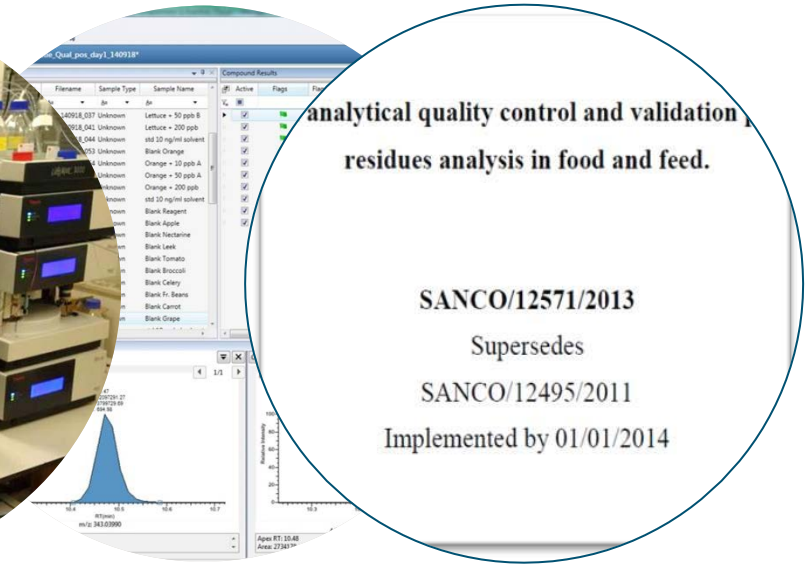
Simultaneous quantitative determination and screening of pesticides using Orbitrap MS Technology



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1st International Symposium on Recent Developments in Pesticide Analysis, Prague 27-28 April 2015

Thermo SCIENTIFIC

Outline

Introduction pesticide residue analysis

Instrument and method (LC)

Quantitative analysis

Identification

Qualitative screening

What about GC?

Conclusions

Pesticide residue analysis in food

The analytical challenge: theory

Pesticide Manual: **1630 entries**

↓ World: ~700 in use, others obsolete

↓ EU: 462 approved

But: residues imported ↑

illegal pesticides ↑ but not gone

100s of different food matrices of varying complexity

MRLs: 0.01-10 mg/kg

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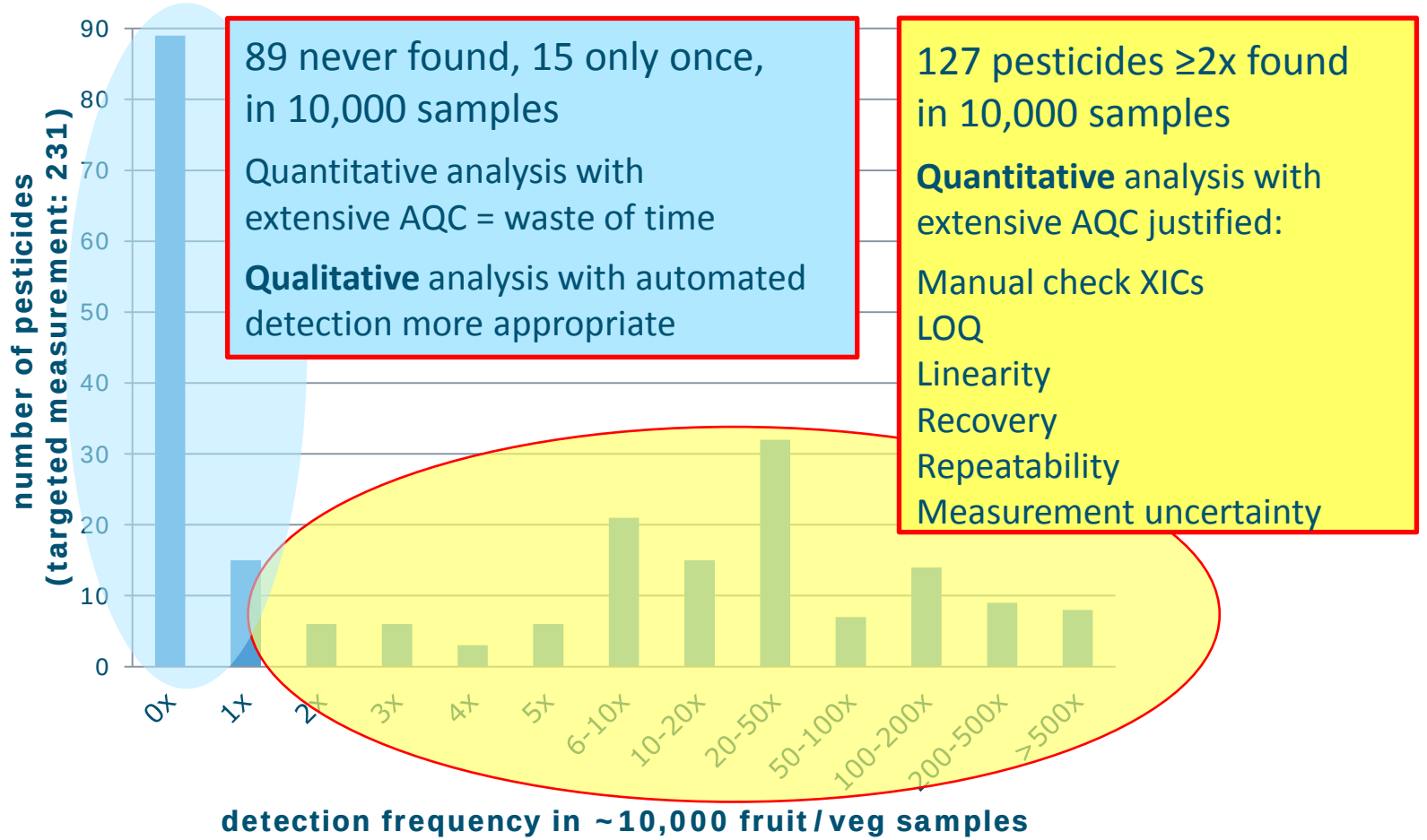
Pesticide residue analysis in food

The analytical challenge: practice

Detection rate of pesticides amenable to LC-MS based multi-residue analysis



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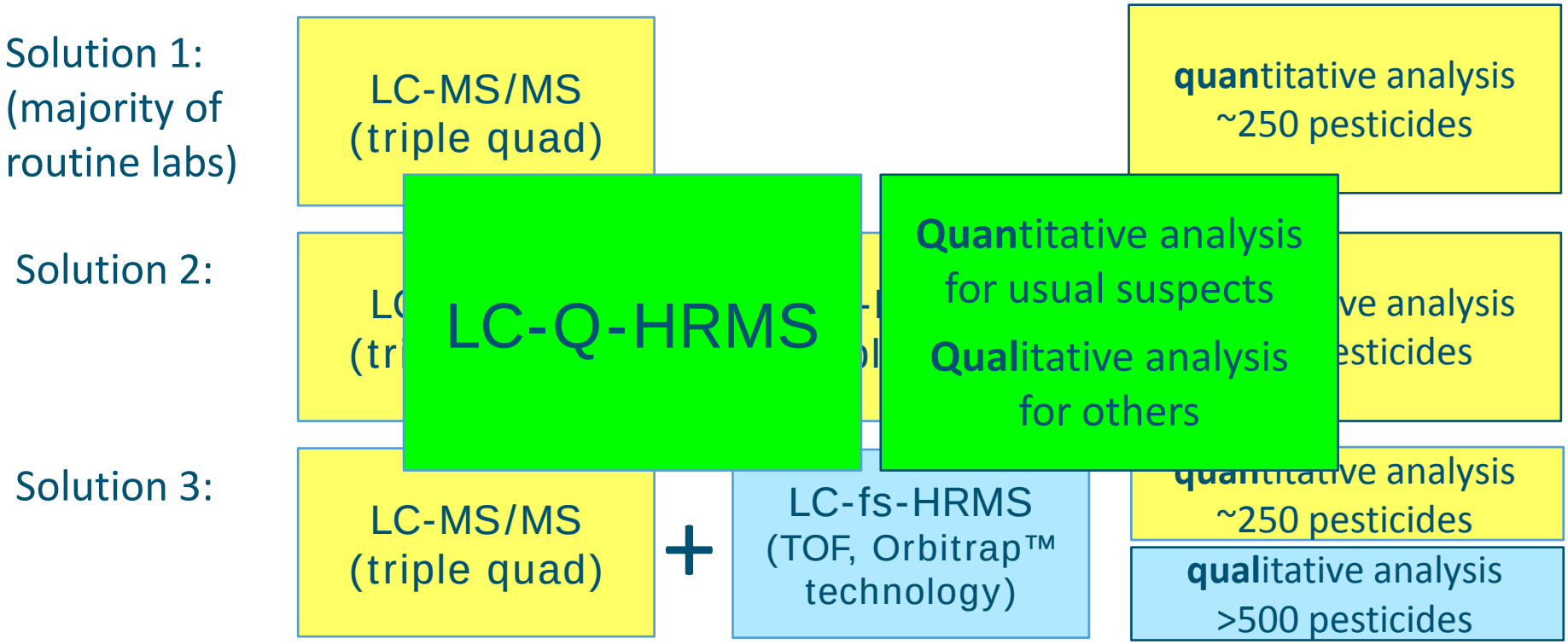
Data 2011-2013 compiled from NVWA, https://www.vwa.nl/

