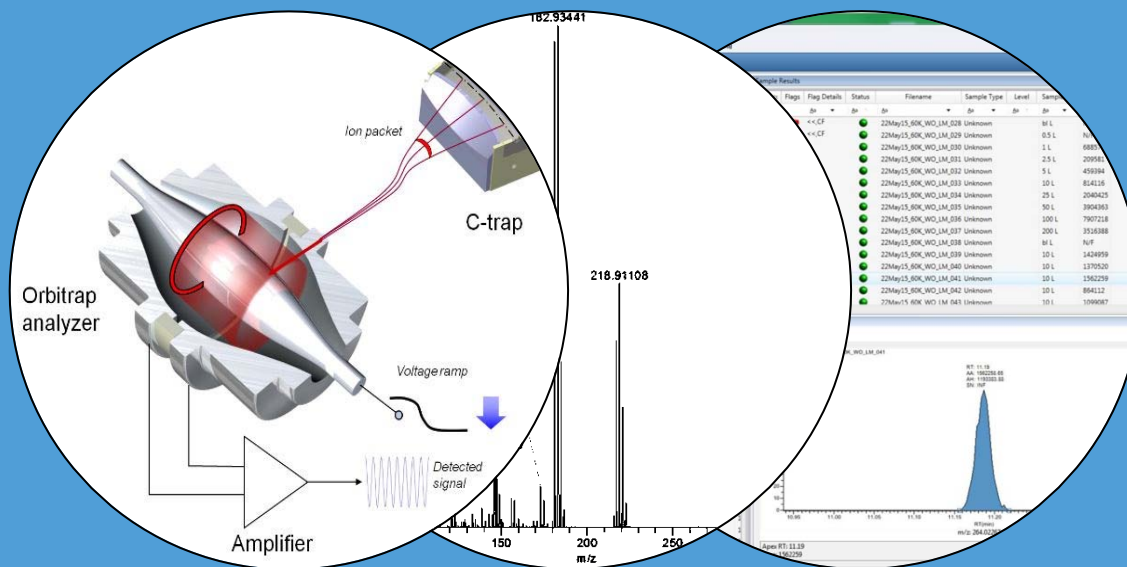


Experiences with application of full scan high resolution MS for pesticide residue analysis

Marc Tienstra, Hans Mol, Paul Zomer



Current routine practice

Chromatography with mass spectrometric detection



Pesticide Residue analysis

Pesticide Manual:

1630 entries

Current golden standard:

Targeted quantitative measurement by LC-MS/MS and GC-MS/MS

Multi-residue methods, ~150-250 analytes/method

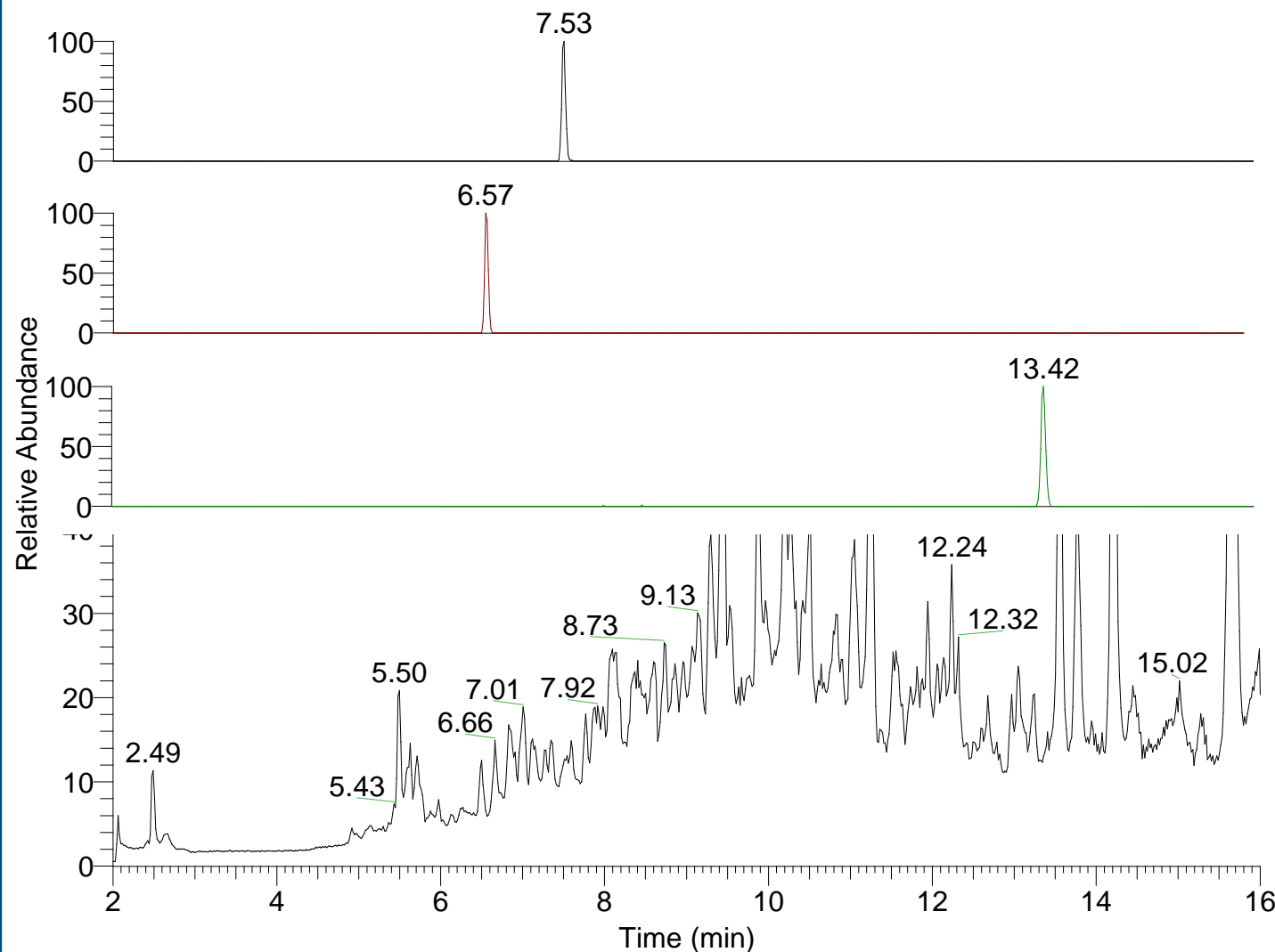
Emerging:

Non-targeted measurement by LC and GC + full scan MS

for better coverage of pesticide scope and easier measurement

Selectivity using HR-MS

Extract signal of exact mass $\pm x$ Da (ppm), e.g. Dimethoate $[M+H]^+$ 230.0069 ± 5 ppm (± 0.0012 Da)



m/z 230.0069
C5H12NO3PS2
dimethoate

m/z 230.0536
C9H6F3N3O
flonicamid

m/z 365.1449
C19H25ClN2OS
pyridaben



Work flow

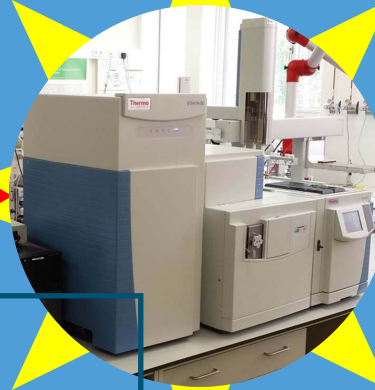
Sample

Extract

QuEChERS extraction



LC-ESI-Q-Orbitrap-MS



(2015)

GC-EI-Q-Orbitrap-MS

Raw data

Quan (usual suspects):

*XICs, MEW ± 5 ppm, 2 ions
Manual verification of
all targets in all samples*

*Extensive AQC:
Linearity, LOQ
recoveries/RSDs*

*Identification: peaks 2 ions fully overlap
RT ± 0.1 min from sequence, ion ratio
 $\pm 30\%$ (rel)*

Qual (others):

*XICs, MEW ± 5 ppm, 2 ions
Fully automated by software*

*Detection: RT ± 0.5 min from
database, peaks detected for
both ions*

LC-HRMS: Identification

LC-ESI-MS: soft ionisation → no fragments

Generation of fragments:

