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Setting up a liquid chromatography-Orbitrap mass spectrometer in full scan and MS/MS mode for the detection of pesticide residues in fruit and vegetables

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INTRODUCTION

High resolution mass spectrometry is a technique which helps to overcome some typical limitations of triple quadrupole mass spectrometers. High resolution instruments provide accurate mass measurement. Spectrometers working in full scan mode can register unlimited number of compounds. This feature allows to perform non-target analysis and retrospective analysis. Hybrid instruments are also equipped in quadrupole mass filter and collision cell. Thanks to this it is possible to perform MS^2 experiments.

Amongst the several workflows which are available in QExactive™ very convenient is Full scan/Data Dependent-MS^2. In this mode user defines list of target parent ions and retention time windows when the ions are expected. During the analysis data acquisition is carried out in full scan mode. However if any of the parent ions from the target list is detected in expected retention time window QExactive™ switch to MS^2 mode, carries out one scan and goes back to full scan mode. Data obtained in full scan mode are used for quantitation whereas data from MS^2 mode for identification. In Full scan/Targeted-MS^2 is similar to Data Dependent however full scans and MS^2 scans are carried out alternately.

EXPERIMENTAL

Extraction method: Citrate QuEChERS
Number of spiked pesticides: 162
Final sample dilution: 5 times (0.2 g/mL)

Analysed matrices:
- Tomato
- Pepper
- Orange
- Green tea

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: 0.4 mL/min
Gradient time: 13 min
Column: Thermo Accucore C18 150 mm x 2.1mm x 2.6µm

Acquisition mode: full scan
Resolutions (FWHM at m/z 200):
-17500
-35000
-**70000**
AGC target: 1e6
Maximum IT: 200 ms
Scan range: 100 – 800 m/z
Mass calibration: external

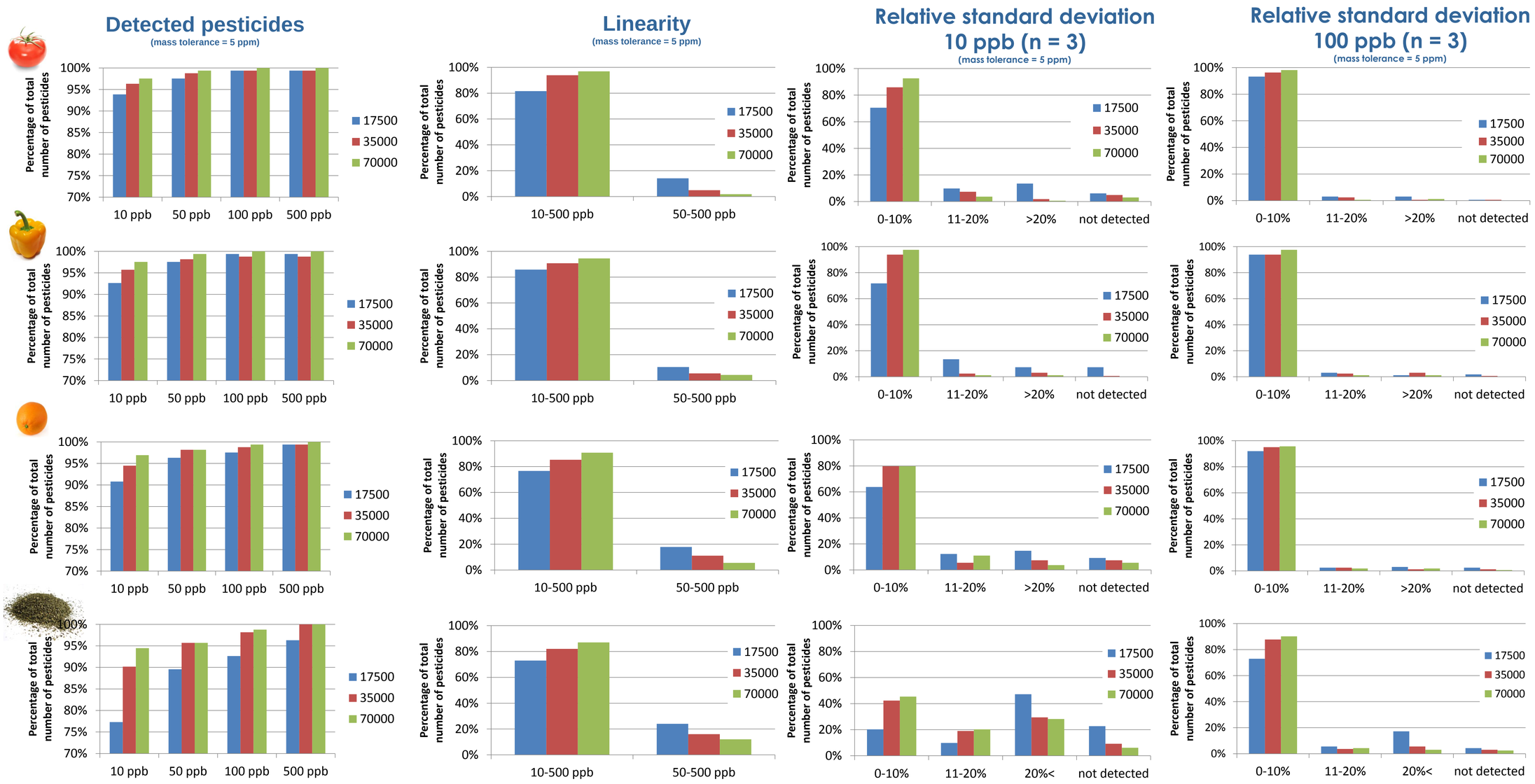
Acquisition mode: /MS^2
Resolutions 17500 (at m/z 200):
AGC target: 2e4
Maximum IT: 50ms
Underfill ratio: 1%
Isolation window: 1.3 m/z
MSX count: 1
Apex trigger: 2-4 sec

