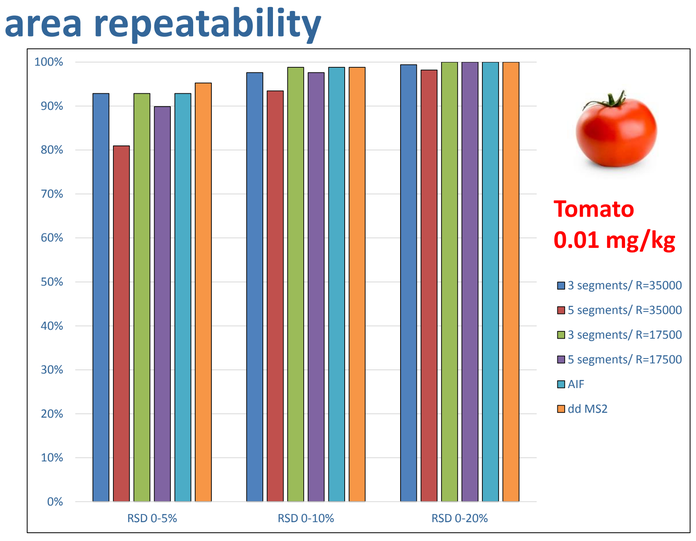
Acquisition mode: full scan MS
-resolution 70,000
-AGC target 1e6
-max IT auto
-scan range 120-1000 Da

Acquisition mode: MS²
-**dd MS²** resolution 17,500
-**vDIA** resolution 17,500 or 35,000, 3 or 5 mass segments
- **AIF** resolution 70,000

RESULTS

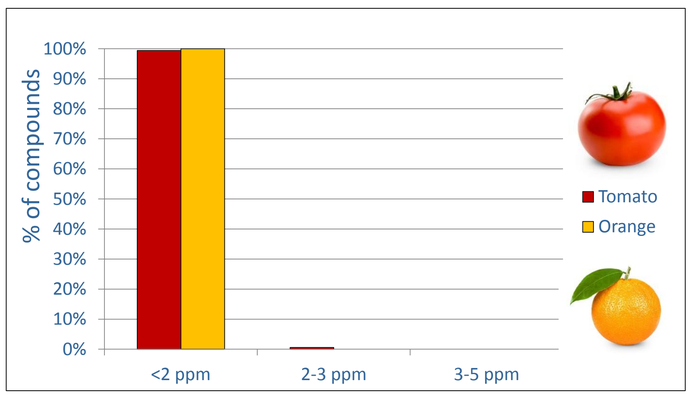
Peak area repeatability



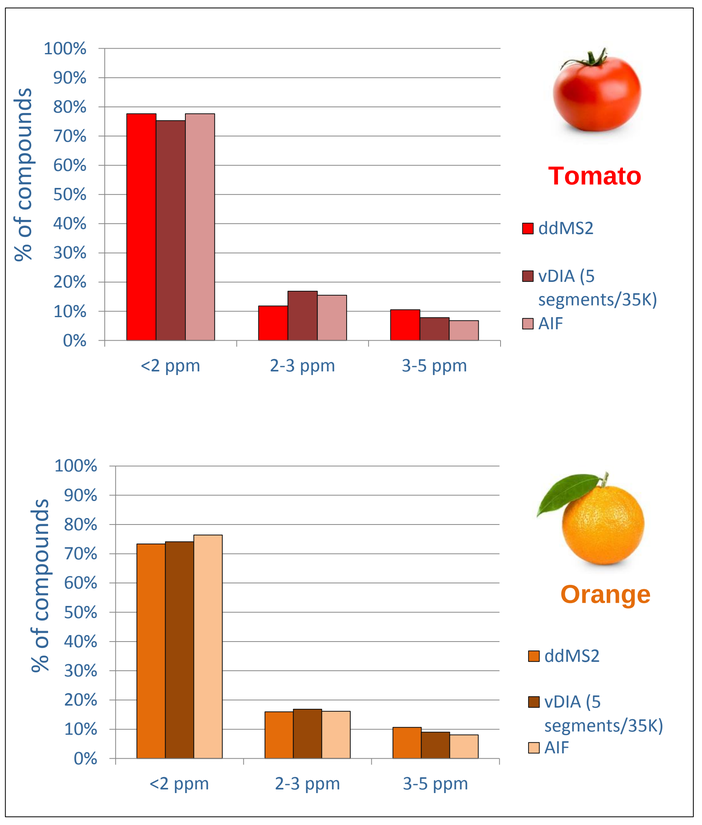


In workflows with shorter cycle times more points per chromatographic peak is obtained, by that peak area repeatability is better.