1) needed for identification, 2) improve screening selectivity

For optimum detection and identification:

full scan acquisition without and with fragmentation in 1 run

Non-targeted fragmentation:

two options: AIF and vDIA

Combined Full scan + vDIA acquisition

FS: m/z 100-1000

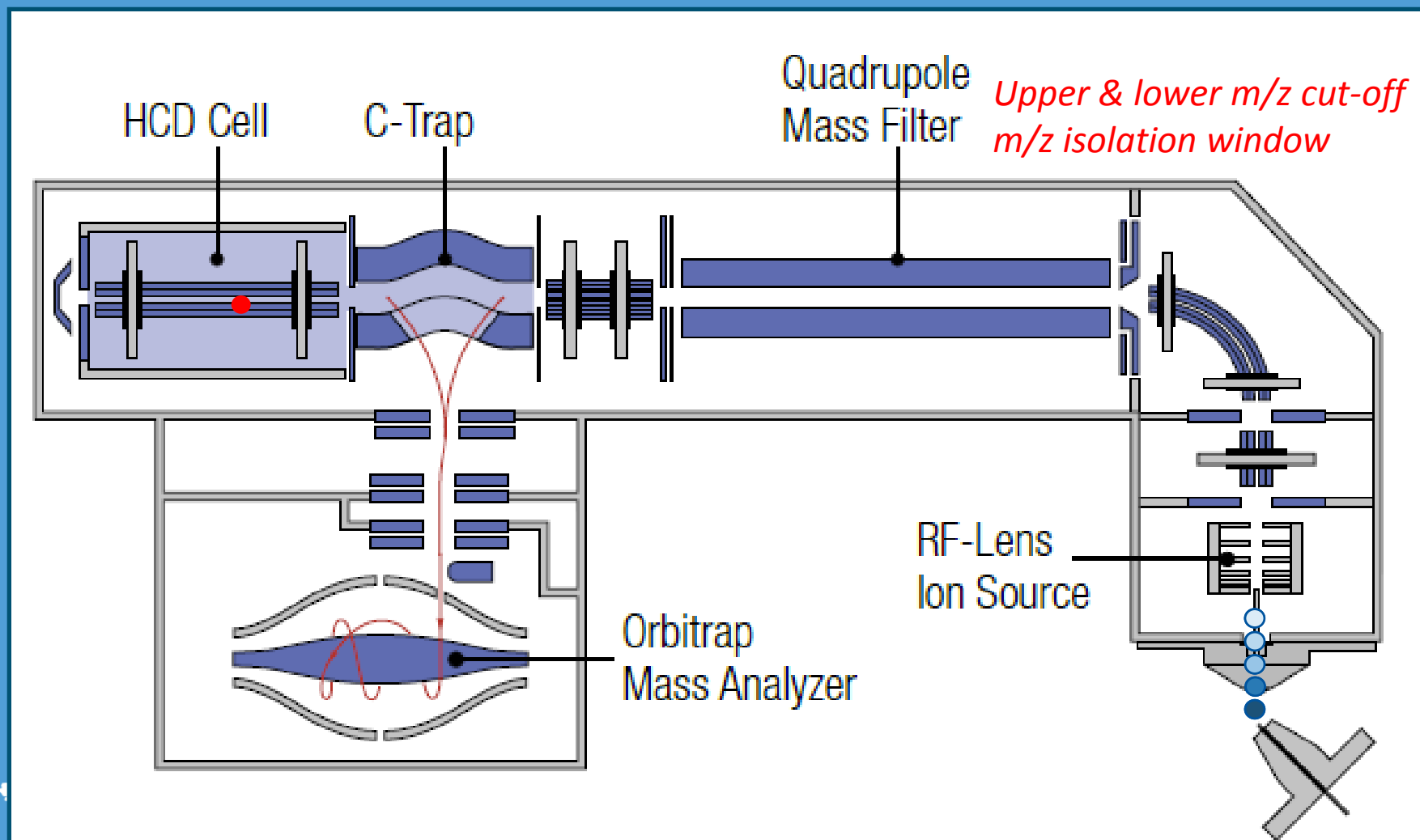
↳: 100-200

↳: 200-300

↳: 300-400

↳: 300-400

↳: 500-1000

FS: m/z 100-1000

Combined Full scan + vDIA acquisition

FS: m/z 100-1000

↳: 100-200

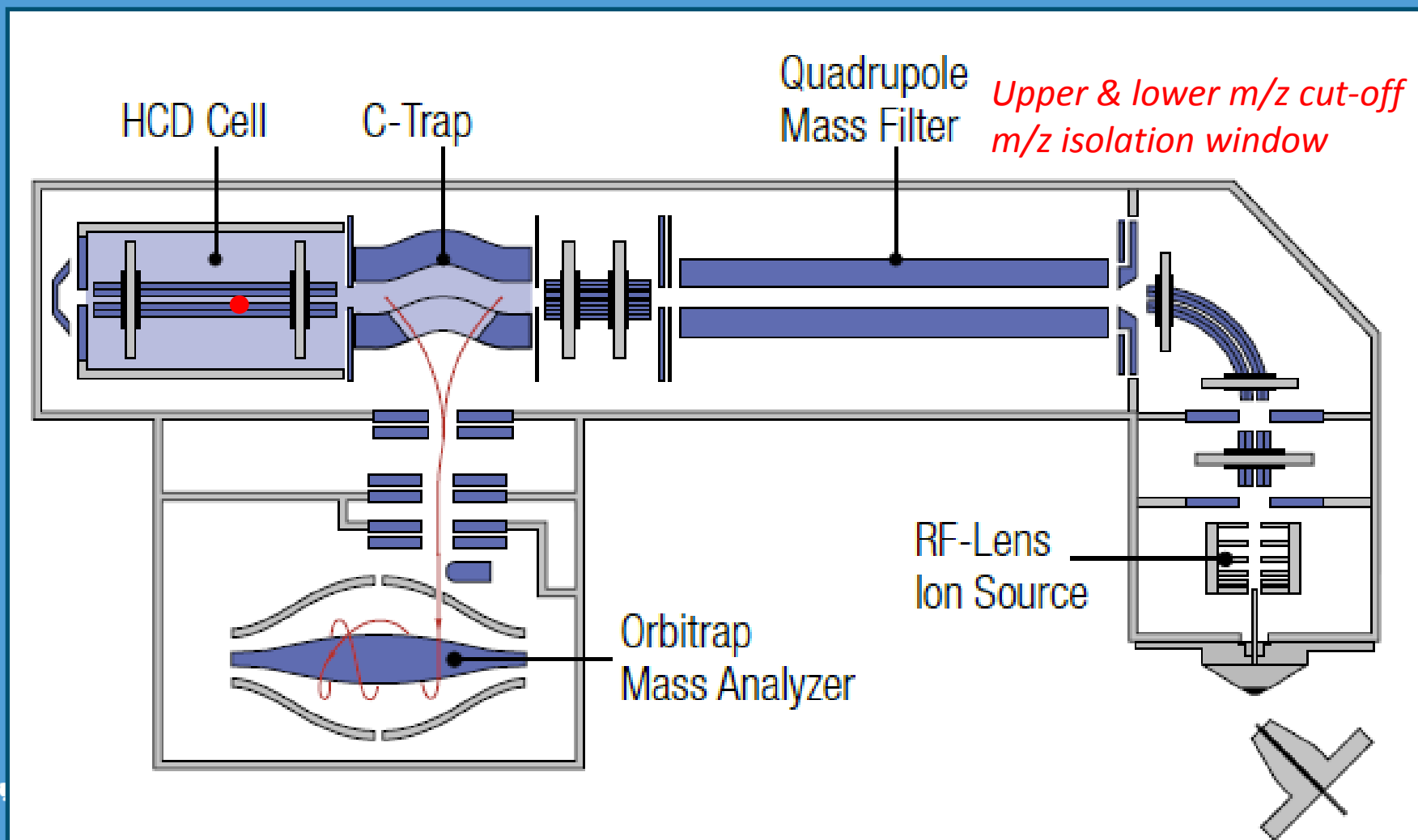
↳: 200-300

↳: 300-400

↳: 300-400

↳: 500-1000

FS: m/z 100-1000



Combined Full scan + vDIA acquisition

FS: m/z 100-1000

↳: 100-200

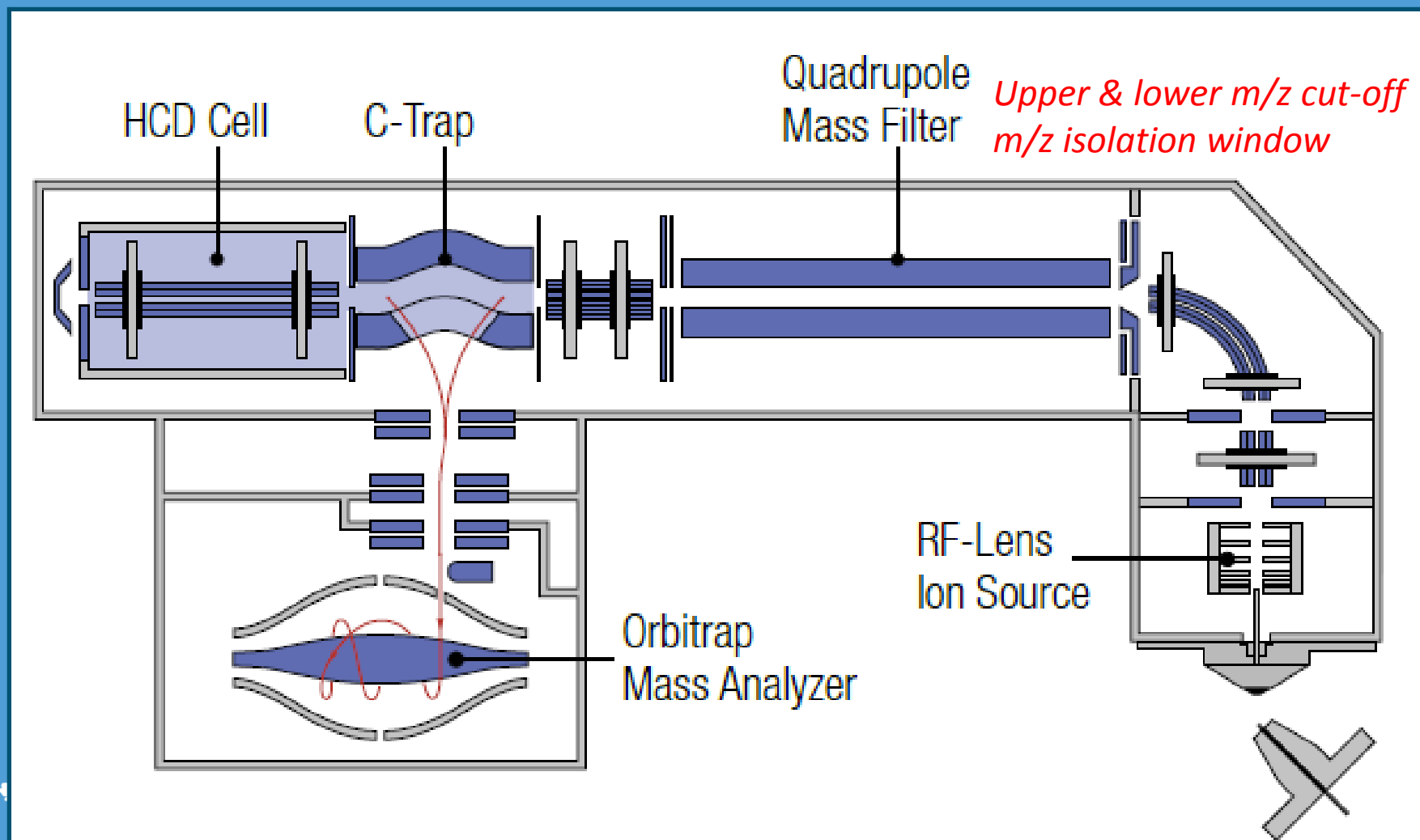
↳: 200-300

↳: 300-400

↳: 300-400

↳: 500-1000

FS: m/z 100-1000



Scan speed sufficient (FS + vDIA)?

