PESTICIDE RESIDUE RESEARCH GROUP

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# Application of LC-QTOF-MS working in simultaneous full scan and MS/MS mode for the analysis of pesticide residues in fruits and vegetables

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## INTRODUCTION

**Accurate mass spectrometers operated in full scan mode have some very important advantages over triple quadrupoles (e.g. in a single run unlimited number of compounds can be registered). However full scan mode not always is able to provide sufficient data for compound identification. It is common that only [M+H]+ ion is detected and no other adducts nor in-source generated fragments are available. In this cases identification criteria cannot be fulfilled. That problem can be solved be using simultaneously full scan and MS/MS analysis. This combination can be realized with or without target list of analytes. In this work two adquisition modes has been studied:**

1) **All Ions MS/MS. Does not require predefined list. Quadrupole does not select any specific precursor and all ions are fragmented.**
2) **Auto MS/MS. Requires target list. The spectrometer works in full scan mode, when an ion from the target list is detected the qudrupole selects this specific ion and fragments it**

## EXPERIMENTAL SECTION: SAMPLE TREATMENT AND LC-QTOF-MS ANALYSIS

### SAMPLE TREATMENT

Extraction of blank matrices **Citrate** buffered **QuEChERS**

↓

Blank extract
**Tomato, Zucchini and Orange**

↓

Spiked with **125 pesticides**
At **10 µg/L** and **100 µg/L**

Final sample dilution: 5 (0.2 g/ml)

### LC-QTOF-MS

**Operational conditions**

Full-scan ESI (+) mode

Nebulizer: 30psi

Gas Temp : 160ºC

Cap. Voltage: 4000 V.

Frag. Voltage: 360 V

Inj Volume: 10 µL

**Chromatography**
Agilent 1290 HPLC system

Column: C18 Agilent. 50mm x 2.1 mm (1.8 µm)

**Mobile phase:**

AcN (A) (5% water, 0.1% formic acid) and MiliQ Water (B) (0.1 % formic acid) 20% (A) isocratic t=2 min, then to 100 % (A) in 13 min and maintained for 2 min,Flow rate of 0.3 mL/min.

### All Ions MS/MS Settings

- Polarity: positive
- High Resolution 4GHz
- Mass range: 70 – 950 m/z
- Absolute Threshold: 1000
- Acquisition rate 3 spectra/sec
- Collision energy
  - 0 V
  - 10 V
  - 20 V

### Auto MS/MS Settings

***Full scan MS***

- Polarity: positive
- High Resolution 4GHz
- Mass range: 100 – 950 m/z
- Absolute Threshold: 500
- Acquisition rate 3 spectra/sec

If the pesticide is detected

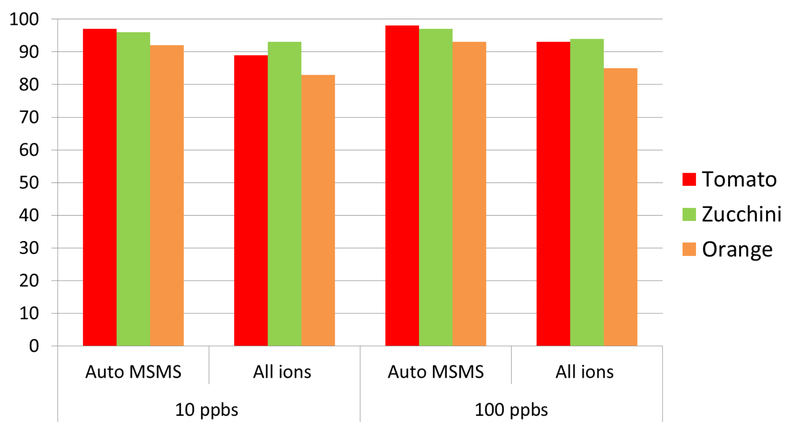
***MS/MS***

- Inclusion list: 125 pesticides
  - Δ m/z 20 ppm
  - Δ Rt 0.35 min
  - Isolation Width 1.3 m/z
- Mass range: 65 – 750 m/z
- Acquisition rate 2 spectra/s
- Absolute Threshold: 50
- Max 5 precursor per cycle
- Active exclusion
  - Excluded after 1 spectrum
  - Released after 0.7 min