The challenge and the solution

Analysis request:

a) are any pesticides present; b) if so: at what level?

New solution:



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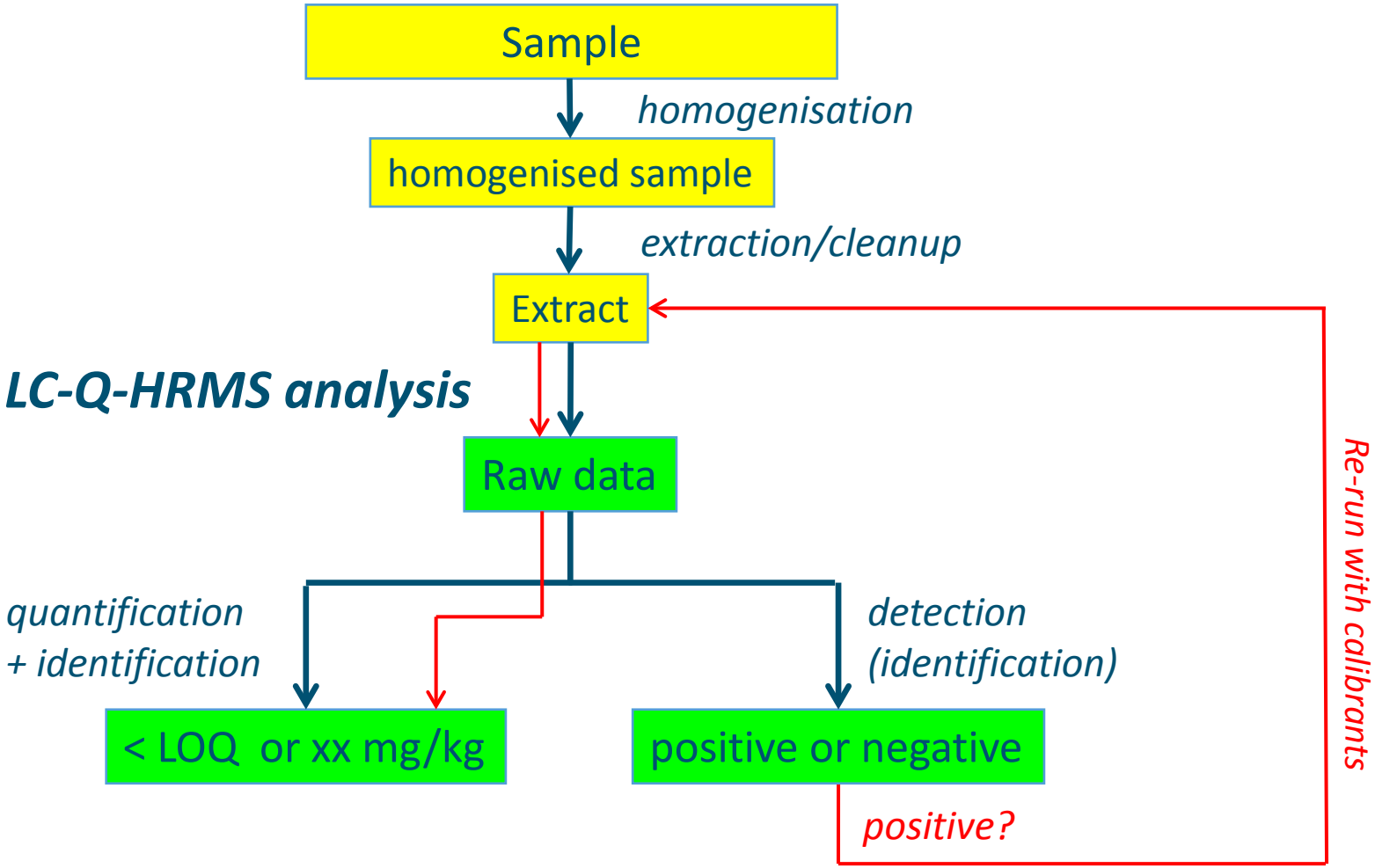
Outline work flow



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Instrument used

Thermo Scientific™ Exactive™ Plus MS

Thermo Scientific™ Q Exactive™ MS

Thermo Scientific™ Q Exactive™ Focus MS

Thermo Scientific™ Q Exactive™ Plus MS

Thermo Scientific™ Exactive™ Plus EMR MS

Thermo Scientific™ Q Exactive™ HF MS

Resolution FWHM @ m/z 200 (scan speed)

17,500 (12 Hz); 35,000 (6 Hz); 70,000 (3 Hz); 140,000 (1.5 Hz) [Focus: up to 70,000]

m/z 50-6000 (2000)

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

Polarity switching: one full cycle pos&neg in <1 sec (R=35,000)

Variable precursor ion isolation width selection from 0.4 Da to full mass range

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Various acquisition options

Non-target acquisition

without fragmentation (Full Scan)

with fragmentation in HCD cell

AIF = all-ion-fragmentation

vDIA = variable Data Independent Acquistion

Targeted acquisition

without fragmentation (SIM = Selected Ion Monitoring)