full scan: no fragmentation
m/z 135-1000@70K

Fragments of
95-205@35K

Fragments of
195-305@35K

Fragments of
295-405@35K

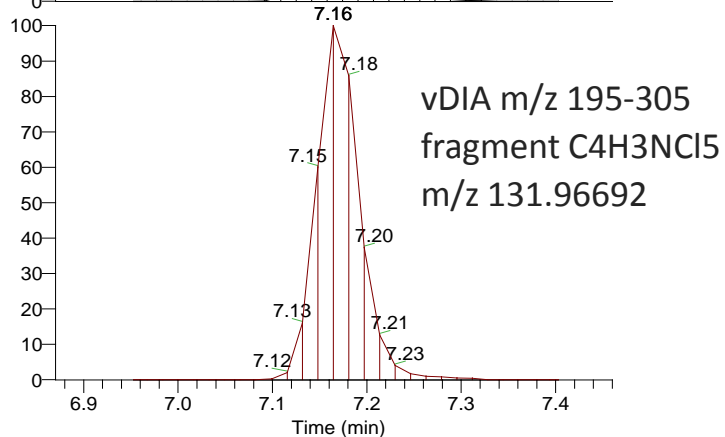
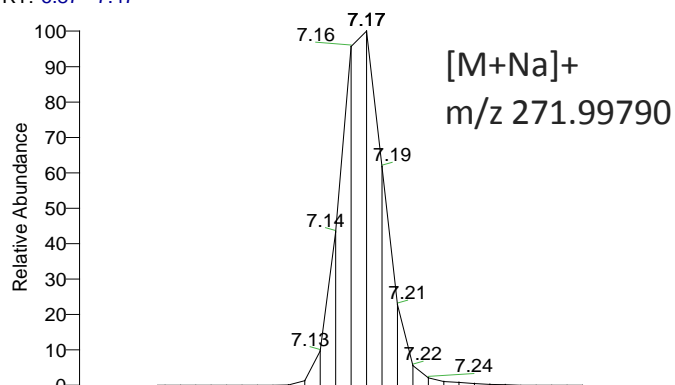
Fragments of
395-505@35K

Fragments of
495-1005@35K

} 978 ms

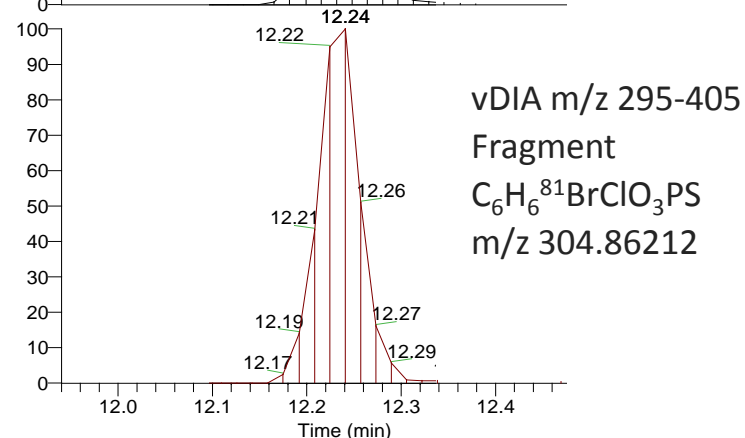
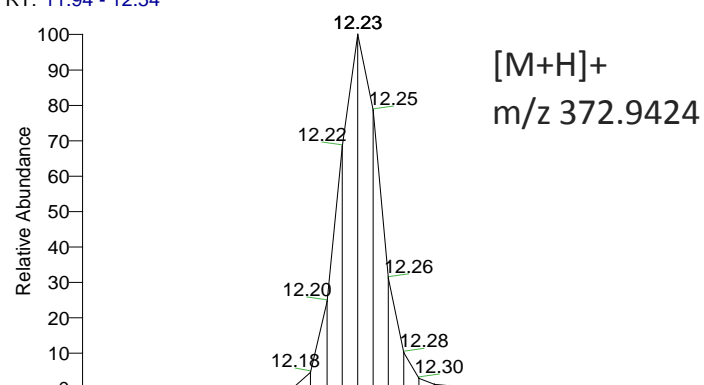
50 ppb Clothiadinin ($C_6H_8ClN_5O_2S$) in lettuce

RT: 6.87 - 7.47



50 ppb Profenofos ($C_{11}H_{15}BrClO_3PS$) in lettuce

RT: 11.94 - 12.54



Quantitative data review

Tracefinder (Thermo Scientific™ software)

Thermo TraceFinder EFS LC

File View Tools Help

Analysis

Data Review - QEx_Validatie_Qual_pos_day1_140918

Batch View

Samples

Auto Samples

Reference Sample

Threshold Samples

Data Review

Sample View

Compound View

Comparative View

Qualitative View

Report View

Local Method

Acquisition

Quantitation

Processing

Compounds

QAQC

Groups

Intel Seq

Reports

Acquisition

Analysis

Method Development

Compounds

| Flags | Compound |
|-------|-------------------|
| 111 | Mevinphos |
| 112 | Myclobutanil |
| 113 | Nicosulfuron |
| 114 | Omethoate |
| 115 | Oxamyl |
| 116 | Oxydemeton-methyl |
| 117 | Pacllobutrazol |
| 118 | Penconazole |
| 119 | Pencycuron |
| 120 | Phenmedipham |
| 121 | Picoxystrobin |
| 122 | Pinoxaden |
| 123 | Pirimicarb |
| 124 | Pirimiphos-methyl |
| 125 | Prochloraz |
| 126 | Profenofos |
| 127 | Propamocarb |
| 128 | Propiconazole |
| 129 | Propyzamide |
| 130 | Prosulfocarb |
| 131 | Pymetrozine |
| 132 | Pyraclostrobin |
| 133 | Pyridaben |
| 134 | Pyridalyl |
| 135 | Pyridate |
| 136 | Pyrimethanil |
| 137 | Pyriproxyfen |
| 138 | Pyroxulam |
| 139 | Quinmerac |
| 140 | Quinoclamine |
| 141 | Quinoxyfen |
| 142 | Quizalofop-ethyl |
| 143 | Rimsulfuron |
| 144 | Silthiofam |
| 145 | Simazine |
| 146 | Spinosyn-A |
| 147 | Spinosyn-D |

Sample Results

| Acc | Flags | Flag Details | Status | Filename | Sample Type | Sample Name | Height | Area | Expected RT |
|-----|-------|--------------|--------|----------------|-------------|----------------------|----------|-----------|-------------|
| 18 | 18 | | | QEx_140918_064 | Unknown | Orange + 200 ppb | 23627272 | 152022784 | 12.31 |
| 19 | 19 | | | QEx_140918_067 | Unknown | std 10 ng/ml solvent | 2304051 | 15000818 | 12.31 |
| 20 | 20 | <<.CF | | QEx_140918_069 | Unknown | Blank Reagent | N/F | N/F | 12.31 |
| 21 | | | | | | | | | |
| 22 | | | | | | | | | |
| 23 | | | | | | | | | |
| 24 | | | | | | | | | |
| 25 | | | | | | | | | |
| 26 | | | | | | | | | |
| 27 | | | | | | | | | |
| 28 | | | | | | | | | |
| 29 | | | | | | | | | |
| 30 | 30 | | | QEx_140918_079 | Unknown | std 10 ng/ml solvent | 4320728 | 28071293 | 12.31 |
| 31 | 31 | | | QEx_140918_080 | Unknown | Apple + 10 ng/g | 2100040 | 12669539 | 12.31 |
| 32 | 32 | | | QEx_140918_081 | Unknown | Nectarine + 10 ng/g | 2221103 | 15338374 | 12.31 |
| 33 | 33 | | | QEx_140918_082 | Unknown | Leek + 10 ng/g | 1538081 | 10217795 | 12.31 |

Review by pesticide (compound view):
For each quan pesticide: click through the samples and check assignment/integration of quantifier (main adduct) and qualifier (fragment), adjust when needed