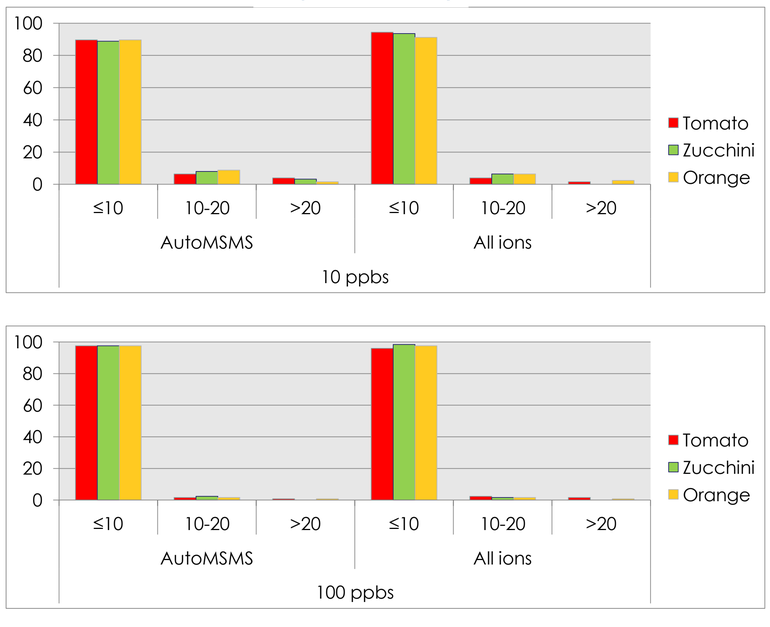
## RESULTS

| Pesticides | | |
|---|---|---|
| Acetamiprid | Fenhexamid | Penconazole |
| Aldicarb | Fenpropimorph | Pencycuron |
| Aldicarb sulfone | Fenpyroximate | Phenthoate |
| Aldicarb sulfoxide | Fenthion | Phosalone |
| Azoxystrobin | fenthion sulfoxide | Phosmet |
| Bitertanol | Flonicamid | Pirimicarb |
| Boscalid | Fluazifop | Pirimicarb desmethyl |
| Bromuconazole | Flufenoxuron | Pirimiphos-methyl |
| Bupirimate | Fluopyram | Prochloraz |
| Buprofezin | Fluquinconazole | Profenofos |
| Carbaril | Flusilazole | Propamocarb |
| Carbendazim | Flutriafol | Propiconazole |
| Carbofuran | Formetanate | Propoxur |
| Chlorantraniliprole | Fosthiazate | Propyzamide |
| Chlorfenvinphos | Haloxyfop | Pymetrozine |
| Clofentezine | Hexaconazole | Pyraclostrobin |
| Clothianidin | Hexythiazox | Pyridaben |
| Cyproconazole | Imazalil | Pyrimethanil |
| Cyprodinil | Imidacloprid | Pyriproxyfen |
| Cyromazine | Indoxacarb | Quinoxyfen |
| Demeton-S-methylsulfone | Iprovalicarb | Rotenone |
| Diazinon | Isocarbofos | Spinosyn A |
| Dichlorvos | Isophenphos methyl | Spinosyn D |
| Dicrotophos | Kresoxim methyl | Spirodiclofen |
| Diethofencarb | Linuron | Spiromesifen |
| Difenoconazole | Malathion | Spiroxamine |
| Diflubenzuron | Mandipropamid | Tebuconazole |
| Dimethoate | Mepanipyrin | Tebufenozide |
| Dimethomorph | Metalaxyl-M | Tebufenpyrad |
| Diniconazole | Metconazole | Terbuthylazine |
| Dodine | Methidathion | Tetraconazole |
| Epoxiconazole | Methiocarb | Thiabendazole |
| Ethion | Methiocarb sulfone | Thiacloprid |
| Ethirimol | Methiocarb sulfoxide | Thiamethoxam |
| Ethoprophos | Methoxyfenozide | Thiodicarb |
| Fenamidone | Metobromuron | Triazophos |
| Fenamiphos | Monocrotophos | Trichlorfon |
| Fenamiphos sulfone | Myclobutanil | Trifloxystrobin |
| Fenamiphos sulfoxide | Nitenpyram | Triflumuron |
| Fenarimol | Omethoate | Triticonazole |
| Fenazaquin | Oxamyl | Zoxamide |
| Fenbuconazole | Paclobutrazol | |