with fragmentation

ddMS/MS = data-dependent MS/MS with inclusion list

t-MS/MS = targeted MS/MS

PRM = Parallel Reaction Monitoring

Combinations of the above

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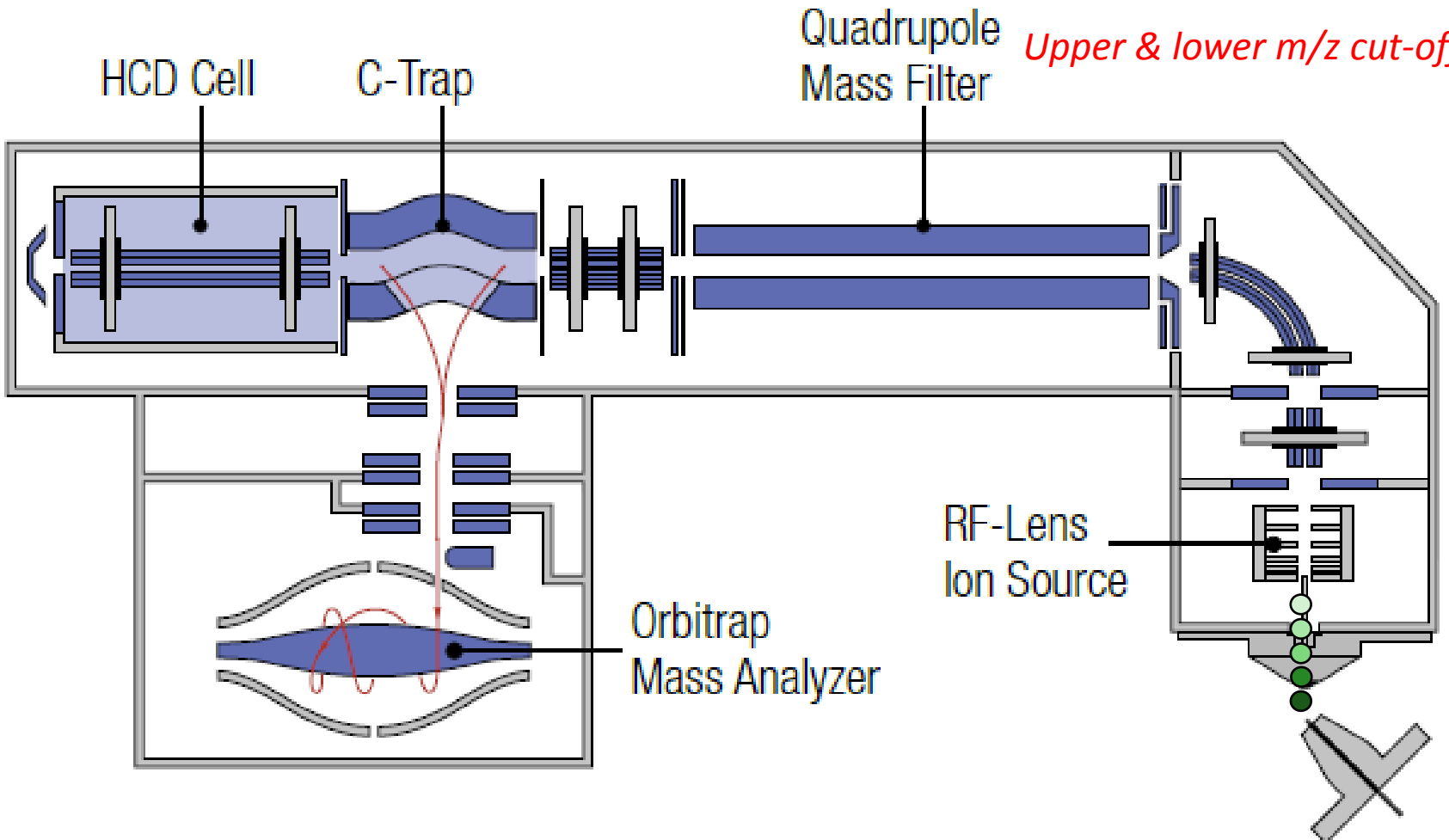
Full scan acquisition

FS: m/z 100-1000	FS: m/z 100-1000	FS: m/z 100-1000	FS: m/z 100-1000



Set up of acquisition method: full scan

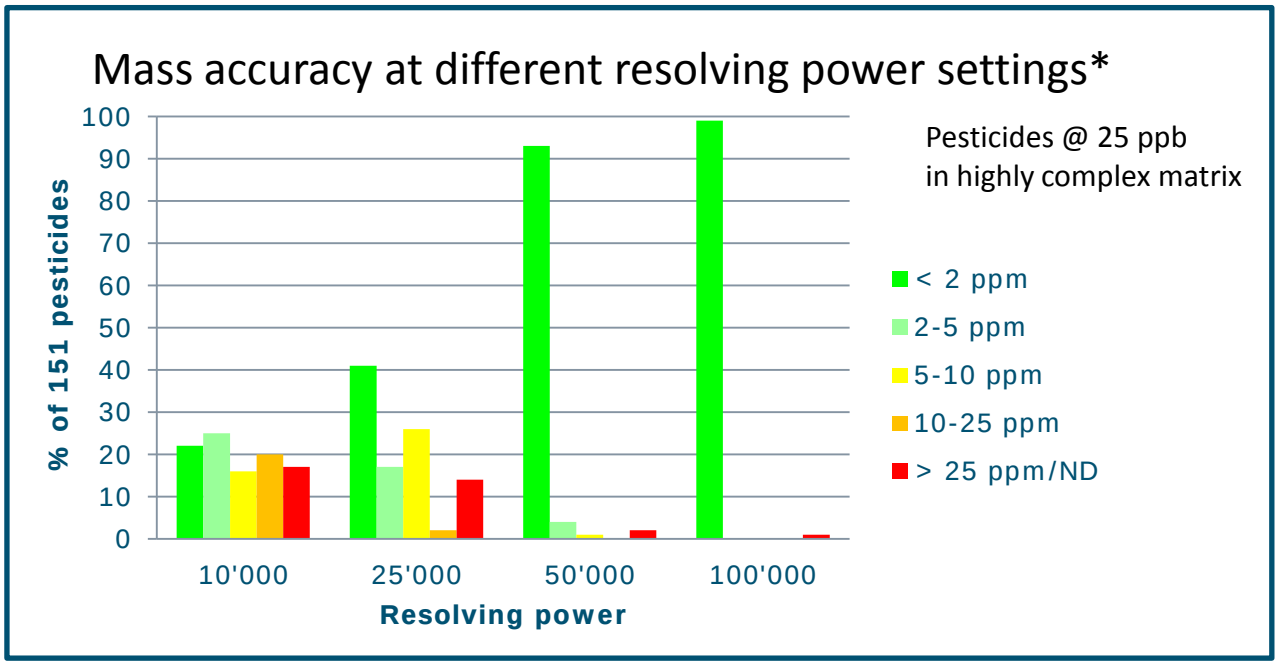
General source parameters, AGC settings: TFS default recommendations

Full scan measurement:

m/z range: 135-1000

mass resolution: ≥50,000 for reliable mass accuracy in complex samples to ensure for selectivity and quantification*

Here: 70,000 FWHM @ m/z 200



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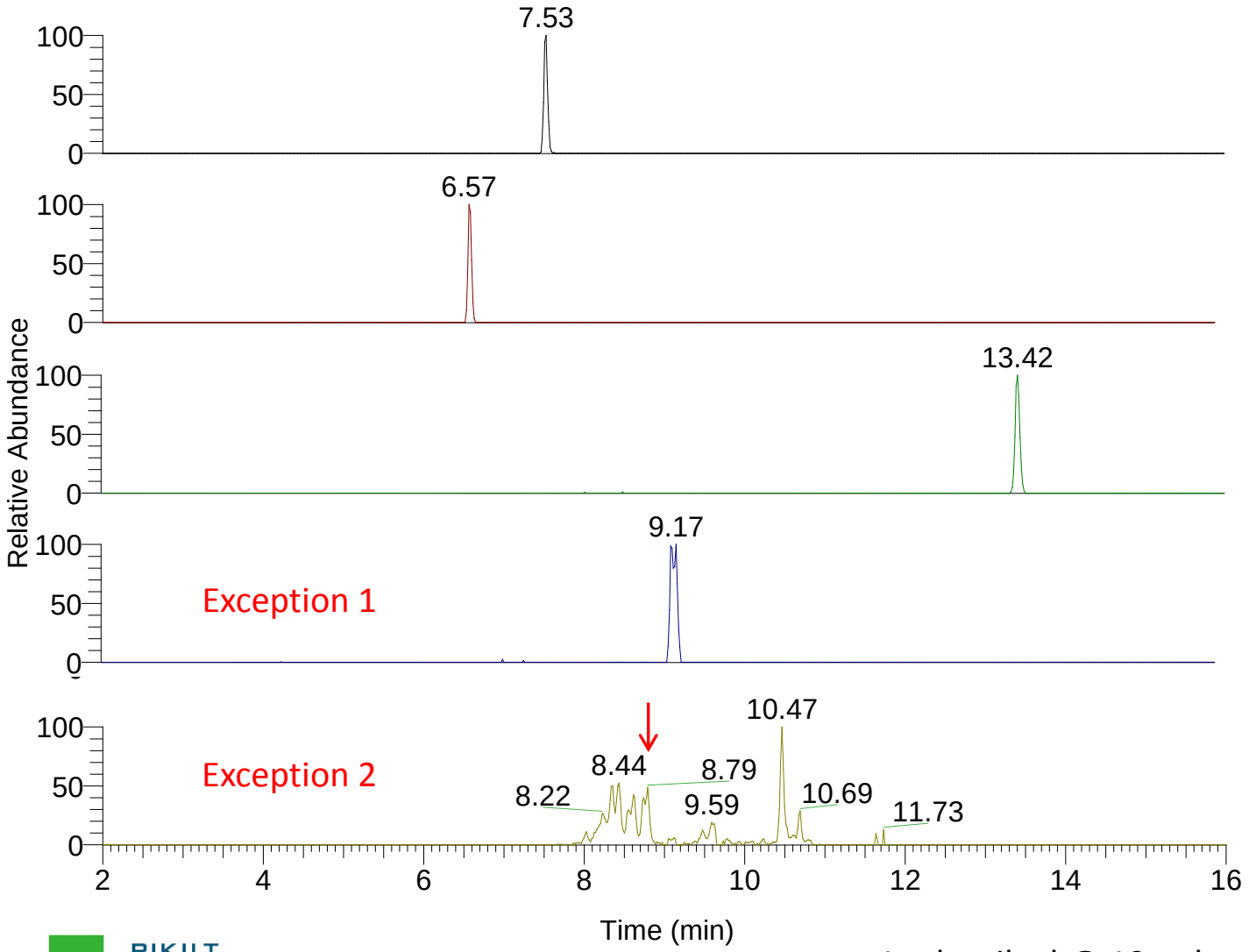
* Kellmann et al, JASMS, 2009, 20, 1464–1476