Compound Details

Quan Peak

Spinosyn-A RT: 12.49 | QEx_140918_081

RT: 12.49
AA: 15338373.80
AH: 2221102.75
SN: INF

Relative Intensity

Quantifier OK

RT (min)

m/z: 732.46810

Apex RT: 12.49
Area: 15338374

Confirming Ions

RT: 12.48 | QEx_140918_081

RT: 12.48
AA: 6337946.54
AH: 890975.50
SN: 1371.23

Relative Intensity

Qualifier OK

RT (min)

m/z: 142.12264
4.00% - 6.00% 142.12264/732.46810 = 41.32%

Apex RT: 12.48
Area: 6337947

Quantitative data review

Thermo TraceFinder EFS LC

File View Tools Help Real time status | User: zomer003

Analysis Data Review - QEx_Validatie_Qual_pos_day2_141017*

Batch View

- Samples
- Auto Samples
- Reference Sample
- Threshold Samples
- Data Review**
- Sample View
- Compound View
- Comparative View
- Qualitative View

Report View

- Local Method
- Acquisition
- Quantitation
- Processing
- Compounds
- QAQC
- Groups
- Intel Seq
- Reports

Acquisition

Analysis

Method Development

Compounds

| Flags | Compound |
|-------|----------------------|
| 22 | Carbaryl |
| 23 | Carbendazim |
| 24 | Carbetamide |
| 25 | Carbofuran |
| 26 | Carfentrazone-ethyl |
| 27 | Chlorantraniliprole |
| 28 | Chlorbromuron |
| 29 | Chloridazon |
| 30 | Clodinafop-propargyl |
| 31 | Clofentezine |
| 32 | Clomazone |
| 33 | Clopyralid |
| 34 | Clothianidin |
| 35 | Cyazofamid |
| 36 | Cybutryne |
| 37 | Cymoxanil |
| 38 | Cyproconazole I |
| 39 | Cyprodinil |
| 40 | Cyromazine |
| 41 | Cythioate |
| 42 | Dichlofluanid |
| 43 | Difenoconazole |
| 44 | Diflubenzuron |
| 45 | Diflufenican |
| 46 | Dimethenamid |
| 47 | Dimethoate |
| 48 | Dimethomorph |
| 49 | Diuron |
| 50 | Dodemorph |
| 51 | Dodine |
| 52 | Emamectin B1a |
| 53 | Epoxiconazole |
| 54 | Ethirimol |
| 55 | Ethoprophos |
| 56 | Etoxazole |
| 57 | Famoxadone |
| 58 | Fenamidone |

Sample Results

| Acc | Flags | Flag Details | Status | Filename | Sample Type | Level | Sample ID | Sample Name | Comments | Height | Area |
|-----|-------|--------------|--------|----------------|-------------|-------|-----------|-----------------------|----------|-----------|-------|
| 1 | 1 | <<,CF | ● | QEx_141017_047 | Unknown | 1 | 1 | std 0 ng/ml solvent | | N/F | N/F |
| 2 | 2 | | ● | QEx_141017_048 | Unknown | 1 | 1 | std 5 ng/ml solvent | | 2108051 | 86004 |
| 3 | 3 | | ● | QEx_141017_049 | Unknown | 1 | 1 | std 10 ng/ml solvent | | 4543783 | 21085 |
| 4 | 4 | | ● | QEx_141017_050 | Unknown | 1 | 1 | std 50 ng/ml solvent | | 20706800 | 81461 |
| 5 | 5 | | ● | QEx_141017_051 | Unknown | 1 | 1 | std 100 ng/ml solvent | | 43425516 | 17377 |
| 6 | 6 | | ● | QEx_141017_052 | Unknown | 1 | 1 | std 250 ng/ml solvent | | 100221320 | 42270 |
| 7 | 7 | <<,CF | ● | QEx_141017_054 | Unknown | 1 | 1 | Blank Reagent day 2 | | N/F | N/F |
| 8 | 8 | <<,CF | ● | QEx_141017_055 | Unknown | 1 | 1 | Blank Apple | | N/F | N/F |
| 9 | 9 | <<,CF | ● | QEx_141017_056 | Unknown | 1 | 1 | Blank Necatarine | | N/F | N/F |
| 10 | 10 | <<,CF | ● | QEx_141017_057 | Unknown | 1 | 1 | Blank Leek | | N/F | N/F |
| 11 | 11 | <<,CF | ● | QEx_141017_058 | Unknown | 1 | 1 | Blank Tomato | | N/F | N/F |
| 12 | 12 | <<,CF | ● | QEx_141017_059 | Unknown | 1 | 1 | Blank Broccoli | | N/F | N/F |
| 13 | 13 | <<,CF | ● | QEx_141017_060 | Unknown | 1 | 1 | Blank Lettuce | | N/F | N/F |
| 14 | 14 | <<,CF | ● | QEx_141017_061 | Unknown | 1 | 1 | Blank Celery | | N/F | N/F |
| 15 | 15 | <<,CF | ● | QEx_141017_062 | Unknown | 1 | 1 | Blank Beans | | N/F | N/F |
| 16 | 16 | <<,CF | ● | QEx_141017_063 | Unknown | 1 | 1 | Blank Carrot | | N/F | N/F |

Compound Details

Quan Peak

Carbaryl RT: 9.16 | QEx_141017_060

Apex RT: N/F
Area: N/F

Confirming Ions

RT: 9.19 | QEx_141017_060

AA: 177519.79
AH: 16897.95
SN: 78.87

4.00% - 6.00% 145.06479/202.08630 = NaN%

Apex RT: 9.19
Area: 177520

Qualitative screening: method set up

Same raw data, different data review

High number of target pesticides, low probability of detection

Manual verification of all XICs too time consuming

⇒ Automated pesticide detection by the software (Tracefinder; Thermo Scientific™)

Default settings for pesticide detection (quan module used without quantification)

| | |
|-------------------------|--|
| Mass extraction window: | exact m/z ± 5 ppm |
| Time window: | database RT ± 0.5 min |
| Requirement: | signal found for pre-set adduct AND fragment ion |
| Output: | report of samples showing only pesticides found |

Screening: data review

Thermo TraceFinder EFS LC

File View Tools Help Real time status | User: zomer003 | ?

Analysis Data Review - QEx_Validatie_Qual_pos_day1_140918*

Batch View

- Samples
- Auto Samples
- Reference Sample
- Threshold Samples
- Data Review
 - Sample View
 - Compound View
 - Comparative View
 - Qualitative View
- Report View
- Local Method
 - Acquisition
 - Quantitation
 - Processing
 - Compounds
 - QAQC
 - Groups
 - Intel Seq
 - Reports

Samples

| Acc | Flags | Status | Filename | Sample Type | Sample Name |
|-----|-------|--------|----------------|-------------|-----------------------|
| 7 | 7 | ● | QEx_140918_021 | Unknown | std 250 ng/ml solvent |
| 8 | 8 | ● | QEx_140918_029 | Unknown | spoel |
| 9 | 9 | ● | QEx_140918_030 | Unknown | Blank Lettuce |
| 10 | 10 | | | | |
| 11 | 11 | | | | |
| 12 | 12 | | | | |
| 13 | 13 | | | | |
| 14 | 14 | | | | |
| 15 | 15 | | | | |
| 16 | 16 | | | | |
| 17 | 17 | | | | |
| 18 | 18 | | | | |
| 19 | 19 | ● | QEx_140918_067 | Unknown | std 10 ng/ml solvent |
| 20 | 20 | ● | QEx_140918_069 | Unknown | Blank Reagent |
| 21 | 21 | ● | QEx_140918_070 | Unknown | Blank Apple |
| 22 | 22 | ● | QEx_140918_071 | Unknown | Blank Nectarine |
| 23 | 23 | ● | QEx_140918_072 | Unknown | Blank Leek |
| 24 | 24 | ● | QEx_140918_073 | Unknown | Blank Tomato |

Compound Results

| Active | Flags | Flag Details | Compound | Height | Area | Expected RT | Actual RT |
|-------------------------------------|-------|--------------|---------------|--------|--------|-------------|-----------|
| <input checked="" type="checkbox"/> | | | Prosulfocarb | 153521 | 488041 | 12.13 | 12.17 |
| <input checked="" type="checkbox"/> | | | Terbutylazine | 49706 | 111306 | 10.64 | 10.67 |

Review by sample (sample view):
 For each sample, click through the pesticides found:
 Check: 2 peaks present? Matching peak profile/RT?
 Optional: isotope pattern, additional fragments

Compound Details

Quan Peak RT: 12.17 | QEx_140918_073

Confirming Ions

Prosulfocarb RT: 12.17

AA: 488041.25
AH: 153520.84
SN: INF

Apex RT: 12.17
Area: 488041

RT: 12.31 | QEx_140918_073

AA: 11641639.72
AH: 2140913.01
SN: 1143.84

Apex RT: 12.31
Area: 11641640

Prosulfocarb?