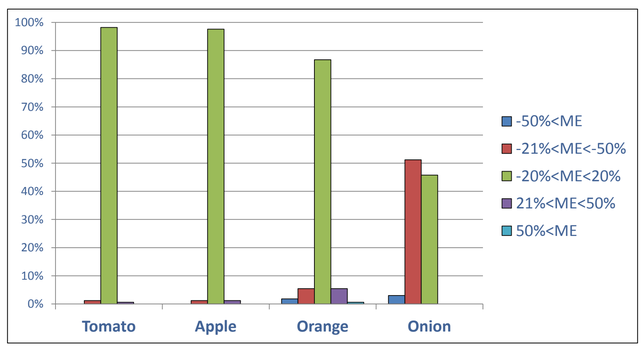
Mass errors in full scan MS



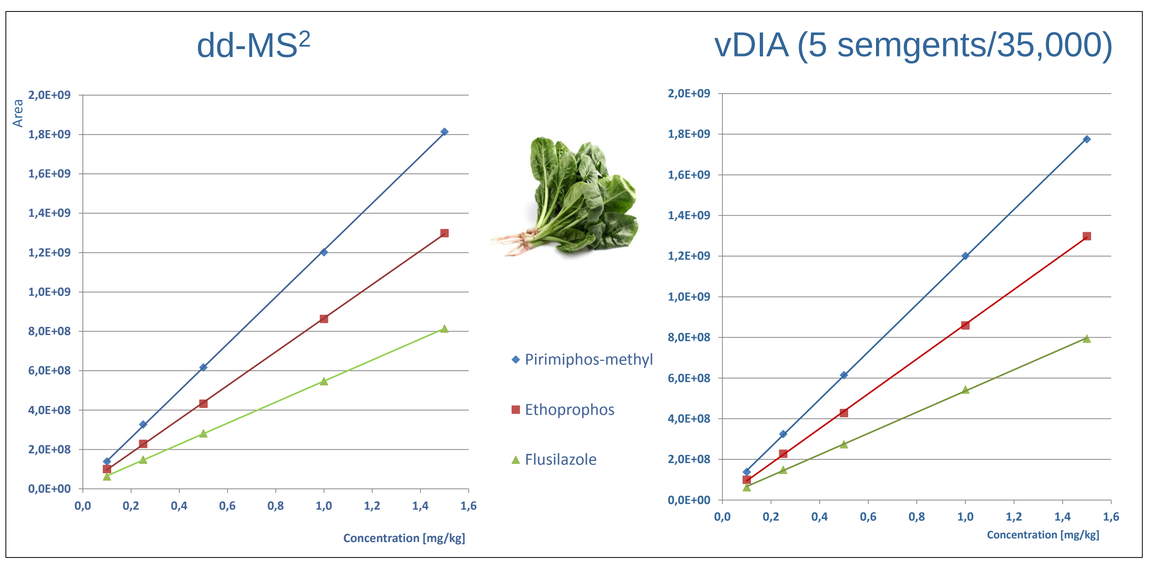
Mass errors in MS²



Matrix effects

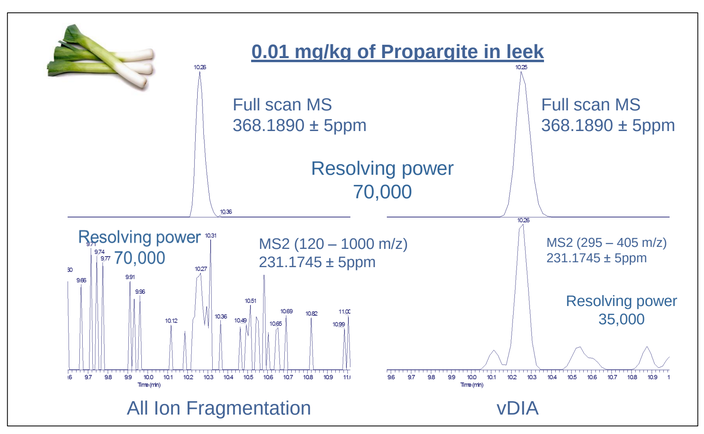


Linearity



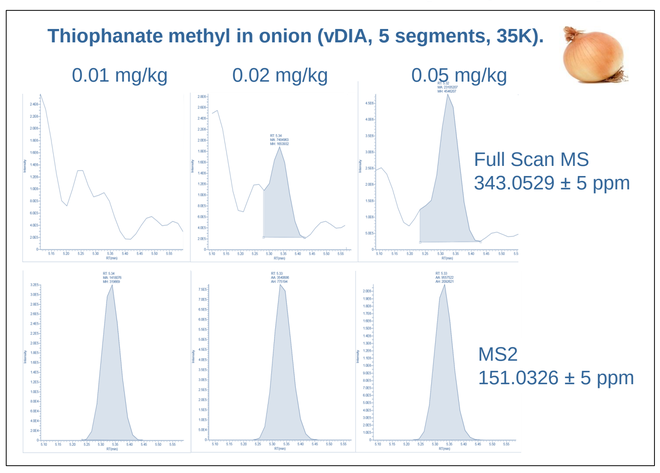
Independently of the workflow selected the detector response is characterised by very good linear range and no saturation is observed.