RESULTS

Target list

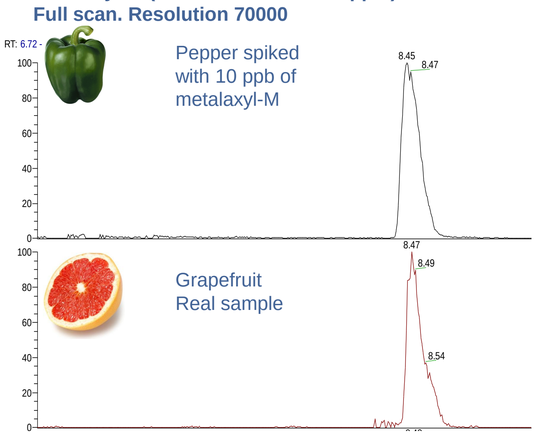
2,4-D	Indoxacarb
3-hidroxycarbofuran	Iprovalicarb
Acephate	Isofenphos-methyl
Acetamiprid	Isoprocarb
Aldicarb	Kresoxim-methyl
Aldicarb Sulfone	Linuron
Aldicarb Sulfoxide	Lufenuron
Azinphos-methyl	Malaoxon
Azoxystrobin	Malathion
Benomyl	Malathion-d10
Bitertanol	Mandipropamid
Boscalid	Metalaxyl-M
Bromuconazole	Metconazole
Bupirimate	Methamidophos
Buprofezin	Methidathion
Carbaryl	Methiocarb
Carbendazim	Methiocarb Sulfone
Carbofuran	Methiocarb Sulfoxide
Chlorantraniliprole	Methomyl
Chlorfenvinphos	Methomyl
Chlorpyrifos	Methoxyfenozide
Chlorpyrifos-methyl	Metobromuron
Clofentezine	Monocrotophos
Clothianidin	Myclobutanil
Cymoxanil	Nitenpyram
Cyproconazole	Omethoate
Cyprodinil	Oxadixyl
Cyromazine	Oxydemeton-methyl
Demeton-S-methylsulfone	Paclobutrazol
Desmethyl Pirimicarb	Paraoxon Methyl
Diazinon	Penconazole
Dichlorvos-d6	Pencycuron
Dicrotophos	Pendimethalin
Diethofencarb	Phenthoate
Difenoconazole	Phosalone
Diflubenzuron	Phosmet
Dimethoate	Phosmet Oxon
Dimethomorph	Phoxim
Diniconazole	Pirimicarb
Dithianon	Pirimiphos-methyl
Dodine	Prochloraz
Epoxiconazole	Profenofos
Ethion	Propamocarb
Ethirimol	Propiconazole
Ethoprophos	Propoxur
Fenamidone	Propyzamide
Fenamiphos	Prothioconazole
Fenamiphos Sulfone	Prothioconazole-desthio
Fenamiphos Sulfoxide	Pymetrozine
Fenarimol	Pyraclostrobin
Fenazaquin	Pyrethrin
Fenbuconazole	Pyridaben
Fenhexamid	Pyrimethanil
Fenitrothion	Pyriproxyfen
Fenoxycarb	Quinoxyfen
Fenpropathrin	Rotenone
Fenpropimorph	Spinosad
Fenpyroximate	Spirodiclofen
Fenthion	Spiromesifen
Fenthion Oxon	Spiroxamine
Fenthion Oxon Sulfone	Tebuconazole
Fenthion Oxon Sulfoxide	Tebufenozide
Fenthion Sulfone	Tebufenpyrad
Fenthion Sulfoxide	Teflubenzuron
Fipronil	Terbuthylazine
Flonicamid	Tetraconazole
Fluazifop	Thiabendazole
Flubendiamide	Thiacloprid
Fludioxonil	Thiamethoxam
Flufenoxuron	Thiodicarb
Fluopyram	Thiophanate-methyl
Fluquinconazole	Tolclofos-methyl
Flusilazole	TPP
Flutriafol	Triadimefon
Formetanate	Triadimenol
Fosthiazate	Triazophos
Haloxyfop	Trichlorfon
Hexaconazole	Trifloxystrobin
Hexythiazox	Triflumuron
Imazalil	Triticonazole
Imidacloprid	Zoxamide