⇒ Reject

4.00% - 6.00% 91.05423/252.14170 = 2385.38%



Screening: data review

Samples

| Acq | Flags | Status | Filename | Sample Type | Sample Name | Level |
|-----|-------|--------|----------------|-------------|----------------------|-------|
| 19 | | ● | QEx_140918_067 | Unknown | std 10 ng/ml solvent | |
| 20 | | ● | QEx_140918_069 | Unknown | Blank Reagent | |
| 21 | | ● | QEx_140918_070 | Unknown | Blank Apple | |
| 22 | | ● | QEx_140918_071 | Unknown | Blank Nectarine | |
| 23 | | ● | QEx_140918_072 | Unknown | Blank Leek | |
| 24 | | ● | QEx_140918_073 | Unknown | Blank Tomato | |
| 25 | | ● | QEx_140918_074 | Unknown | Blank Broccoli | |
| 26 | | ● | QEx_140918_075 | Unknown | Blank Celery | |
| 27 | | ● | QEx_140918_076 | Unknown | Blank Fr. Beans | |
| 28 | | ● | QEx_140918_077 | Unknown | Blank Carrot | |
| 29 | | ● | QEx_140918_078 | Unknown | Blank Grape | |
| 30 | | ● | QEx_140918_079 | Unknown | std 10 ng/ml solvent | |
| 31 | | ● | QEx_140918_080 | Unknown | Apple + 10 ng/g | |
| 32 | | ● | QEx_140918_081 | Unknown | Nectarine + 10 ng/g | |
| 33 | | ● | QEx_140918_082 | Unknown | Leek + 10 ng/g | |
| 34 | | ● | QEx_140918_083 | Unknown | Tomato + 10 ng/g | |
| 35 | | ● | QEx_140918_084 | Unknown | Broccoli + 10 ng/g | |
| 36 | | ● | QEx_140918_085 | Unknown | Celery + 10 ng/g | |

Compound Results

| Active | Flags | Flag Details | Compound | Height | Area | Expected RT | Actual RT |
|-------------------------------------|-------|--------------|---------------|--------|--------|-------------|-----------|
| <input checked="" type="checkbox"/> | | | Prosulfocarb | 153521 | 488041 | 12.13 | 12.13 |
| <input checked="" type="checkbox"/> | | | Terbutylazine | 49706 | 111306 | 10.64 | 10.67 |

Compound Details

Terbutylazine RT: 10.67 | QEX_140918_073

RT: 10.67
AA: 111306.20
AH: 49706.30
SN: INF

Relative Intensity vs RT(min)

m/z: 230.11670

Apex RT: 10.67
Area: 111306

Confirming Ions

RT: 10.66 | QEX_140918_073

RT: 10.66
AA: 21854.81
AH: 10694.49
SN: INF

Intensity vs RT(min)

m/z: 174.05410

4.00% - 6.00% 174.05410/230.11670 = 19.63%

Apex RT: 10.66
Area: 21855

Terbutylazine?

(upon quantification: << 1 ppb)



GC-HRMS: introduction

Features/specifications:

Q Exactive GC

Resolution FWHM @ m/z 200 (scan speed)

15,000; 30,000; 60,000; 120,000

~ 18 Hz → 3 Hz

m/z 30-3000

Acquisition options:

Non-targeted (full scan) /

Targeted (SIM, MS/MS, data-dependent MS/MS)

Mass accuracy: internal < 1 ppm RMS; external < 3 ppm RMS

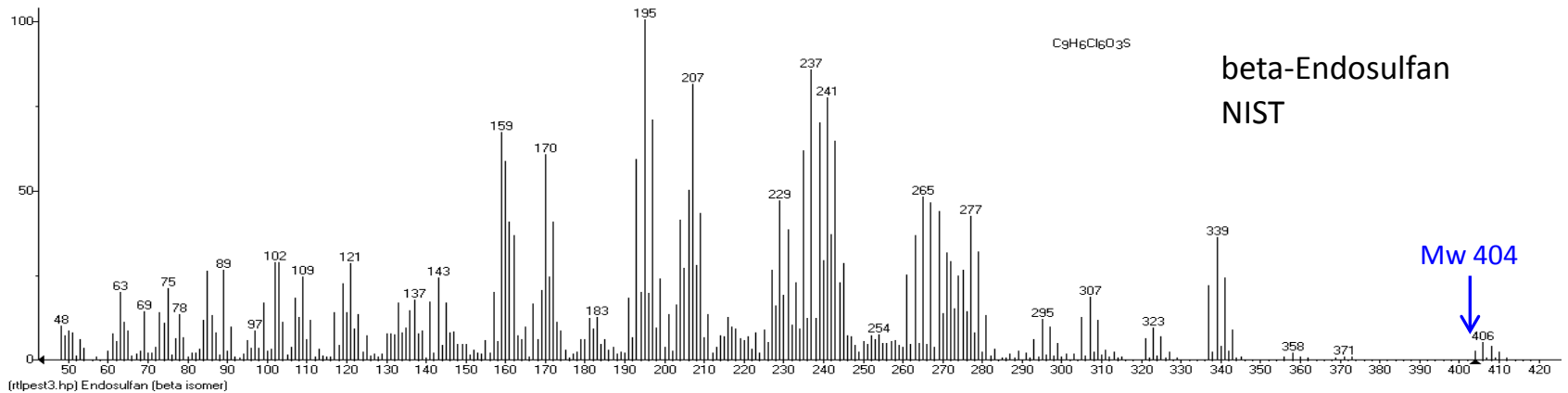
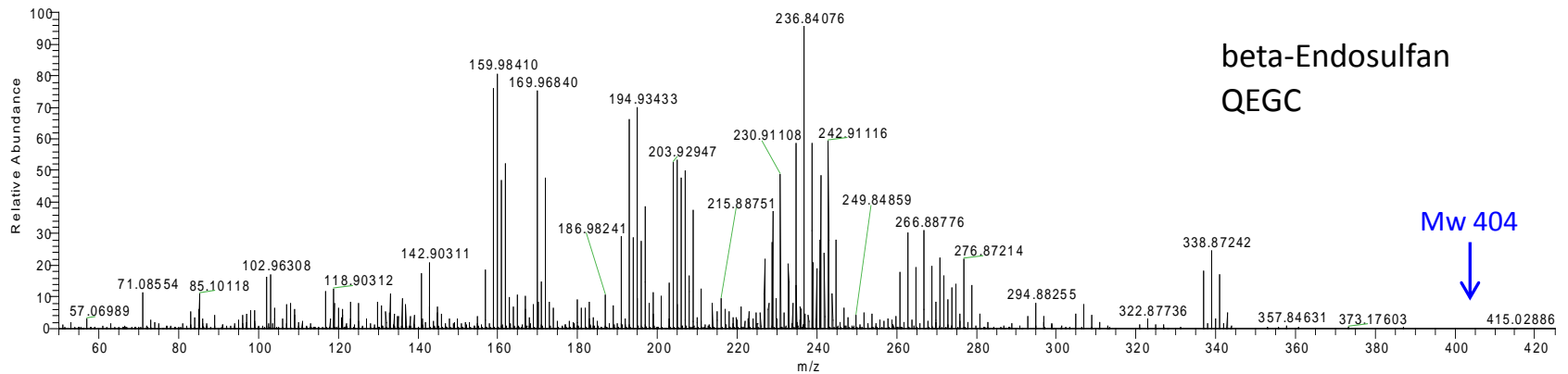
Dissociation in source EI / PCI / NCI



Identification

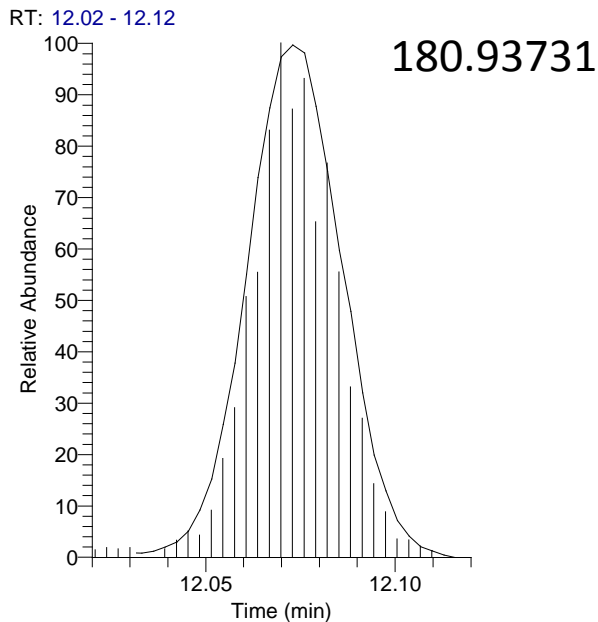
GC-EI-MS: hard ionisation technique, multiple fragments
=> one acquisition event suffices

13April15_60K_WO_LM_001 #3316 RT: 16.68 AV: 1 SB: 142 16.42-16.63, 16.76-17.04 NL: 1.30E6
T: FTMS + p EI Full m.s [50.00-500.00]