### Percentage of identified compounds



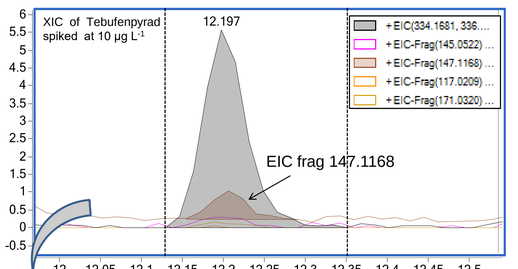

### Repeatability




### Identification examples

#### All ions MS/MS mode

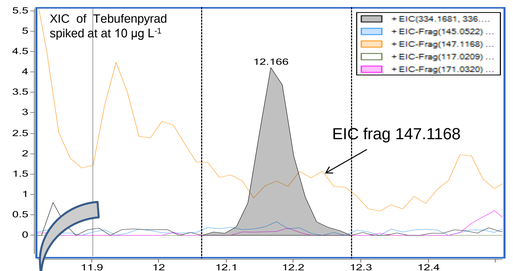
Tebufenpyrad **IDENTIFIED.** Zucchini Matrix




| Name | Diff (ppm) | Formula |
|---|---|---|
| Tebufenpyrad | 0.69 | C18 H24 Cl N3 O |

| Coelution Score | m/z | CE | Flags(FIs) |
|---|---|---|---|
| | 145.0522 | | No peaks for EIC |
| 93.7 | 147.1168 | 20 | Qualified |
| | 117.0209 | | No peaks for EIC |
| | 171.032 | | No peaks for EIC |

Tebufenpyrad detected but **NOT IDENTIFIED.** Orange matrix

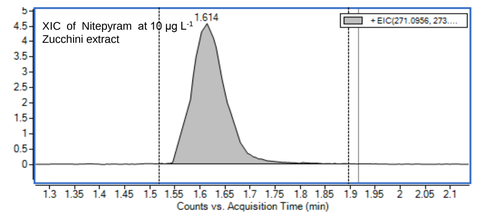


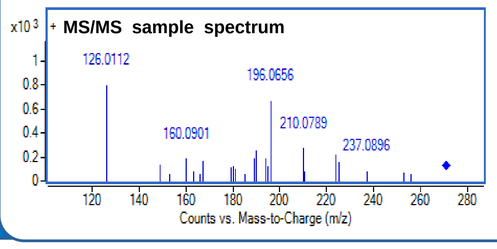

| Name | Diff (ppm) | Formula |
|---|---|---|
| <Tebufenpyrad> | 0.42 | C18 H24 Cl N3 O |

| Coelution Score | m/z | CE | Flags(FIs) |
|---|---|---|---|
| 53 | 145.0522 | | Low coelution score |
| | 147.1168 | | Large RT diff |
| | 117.0209 | | No peaks for EIC |
| | 171.032 | | Large RT diff |

Fragments ions not present or not coeluting

#### Auto MS/MS mode

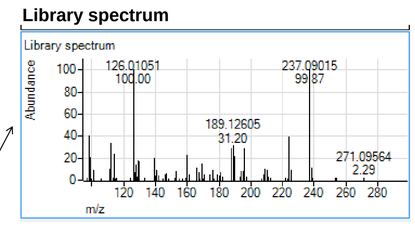


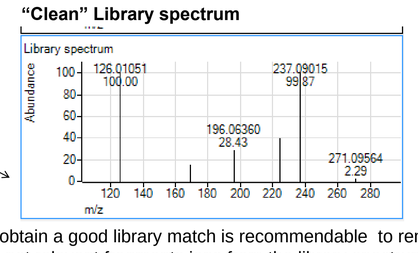

NOT IDENTIFIED

IDENTIFIED

**Library spectrum**




**"Clean" Library spectrum**




To obtain a good library match is recommendable to remove not relevant fragments ions from the library spectrum

## CONCLUSION

**The results show good identification capabilities and repeatability for both acquisition modes. However, identification by Auto MS/MS is more confident, specially in "complex" matrices such as orange. The observed false negative results were mainly as a consequence of a lack of compound sensitivity caused by ion suppression effects. Additionally a few cases of software failure were observed.**

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