Selectivity in AIF and vDIA



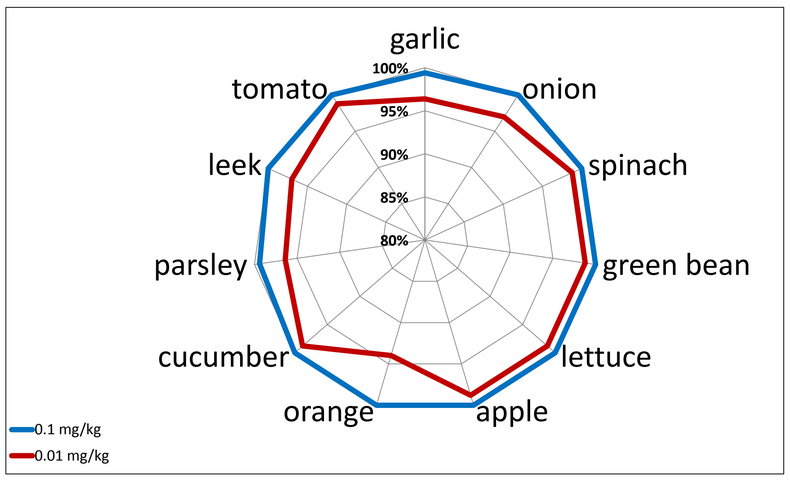
vDIA provides more selectivity than AIF

Quantitation in MS² (AIF, vDIA)

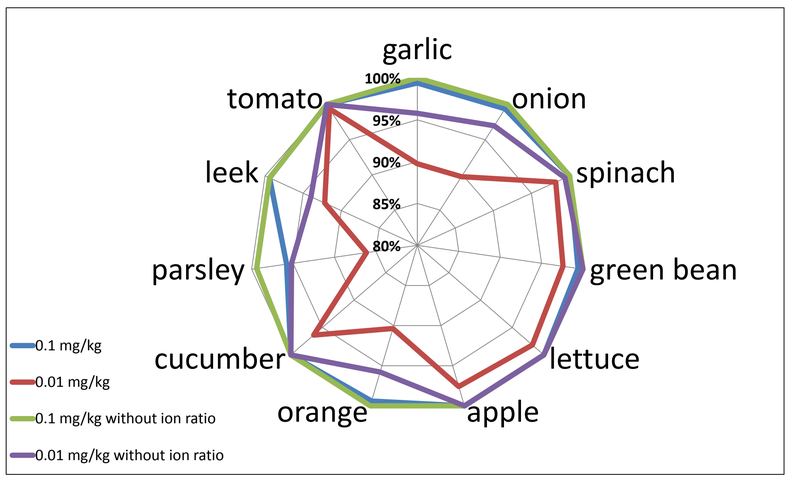


If full scan MS does not have enough selectivity, quantitation is possible in MS²

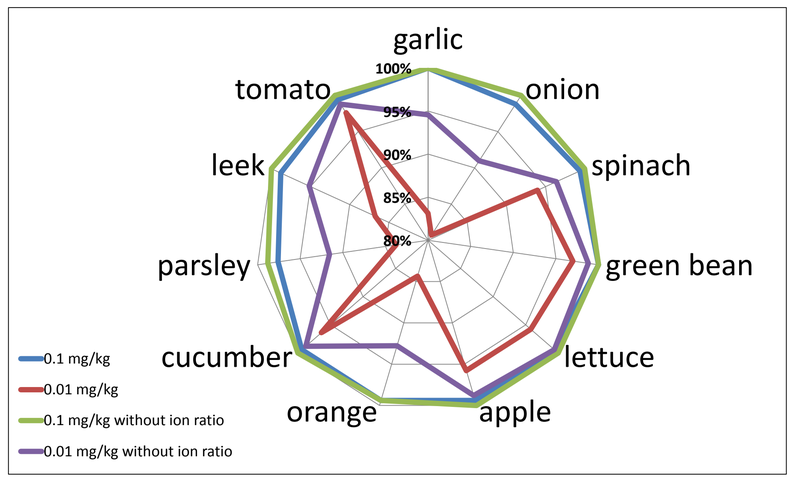
Percentage of identified pesticides



dd-MS²



vDIA (5 semgents/35,000)



AIF

CONCLUSIONS

LC–Q Exactive Focus MS operated in full scan at the resolution of 70,000 detected close to 100% of the selected pesticides in all matrices with mass errors below 2 ppm and mass errors < 5 ppm in MS². From the point of view of peak area repeatability the most robust workflow was dd MS². Matrix effects were lower than 20% in the majority of the cases facilitating quantification. AIF and vDIA offer the possibility to quantify with accurate MS², this can help with "difficult" matrices. Dd MS² had the highest identification rate (96-100%, depending on the matrix). In vDIA it was 86-100% and in AIF 81-100%.

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