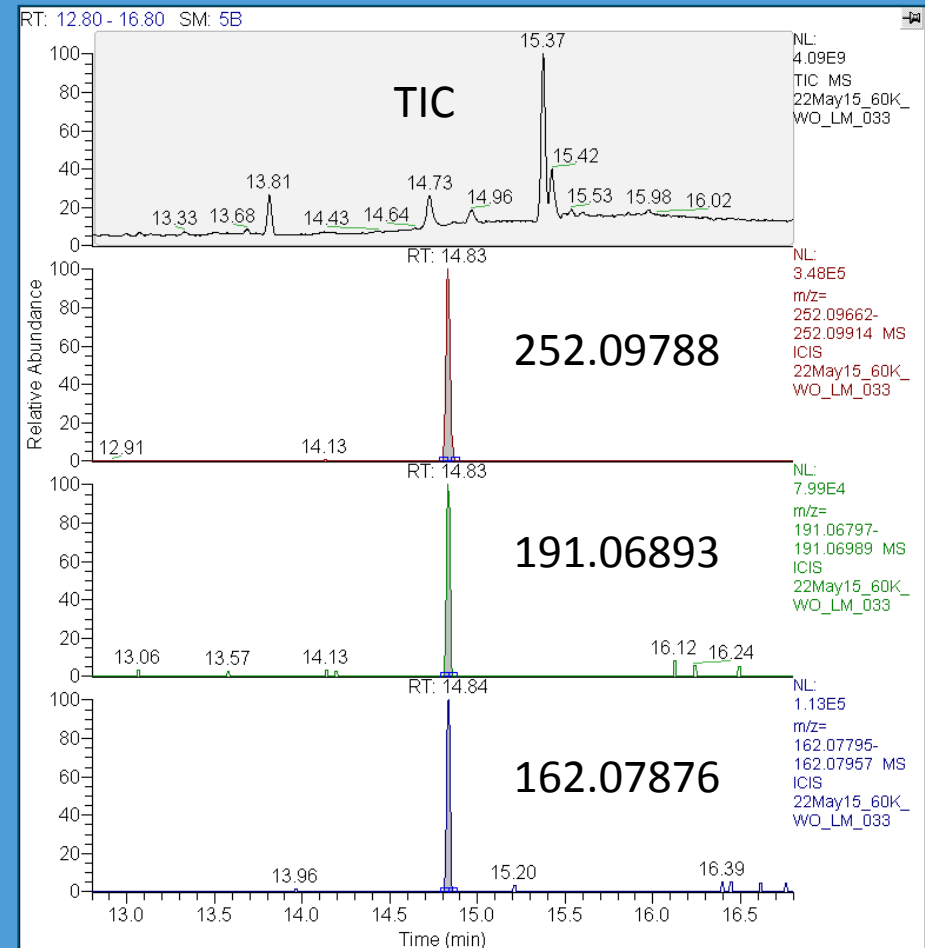
Scanspeed and XICs vs TIC

Lindane
 $C_6Cl_3H_4$
 10 ppb in leek



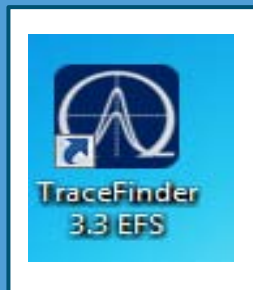
60K \approx 5 Hz

Pendimethalin
 $C_{11}H_{14}N_3O_4$
 10 ppb in leek



Method (datahandling)

Thermo Scientific™ Software:
XCalibur
TraceFinder 3.3 EFS



NIST library

Pesticide database with t_r and exact masses of (fragment) ions
On-going (currently 574 pesticides)



Method development:

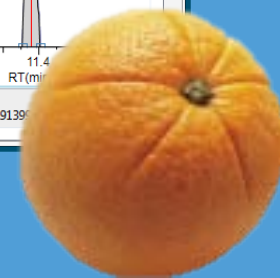
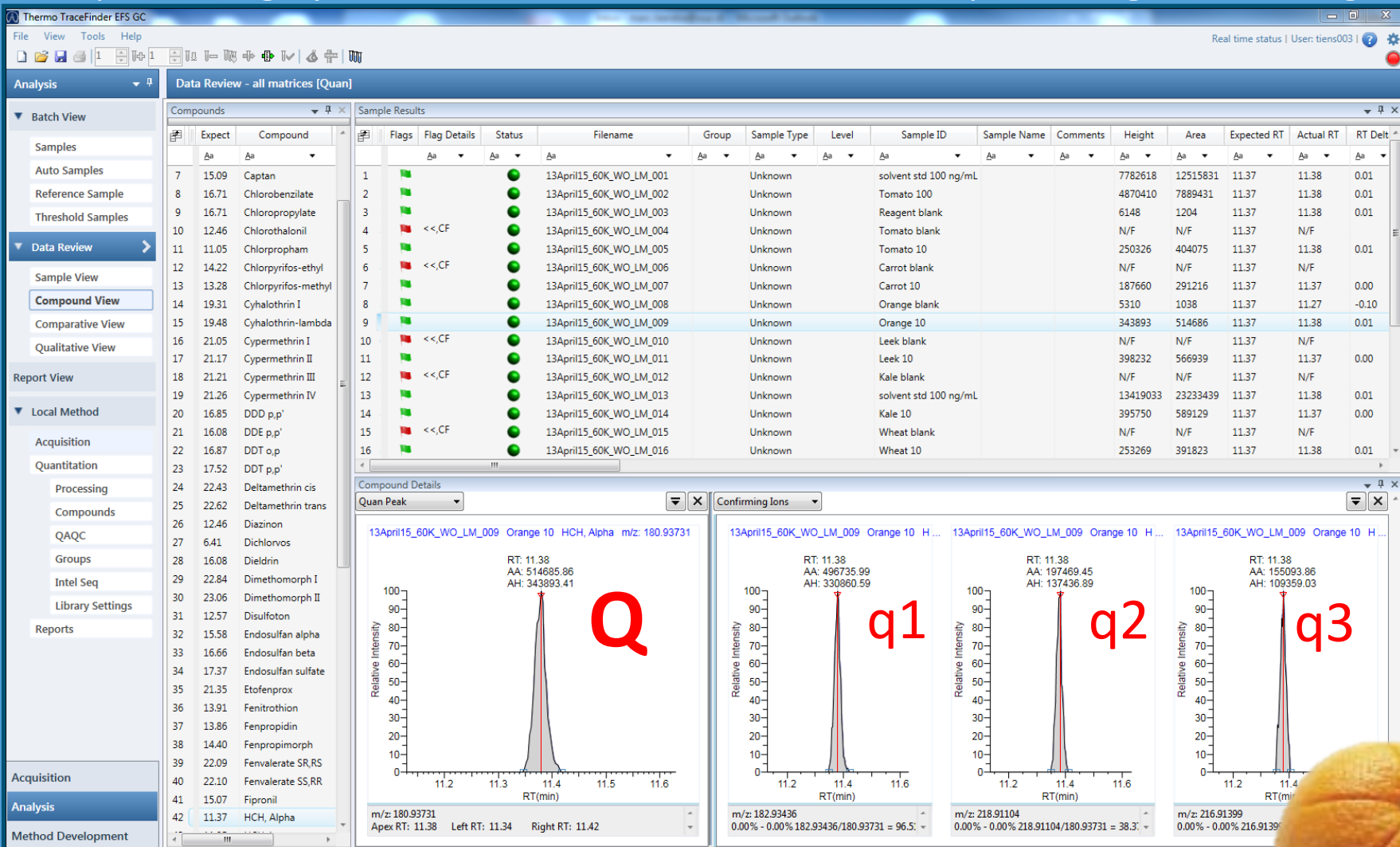
Default MEW: ± 5 ppm

Assess sensitivity/selectivity of the different ions available for each pesticide