Extracting pesticides from the raw data

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



m/z 230.0069
$C_5H_{12}NO_3PS_2$
dimethoate

m/z 230.0536
$C_9H_6F_3N_3O$
flonicamid

m/z 365.1449
$C_{19}H_{25}ClN_2OS$
pyridaben

m/z 202.0854
$C_7H_{12}ClN_5$
simazine

m/z 343.5290
$C_{12}H_{14}N_4O_4S_2$
Thiophanate-methyl

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Leek spiked @ 10 ppb,
Full scan m/z 135-1000; Res = 70,000

Set up of acquisition method: fragmentation

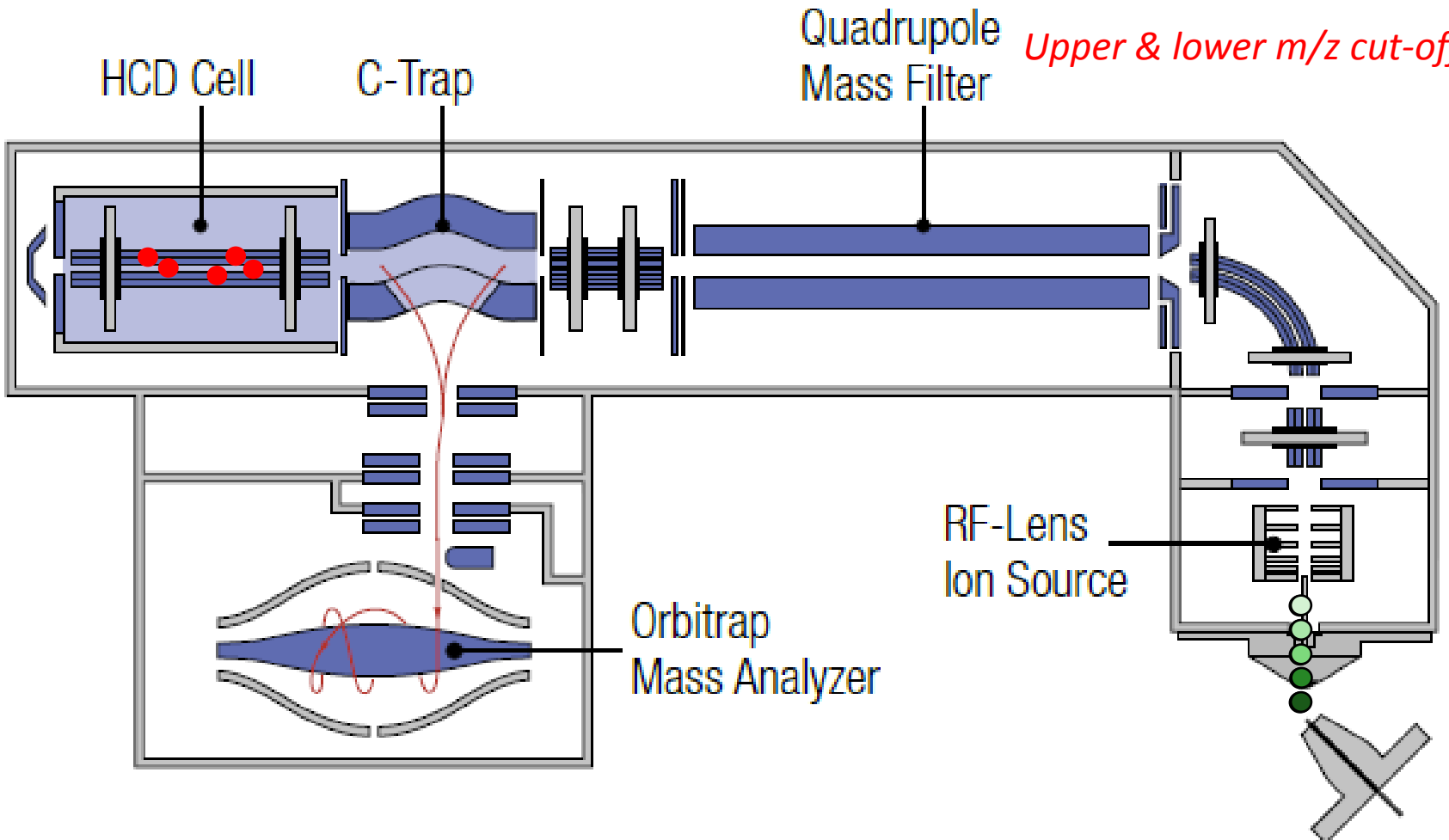
Generation of fragments:
1) needed for identification, 2) improve screening selectivity

For optimum detection and identification:
full scan acquisition without and with fragmentation in 1 run