Full scan (detection and quantitation)



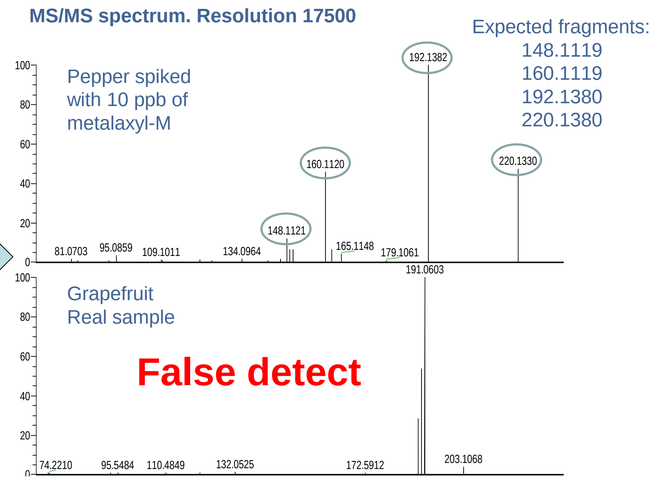
MS^2 (identification)

Metalaxyl-M (XIC m/z 280.1543 ± 5 ppm). Full scan. Resolution 70000



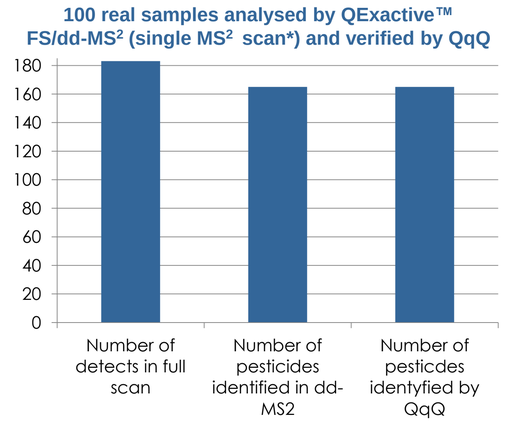
MS^2

MS/MS spectrum. Resolution 17500



Real samples

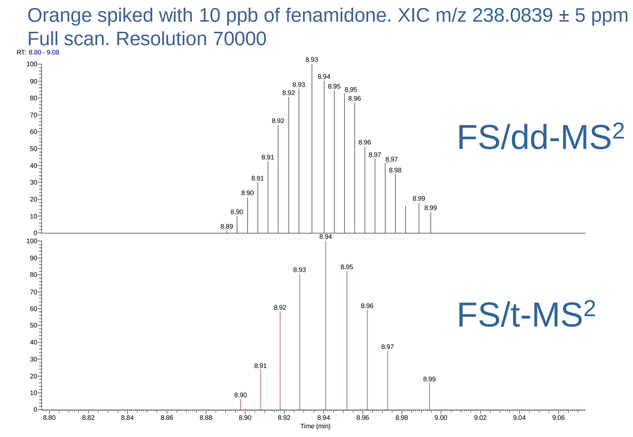
100 real samples analysed by QExactive™ FS/dd-MS^2 (single MS^2 scan*) and verified by QqQ



*For identification one MS^2 fragment was necessary

Number of points per peak in Data Dependent (single MS^2 scan) and Targeted MS^2 (multiple MS^2 scans)

Orange spiked with 10 ppb of fenamidone. XIC m/z 238.0839 ± 5 ppm
Full scan. Resolution 70000



CONCLUSIONS

- Increase of resolution improved limit of detection and repeatability of peak area. Resolution of 35000 was sufficient to detect (with mass tolerance of 5 ppm) 95% of analysed pesticides in tomato, pepper and orange.
- To obtain good repeatability of peak area at level 10 ppb resolution of 35000 or 70000 was required.
- High sensitivity of the QExactive™ allowed to dilute samples 5 times. This dilution reduced potential matrix effects.
- Even with resolution of 70000 false detects can be found. Data Dependent MS^2 mode is very convenient way to identify peak detected in full scan mode.
- QExactive™ working in full scan/Data Dependent-MS^2 (resolution of 70000 in full scan and one MS^2 fragment for identification) has at least the same identification potential as two transitions and ion ratio applied in QqQ.
- In Data Dependent only one MS^2 scan is carried out, by that peaks in full scan have more points than in case of Targeted-MS^2.

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