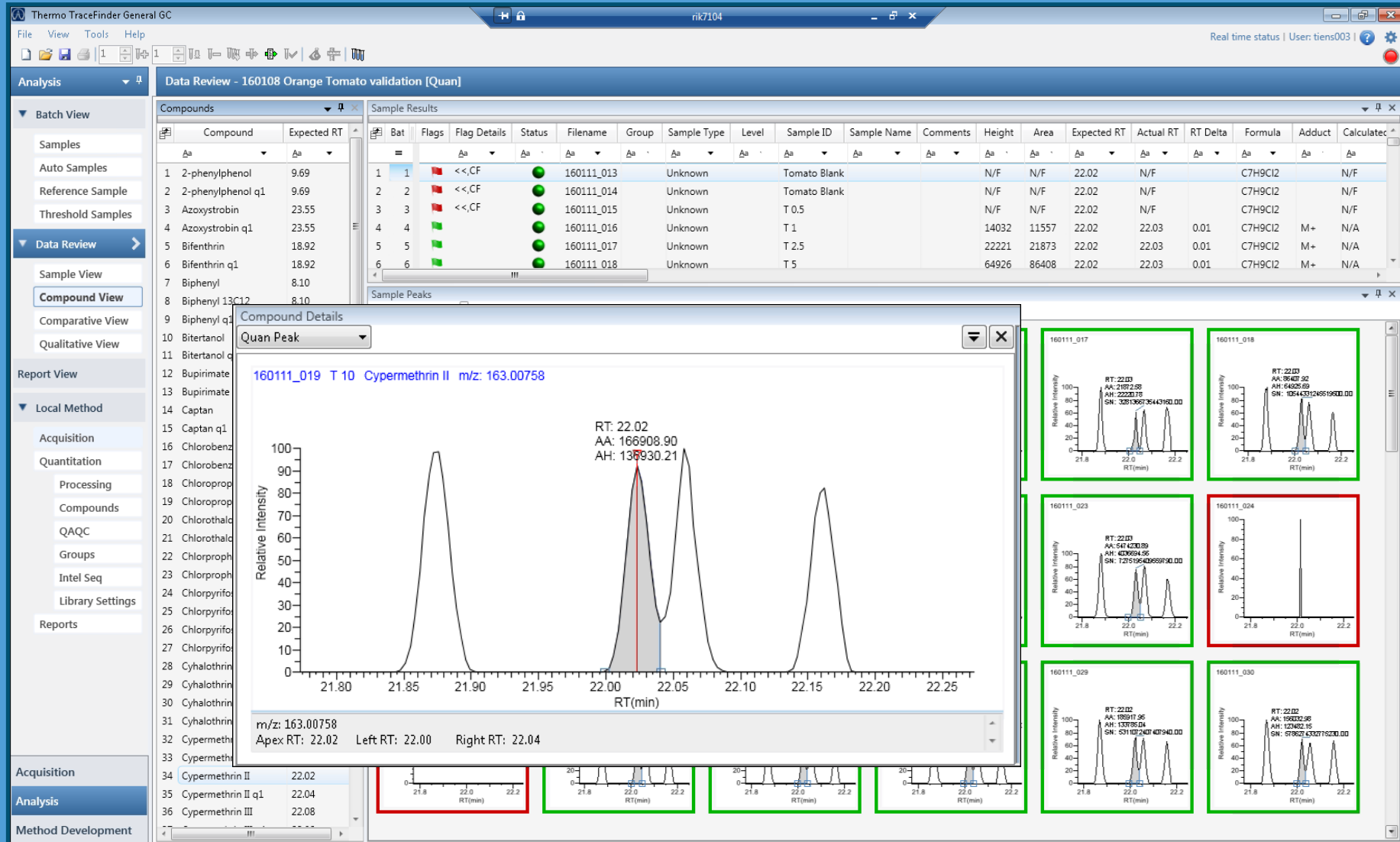
| CompoundNa | RT | Q;q1;q2;q3;q4;q5;q6 | Q | Q | q1 | q1 | q2 | q2 | q3 | q3 | q4 | q4 | q5 | q5 |
|---------------------|-------|-----------------------------|---------------|-----------|-----------------|-----------|----------------|-----------|-----------------|-----------|-----------------|-----------|------------|-----------|
| 2-phenylphenol | 9.47 | 170;141;115 | C12H9O | 169.06479 | C12H100 | 170.07262 | C11H9 | 141.06988 | C9H7 | 115.05423 | | | | |
| Azoxystrobin | 22.76 | 344;388;329;172;360;403 | C20H14N3O3 | 344.10297 | C21H14N3O5 | 388.09280 | C19H11O3N3 | 329.07949 | C10H6O2N | 172.03931 | C20H14O4N3 | 360.09788 | C22H17N3O5 | 403.11627 |
| Bifenthrin | 18.51 | 181;166;141;165;153 | C14H13 | 181.10118 | C13H10 | 166.07770 | C13H9 | 165.06988 | C12H9 | 153.06988 | | | | |
| Biphenyl | 7.88 | 154;153;152;76 | C12H10 | 154.07770 | C12H9 | 153.06988 | C12H8 | 152.06205 | | | | | | |
| Bitertanol | 20.11 | 170;168;112;(141;152) | C12H10O | 170.07262 | C8H14ON3 | 168.11314 | C4H6ON3 | 112.05054 | C11H9 | 141.06988 | C12H8 | 152.06205 | | |
| boscalid | 21.03 | 140;142;342;344;112 | C6H3ONCl | 139.98977 | C6H3ONCl(37) | 141.98682 | C18H12Cl2N2O | 342.03212 | C18H12Cl(37)N2O | 344.02917 | C5H3NCl | 111.99485 | | |
| Bupirimate | 16.3 | 273;193;208;316;166 | C10H17N4O3S | 273.10159 | C10H17N4 | 193.14477 | C11H18N3O | 208.14444 | C13H24N4O3S | 316.15636 | C8H12ON3 | 166.09749 | | |
| Captan | 15.09 | 79;149;107;80 | C6H7 | 79.05423 | C8H7NO2 | 149.04713 | C7H7O | 107.04919 | C6H8 | 80.06205 | | | | |
| chlorfenvinphos | 15.08 | 267;269;323;295;325 | C8H6O4Cl2P | 266.93753 | C8H6O4Cl(37)P | 268.93458 | C12H14O4Cl2P | 323.00013 | C10H10O4Cl2P | 294.96883 | C12H14O4Cl(37)P | 324.99718 | | |
| Chlorobenzilate | 16.71 | 251;139;253;141;111 | C13H9OCl2 | 251.00250 | C7H4ClO | 138.99452 | C13H9OCl(37) | 252.99955 | C7H4Cl(37)O | 140.99157 | C6H4Cl | 110.99960 | | |
| Chloropropylate | 16.71 | 251;139;253;141;111 | C13H9OCl2 | 251.00250 | C7H4ClO | 138.99452 | C13H9OCl(37) | 252.99955 | C7H4Cl(37)O | 140.99157 | C6H4Cl | 110.99960 | | |
| Chlorothalonil | 12.46 | 266;264;268;124;229 | C8Cl3Cl(37)N2 | 265.87806 | C8Cl4N2 | 263.88101 | C8Cl2Cl(37)N2 | 267.87511 | C8N2 | 124.0056 | C8N2Cl3 | 228.91216 | | |
| Chlorpropham | 11.05 | 127;171;213;154 | C6ClH6N | 127.01833 | C7H6NO2Cl | 171.00816 | C10H12ClNO2 | 213.05511 | C8H9NCl | 154.04180 | | | | |
| Chlorpyrifos-ethyl | 14.22 | 197;199;258;313;125 | C5Cl3H2NO | 196.91965 | C5H2Cl2Cl(37)NO | 198.91670 | C5H3Cl2NO3PS | 257.89428 | C9H11Cl2NO3PS | 313.95688 | C2H6O2PS | 124.98206 | | |
| Chlorpyrifos-methyl | 13.28 | 286;288;125 | C7H7Cl2NO3PS | 285.92558 | C7H7Cl(37)NO3PS | 287.92263 | C2H6O2PS | 124.98206 | | | | | | |
| coumaphos | 20.28 | 226;362;210;109;182 | C10H7O2ClS | 225.98498 | C14H16ClO5PS | 362.01391 | C10H7O3Cl | 210.00782 | C2H6O3P | 109.00491 | C9H7O2Cl | 182.01291 | | |
| Cyhalothrin I | 19.31 | 197;141;208;181 | C8H9ClF3 | 197.03394 | C8H7F2 | 141.05103 | C14H11OON | 208.07569 | C13H9O | 181.06479 | C14H11NO | 209.08352 | | |
| Cyhalothrin-lambda | 19.48 | 197;141;208;181 | C8H9ClF3 | 197.03394 | C8H7F2 | 141.05103 | C14H11OON | 208.07569 | C13H9O | 181.06479 | C14H11NO | 209.08352 | | |
| Cypermethrin I | 21.05 | 163;127;209;181 | C7H9Cl2 | 163.00758 | C7H8Cl | 127.03090 | C14H11NO | 209.08352 | C13H9O | 181.06479 | C12H8 | 152.06205 | | |
| Cypermethrin II | 21.17 | 163;127;209;181 | C7H9Cl2 | 163.00758 | C7H8Cl | 127.03090 | C14H11NO | 209.08352 | C13H9O | 181.06479 | C12H8 | 152.06205 | | |
| Cypermethrin III | 21.21 | 163;127;209;181 | C7H9Cl2 | 163.00758 | C7H8Cl | 127.03090 | C14H11NO | 209.08352 | C13H9O | 181.06479 | C12H8 | 152.06205 | | |
| Cypermethrin IV | 21.26 | 163;127;209;181 | C7H9Cl2 | 163.00758 | C7H8Cl | 127.03090 | C14H11NO | 209.08352 | C13H9O | 181.06479 | C12H8 | 152.06205 | | |
| DDD p,p' | 16.85 | 235;237;199;212;165 | C13Cl2H9 | 235.00758 | C13H9Cl(37) | 237.00463 | C13H8Cl | 199.03090 | C14H9Cl | 212.03873 | C13H9 | 165.06988 | | |
| DDE p,p' | 16.08 | 245;248;318;316;176;210 | C14Cl2H8 | 245.99976 | C14H8Cl(37) | 247.99681 | C14H8Cl3Cl(37) | 317.93451 | C14H8Cl4 | 315.93746 | C14H8 | 176.06205 | C14H7Cl | 210.02308 |
| DDT o,p | 16.87 | 235;237;199;212;165 | C13Cl2H9 | 235.00758 | C13H9Cl(37) | 237.00463 | C13H8Cl | 199.03090 | C14H9Cl | 212.03873 | C14H8Cl2 | 245.99976 | C13H9 | 165.06988 |
| DDT p,p' | 17.52 | 235;237;199;212;165 | C13Cl2H9 | 235.00758 | C13H9Cl(37) | 237.00463 | C13H8Cl | 199.03090 | C14H9Cl | 212.03873 | C14H8Cl2 | 245.99976 | C13H9 | 165.06988 |
| Deltamethrin cis | 27.43 | 253-174-172-251-255-181-209 | C7H9BrRfR11 | 252.90450 | C7H9BrRf(37)R11 | 257.90616 | C7H9Br | 171.98821 | C7H9Br2 | 250.90655 | C7H9BrRfR11 | 254.90246 | C13H9O | 181.06479 |

Quantitative data processing method

Data processing by TraceFinder + manual verification of peak assignment/integration



Quantitative data processing method



Qualitative screening

Two approaches:

1. Library: match of EI-spectra

deconvolution of HR spectra

⇒ cleaned spectrum

Library search (NIST, PEST library)

Software:

Report if match (SI) > user threshold

Analyst: manual review hits

2. Database: RT + 2 exact masses

RT ± 0.5 min

XICs ± 5 ppm

2 ions (w/o ratio criterion)

Software:

