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Performance evaluation of LC-single stage Orbitrap-MS for screening of residues and contaminants in food and feed

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Introduction

During the last years a shift in residue analysis to multi analyte-group – multi matrix methods has taken place. Full scan-high mass accuracy-high resolving power mass spectrometry is very promising for this type of analysis. The suitability of a single stage Orbitrap-MS for automated detection of pesticides, veterinary drugs, mycotoxins and plant toxins in 5 different matrices was evaluated.

Experimental

Egg, tomato, pig meat, wheat and a compound feed were analyzed as such and after spiking with 218 compounds (40% pesticides, 40% veterinary drugs, 20% plant- and mycotoxins).

Extraction

The samples were extracted using a generic acetonitrile extraction [1]. The final extract concentration was 0.25 g/ml [meat, wheat, feed] or 0.4 g/ml [egg, tomato].

LC-MS Detection

A gradient of H_2O:MeOH 10mM Ammonium formate and 20 µl/L formic acid was used on a Waters Atlantis T3 column (3µm; 3x100mm). 10 µl was injected.
Total run time was 20 min.
The Exactive was used at R=50.000, scan time was 0.4 sec. and a 'normal' scan was alternated with an 'all ion fragmentation' scan at 30 eV collision energy in the HCD cell.

Data processing

The data was evaluated using ToxID and an in-house developed software tool ('LCSearch' based on MetAlign software [2]). For screening automated library-based detection based on retention time and accurate mass of the compound was performed.

Results

Optimization of detectability

Lower detection limits can be achieved by injecting more matrix equivalent into the LC-MS system, either by more concentrated extracts or by injecting larger volumes.

However, the gain in detectability may be partly off-set by an increase in ion suppression. This is matrix dependent. An example of the effect of injected amount on observed response is shown in Figure 1.

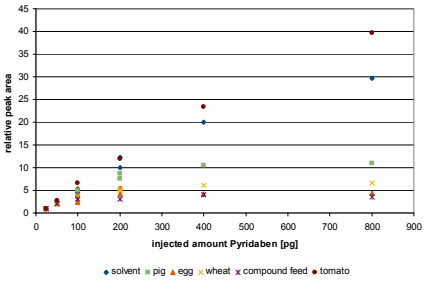


Fig 1: Impact of increasing sample amount on response

Automated library-based detection of analytes

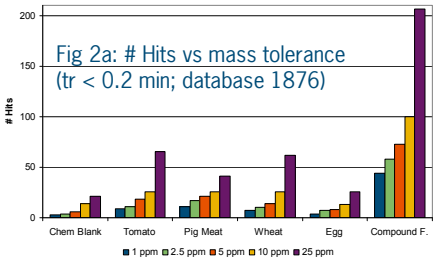
Table 1 summarizes the % of compounds detected in a) a solvent standard and b) in spiked samples relative to the number of detected compounds in de solvent standard.

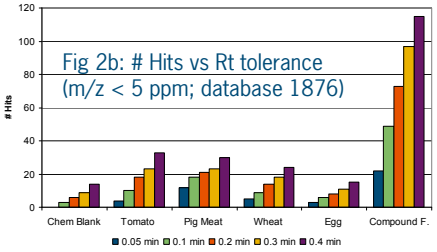
Table 1: % of compounds found

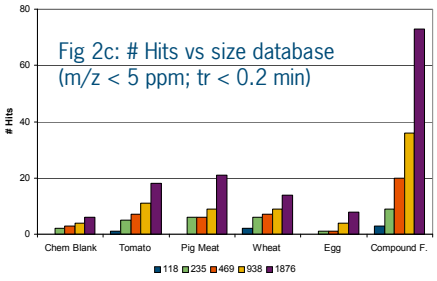
Solvent (ng/ml)	*2.5*	*12.5*	*62.5*
	61%	83%	94%
Matrix (mg/kg)	*0.01*	*0.05*	*0.25*
Tomato	98%	99%	97%
Egg	103%	101%	96%
Pig Meat	89%	92%	93%
Wheat	85%	92%	96%
Feed	50%	70%	80%

False Positives

As any tentatively identified compound will trigger further action, the number of false positives should be minimized. The most obvious way to achieve this through narrow retention time and mass accuracy tolerances. The impact of this, and of the # compounds in library and the complexity of the matrix is shown for the blank samples in Figure 2 a-c.







Conclusions

- With the high resolving power/mass accuracy achieved with the Orbitrap, the intrinsic analyte response and matrix-suppression are the main factors affecting the detectability of the analytes.
- While for veg/fruit matrices LODs ≤ 10 µg/kg can be achieved for the majority of the compounds by introduction of increased sample amounts, analysis below 50 µg/kg in matrices inducing strong ion suppression remain a challenge.
- For automated detection based on retention time and one accurate mass, narrow tolerance windows are essential for minimizing the number of false positives.

References

[1] Mol *et al*, Anal. Chem, 80(24) p.9450 (2008)
[2] www.metalign.nl\uk\

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