Non-targeted fragmentation:
two options: AIF and vDIA

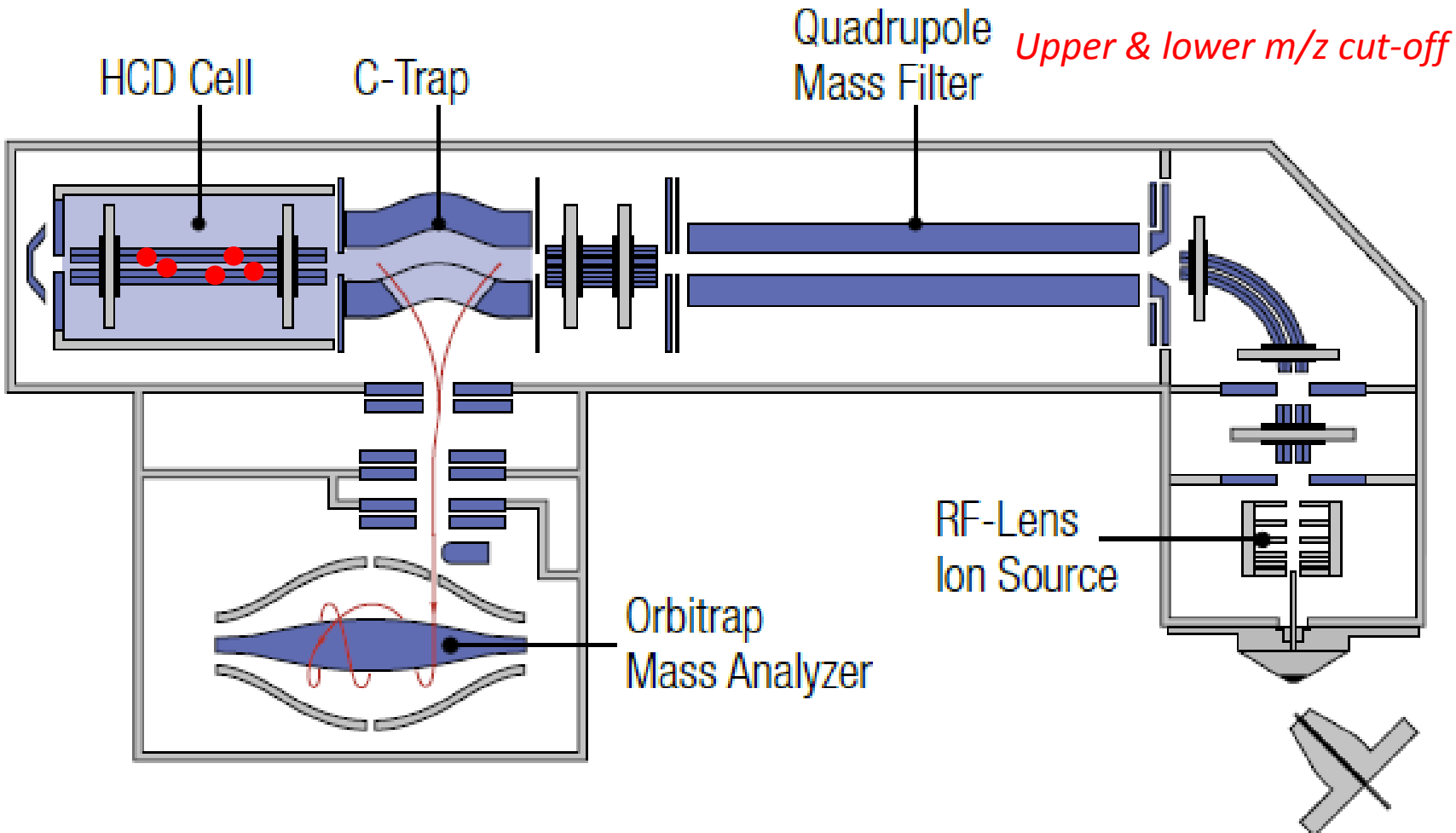
Combined Full scan + AIF acquisition

FS: m/z 100-1000	AIF ϟ m/z 100-1000	FS: m/z 100-1000	AIF ϟ m/z 100-1000



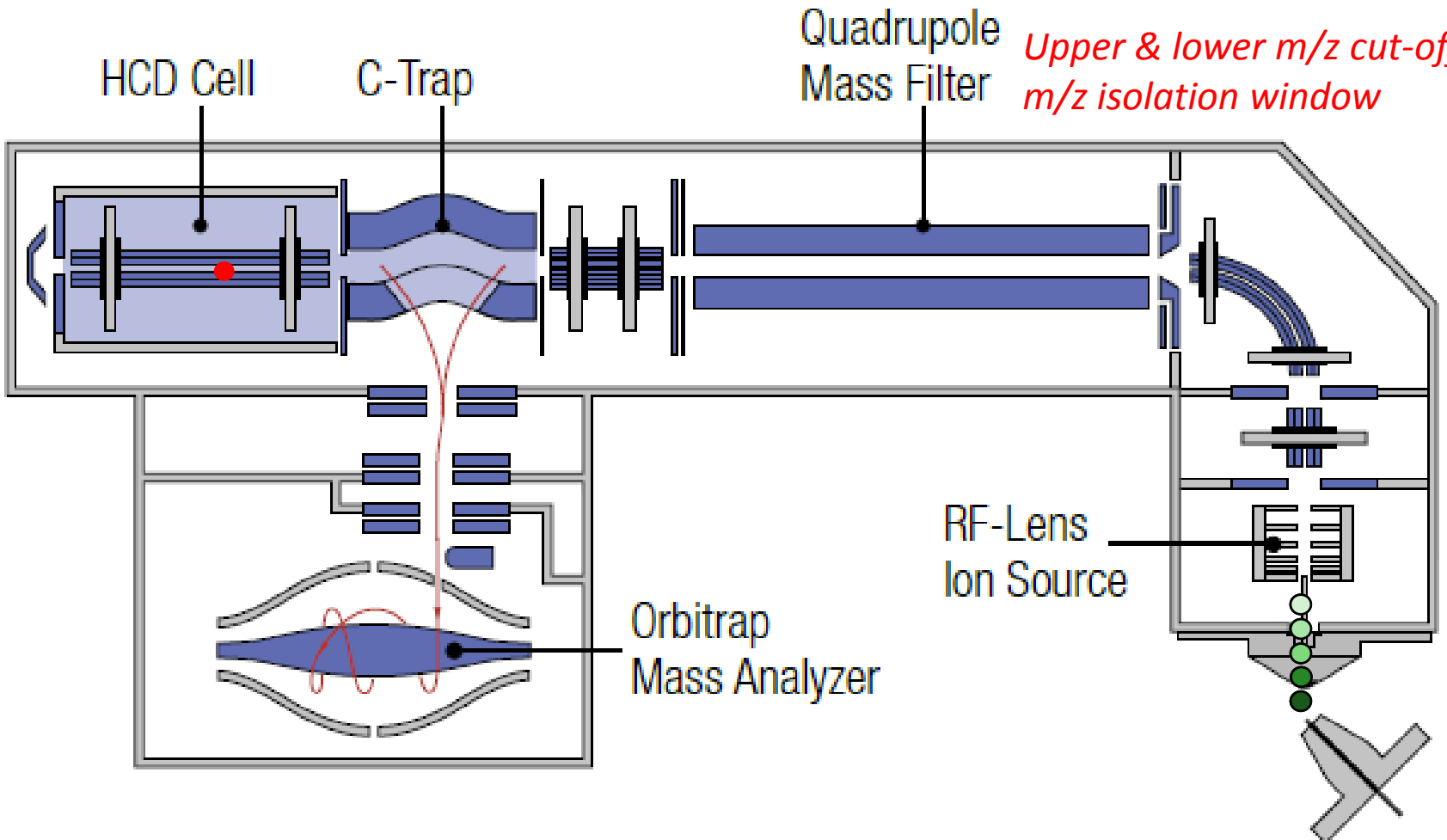
Combined Full scan + AIF acquisition

FS: m/z 100-1000	AIF ϟ m/z 100-1000	FS: m/z 100-1000	AIF ϟ m/z 100-1000