Report if signal is found for both ions

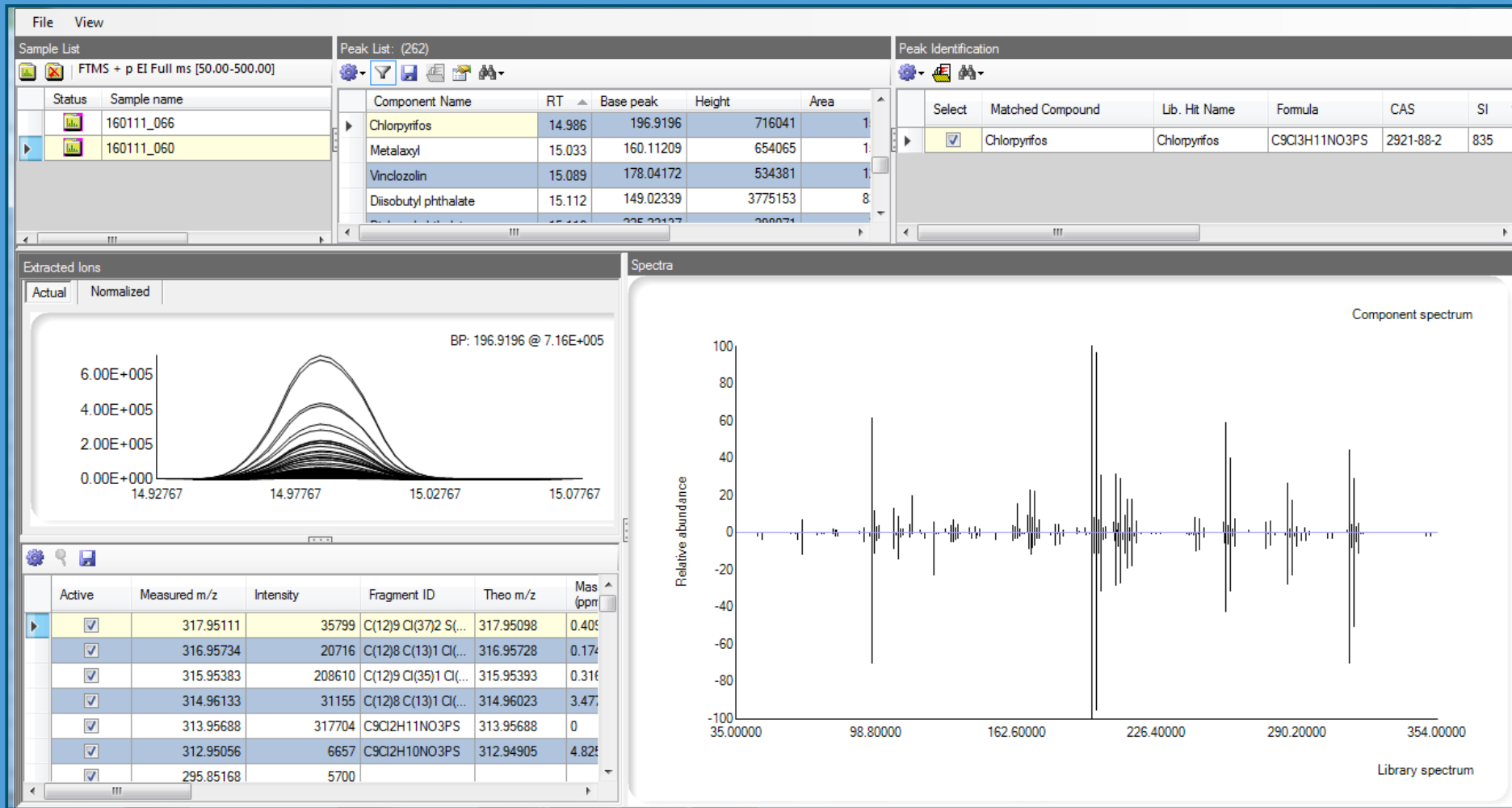
Analyst: manual review hits

Only briefly assessed, preliminary results



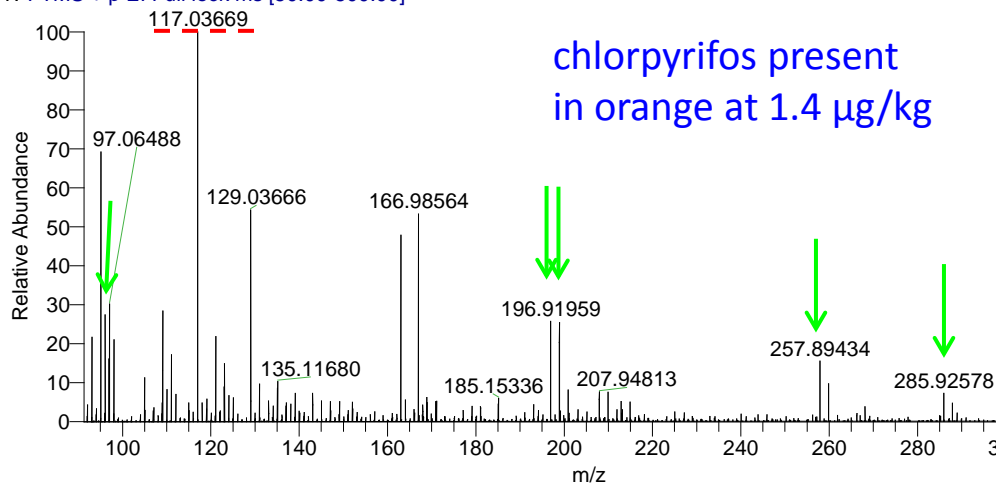
Qualitative screening: approach-1

Orange spiked @ 10 µg/kg: 73% automatically found

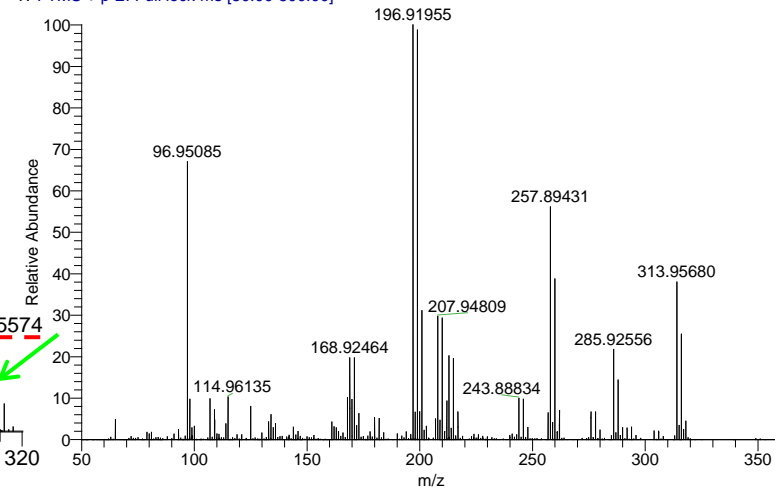


Qualitative screening

160111_066 #2682-2685 RT: 14.98-14.99 AV: 4 SB: 5 14.96 , 15.01-15.02 NL: 3.79E5
T: FTMS + p EI Full lock ms [50.00-500.00]



160106_006 #2370-2373 RT: 15.02-15.03 AV: 4 SB: 4 14.99-15.00 , 15.05 NL: 1.84E7
T: FTMS + p EI Full lock ms [50.00-500.00]

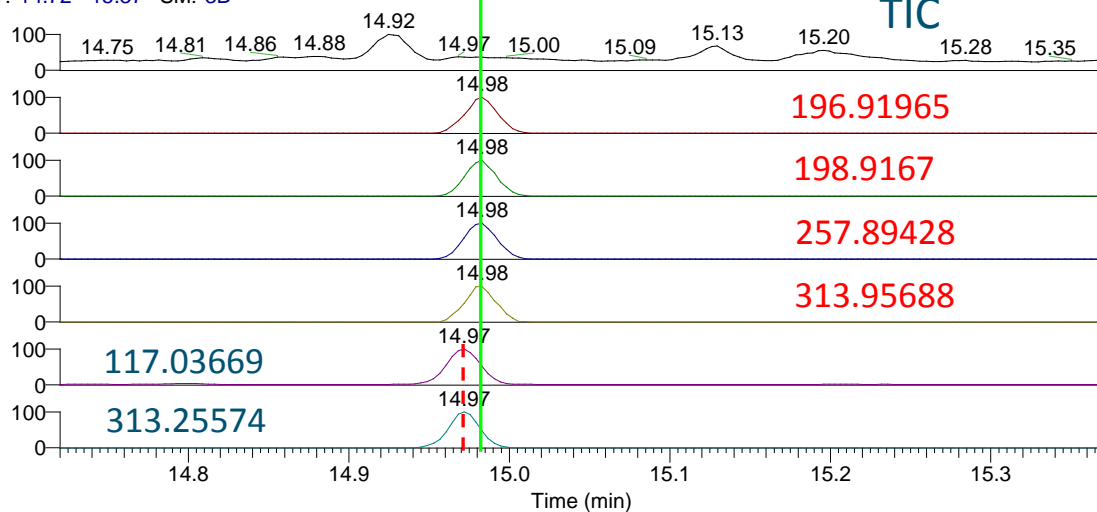


Not automatically found by spectral match....

E:\GC-Orbitrap...\160111_066

01/13/16 03:30:14

RT: 14.72 - 15.37 SM: 3B



easily found through
approach-2

Two approaches:

1. Library: match of EI-spectra

deconvolution of HR spectra

⇒ cleaned spectrum

Library search (NIST, PEST library)

Software:

Report if match (SI) > user threshold

Analyst: manual review hits

+ allows screening for analytes
not (yet) included in dedicated
HR/AM database

- low $\mu\text{g}/\text{kg}$ levels in complex
matrices are challenging

2. Database: RT + 2 exact masses

RT \pm 0.5 min

XICs \pm 5 ppm

2 ions (w/o ratio criterion)

Software:

Report if signal is found for both ions

Analyst: manual review hits

+ better screening sensitivity

- needs database with t_r / exact masses

Conclusions

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<http://dx.doi.org/10.1080/19440049.2015.1085652>



Simultaneous quantitative determination, identification and qualitative screening of pesticides in fruits and vegetables using LC-Q-Orbitrap™-MS

Paul Zomer* and Hans G.J. Mol

Natural Toxins & Pesticides, RIKILT Wageningen UR, Wageningen, the Netherlands

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Hans G.J. Mol, Marc Tienstra, Paul Zomer

Evaluation of gas chromatography - electron ionization - full scan high resolution Orbitrap mass spectrometry for pesticide residue analysis

*GC-Q-Orbitrap-HRMS
submitted 2016*

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**Thank you for
your attention!**



RIKILT

WAGENINGEN UR