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

Mr Łukasz Rajski¹, Ms María Del Mar Gómez-Ramos¹, Mr Víctor Cutillas², Prof Amadeo Fernández-Alba²
¹EURL-FV. University of Almería, Agrifood Campus of International Excellence (ceiA³), ²University of Almería

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). Acetonitrile 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-Orbitrap working with resolution of 70,000 (at m/z 200) in full scan MS and 17,500 or 35,000 in MS2 mode.

Detection and quantitation were carried out in full MS. MS2 data were used for identification. Dd MS2 provided the highest number of points per chromatographic peak and by that peak area repeatability was the best. AIF and vDIA were characterised by longer cycle times thus obtained peak area repeatability was slightly worse but acceptable. All workflows showed very good linearity in the range 0.01 - 0.5 mg/kg. Dd MS2 had the highest identification rate (96-100%, depending on the matrix). In vDIA it was 86-100% and in AIF 81-100%. But, these two last mode offer high screening capabilities.

In terms of identification the best results were obtained with dd MS2. Problems were observed only when precursor ion had low abundance. In AIF and vDIA more false negative results were obtained. AIF and vDIA are less selective than dd MS2 thus more interfering ions is present in MS2 spectra. However great advantage of AIF and vDIA over dd MS2 is non-targeted acquisition of the workflow. For analysis of routine samples dd MS2 seems to be better solution because MS2 identification is more infallible.