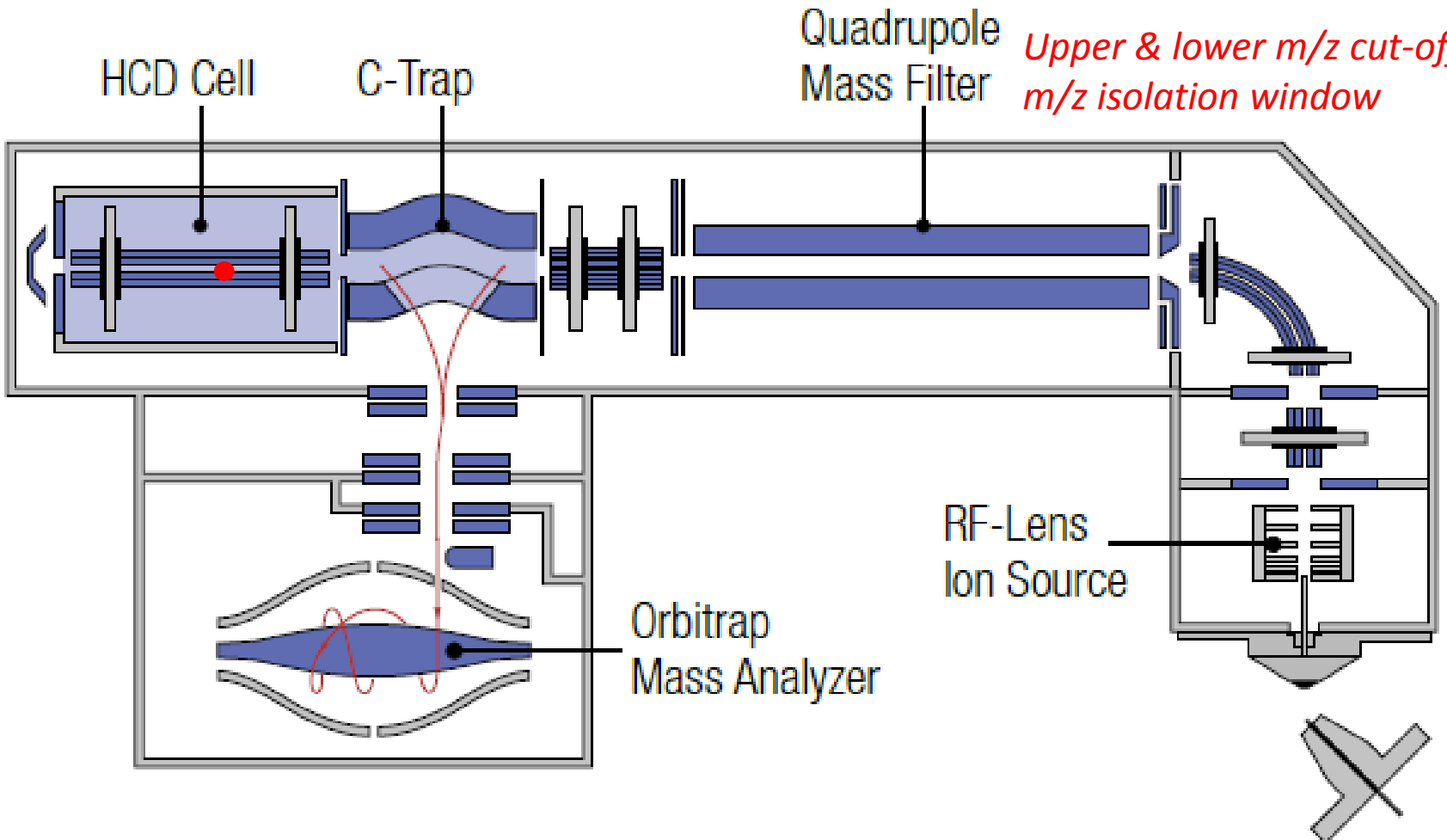
Combined Full scan + vDIA acquisition

FS: m/z 100-1000	ϟ: 100-200	ϟ: 200-300	ϟ: 300-400	ϟ: 300-400	ϟ: 500-1000	FS: m/z 100-1000



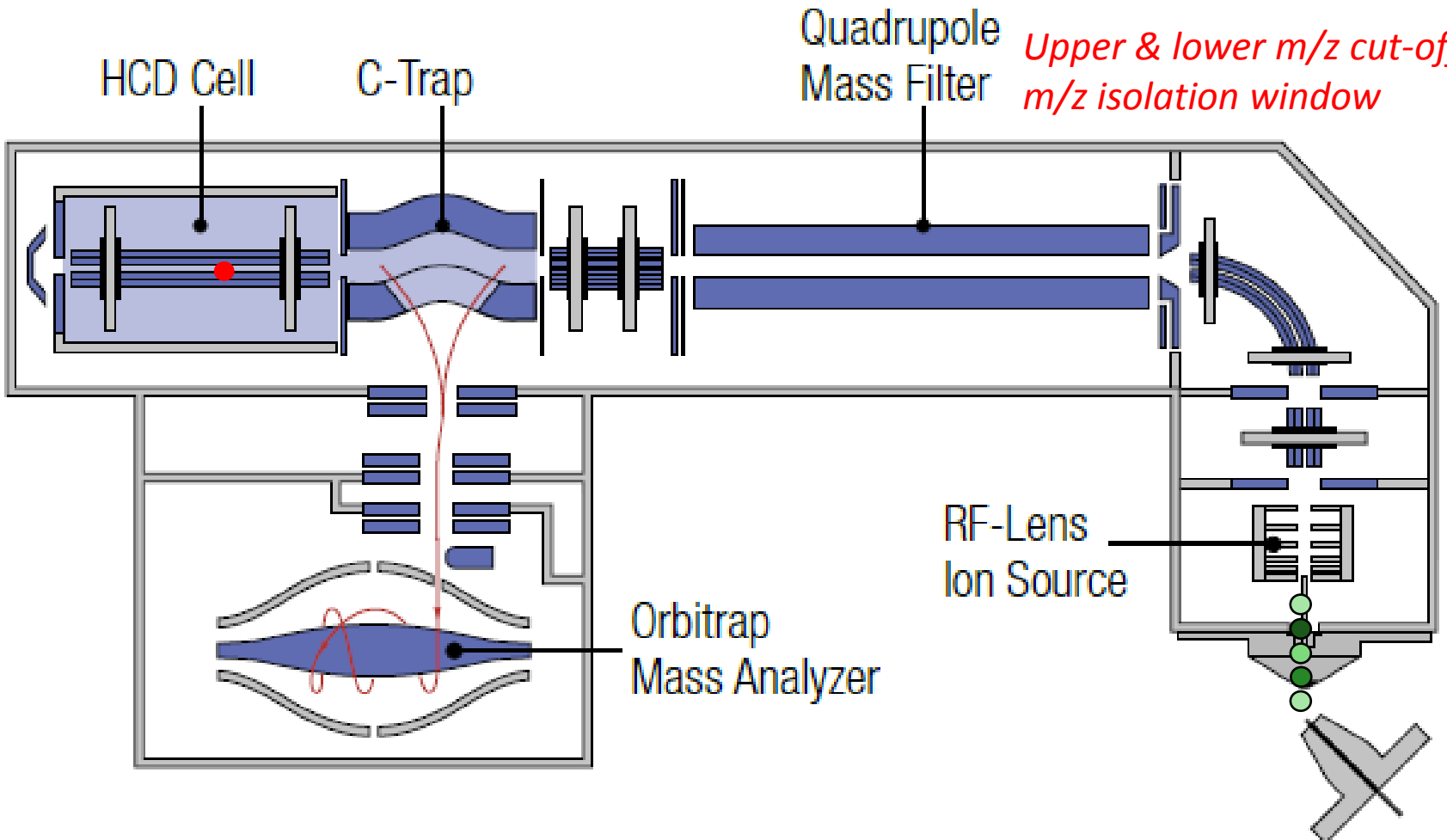
Combined Full scan + vDIA acquisition

FS: m/z 100-1000	ϟ: 100-200	ϟ: 200-300	ϟ: 300-400	ϟ: 300-400	ϟ: 500-1000	FS: m/z 100-1000



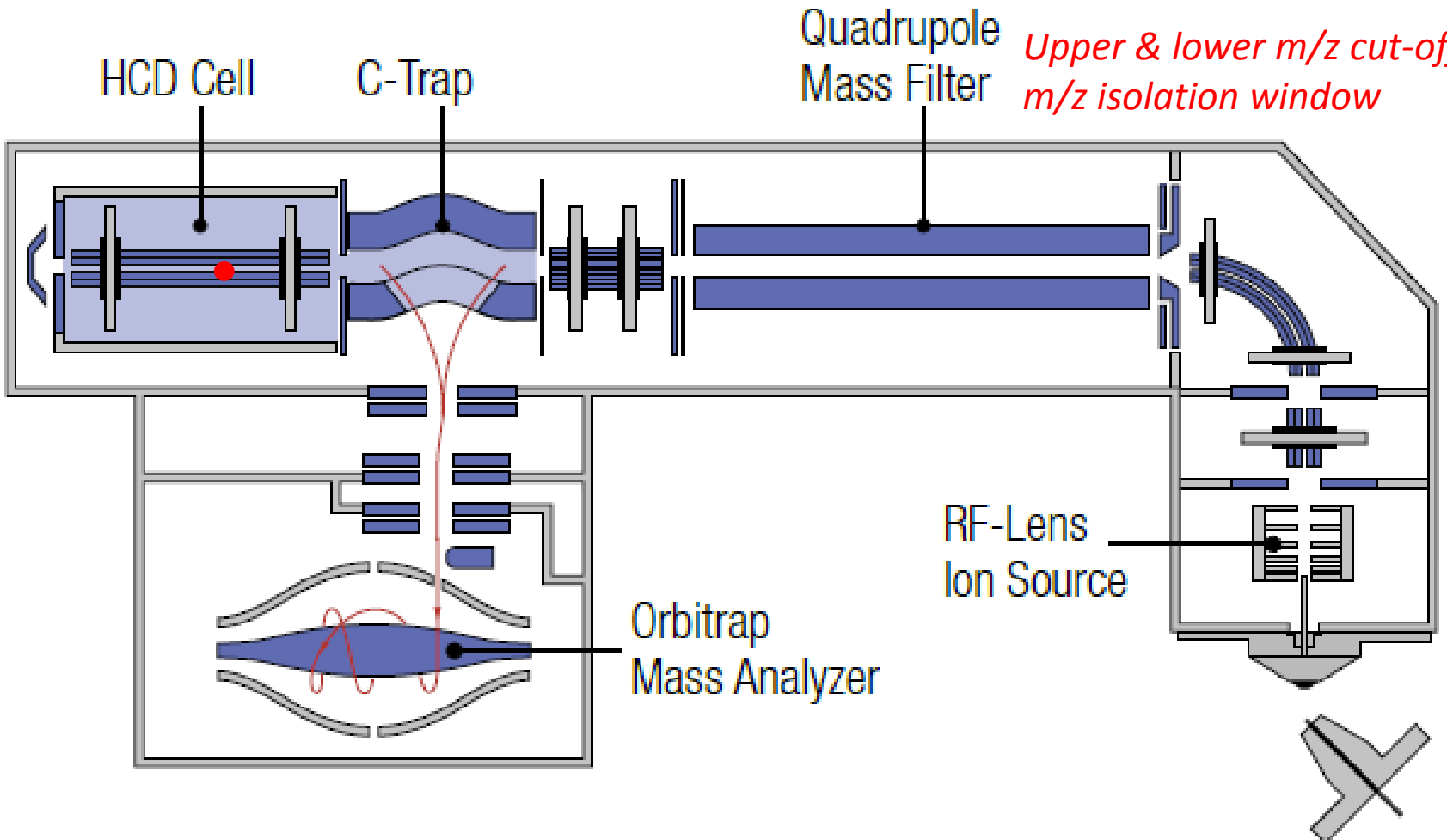
Combined Full scan + vDIA acquisition

FS: m/z 100-1000	ϟ: 100-200	ϟ: 200-300	ϟ: 300-400	ϟ: 300-400	ϟ: 500-1000	FS: m/z 100-1000

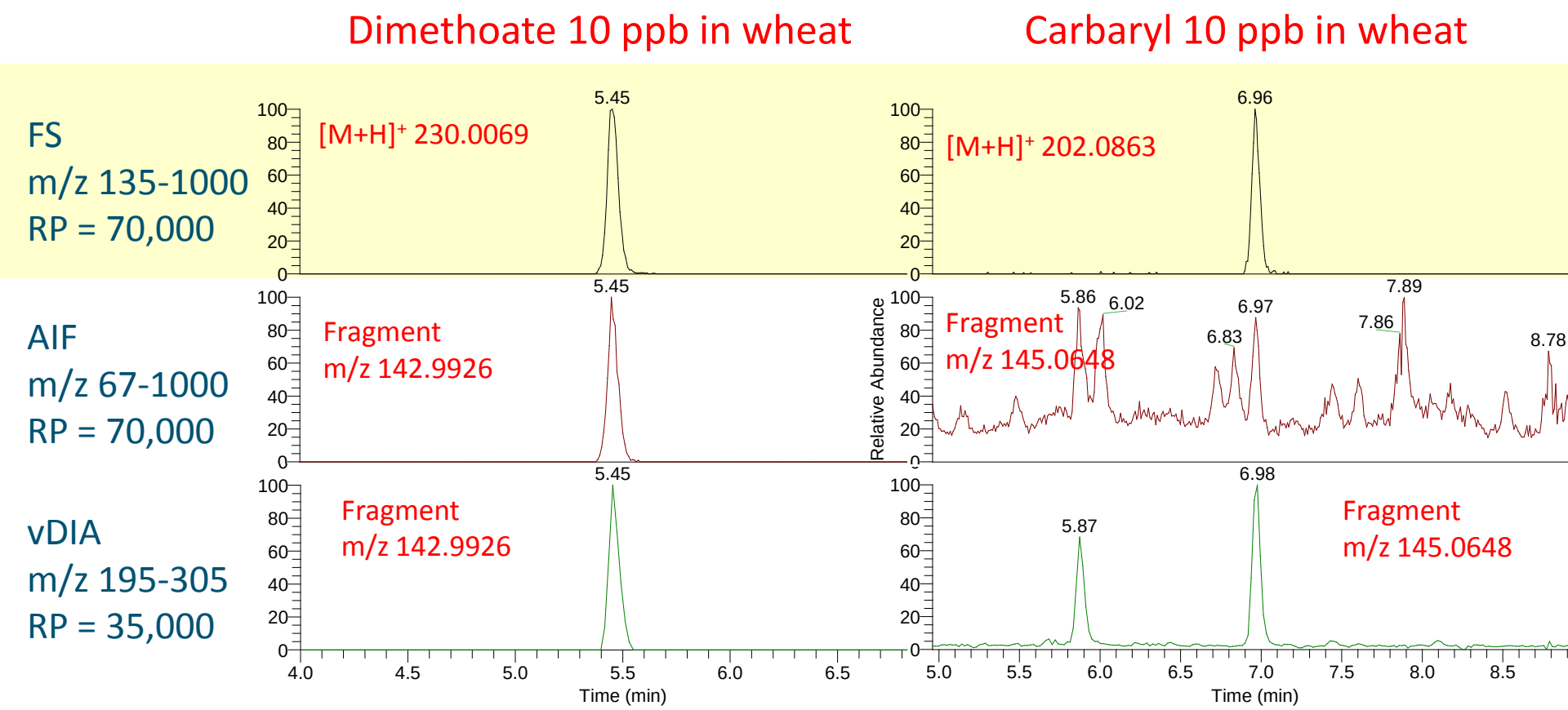


Combined Full scan + vDIA acquisition

FS: m/z 100-1000	ϟ: 100-200	ϟ: 200-300	ϟ: 300-400	ϟ: 300-400	ϟ: 500-1000	FS: m/z 100-1000



AIF vs. vDIA



⇒ vDIA preferred: improved selectivity & sensitivity + beneficial for identification

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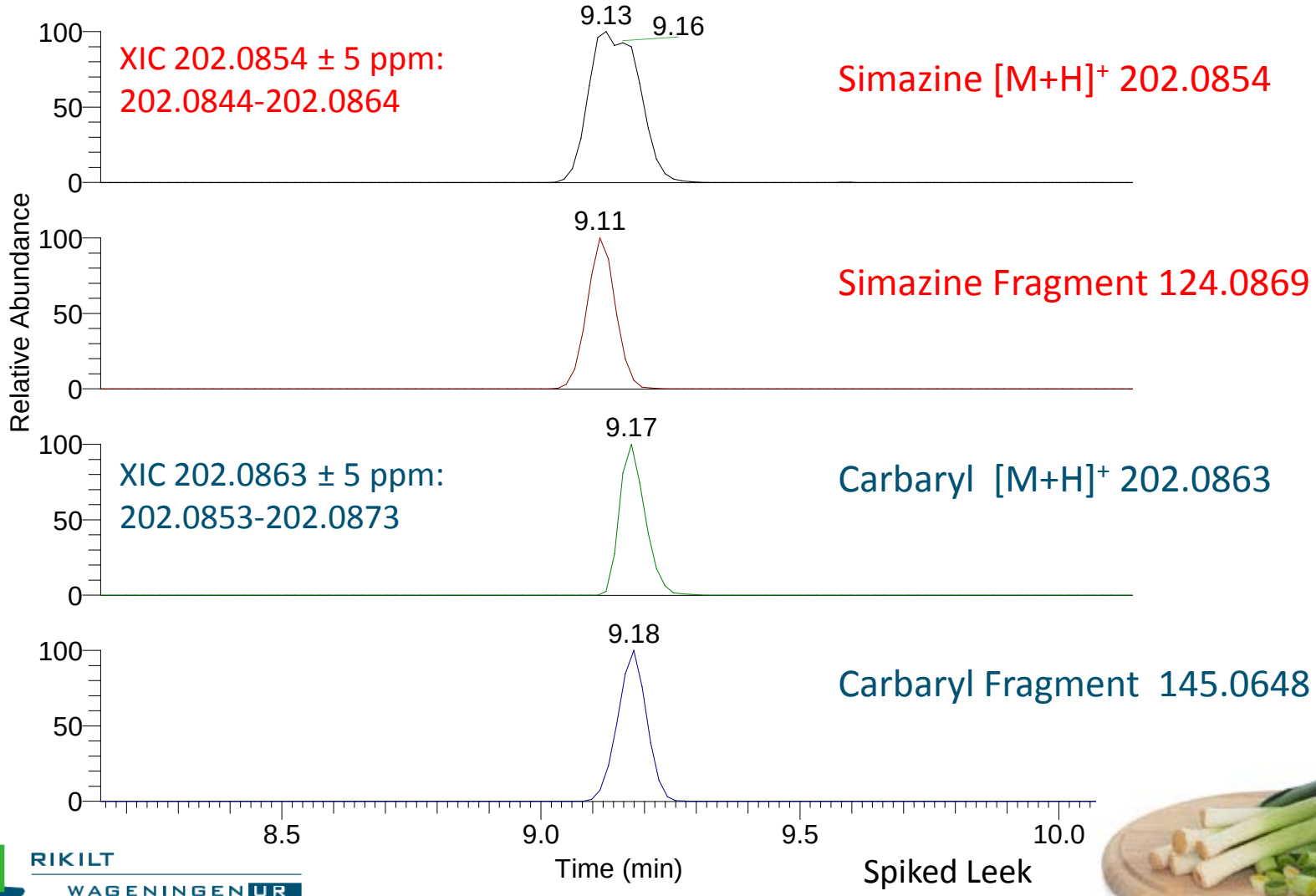
Dealing with exception 1: interfering analytes

Simazine $C_7H_{12}ClN_5$ and Carbaryl $C_{12}H_{11}NO_2$: difference $[M+H]^+$ = 0.9 mDa (4 ppm)



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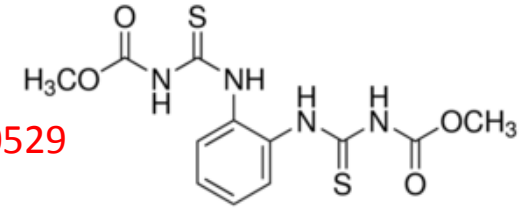
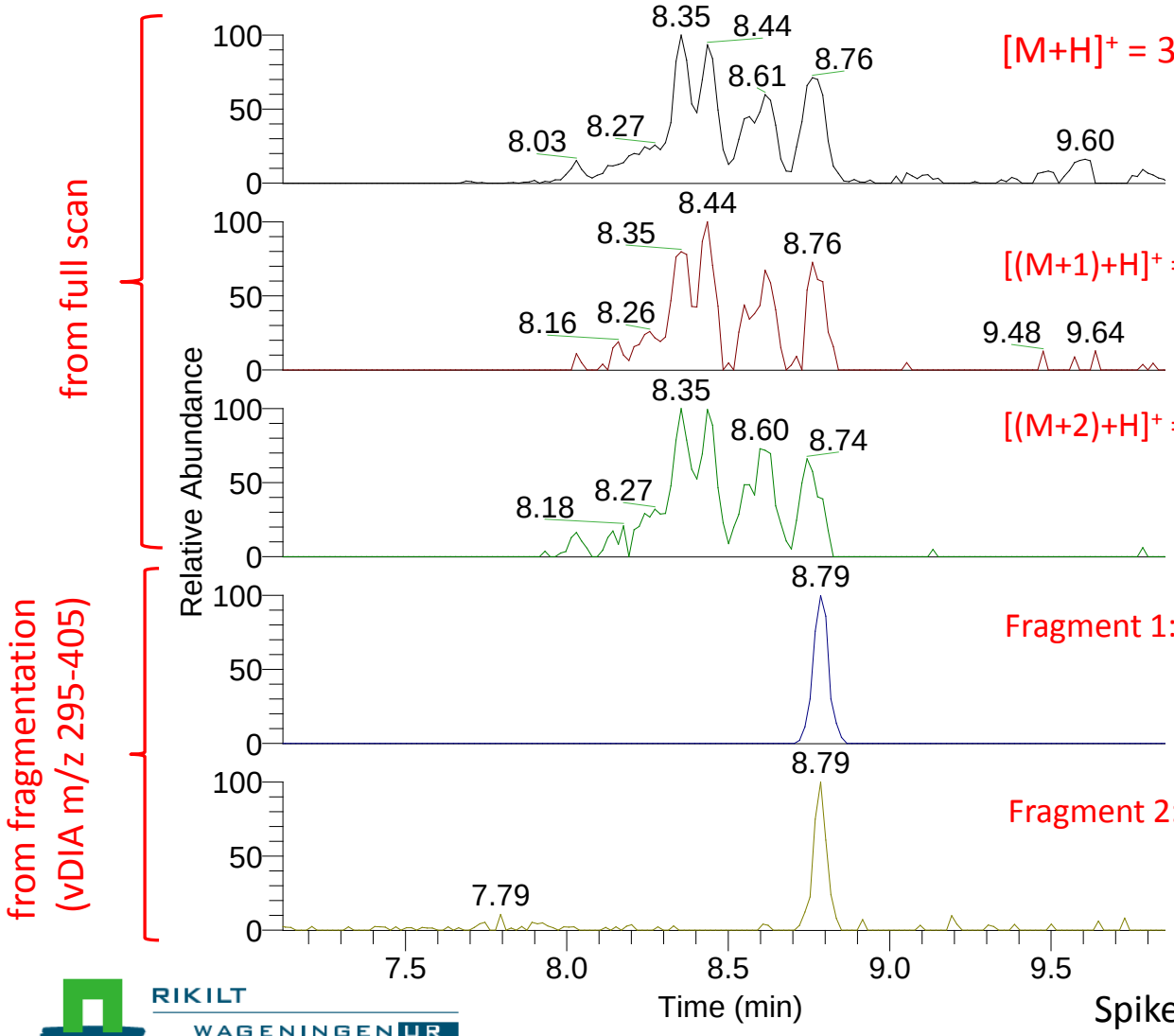
Spiked Leek
FS 70K, vDIA 35K

Dealing with exception 2: interfering matrix

Thiophanate-methyl in leek spiked @10 ppb



$C_{12}H_{14}N_4O_4S_2$



Spiked Leek
FS 70K, vDIA 35K

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Method used

Sample preparation: QuEChERS (AOAC version)

10 g homogenised sample + 10 mL Acetonitrile/1% HAc
Shake 30 min
4 g $MgSO_4$ + 1 g NaAc, centrifuge (no dSPE cleanup)
Dilute acetonitrile phase 1:1 with water

LC: Thermo Scientific™ Dionex™ UltiMate™ 3000 system:

Injection: 5 µL
Column: 100×3 mm ID, 3 µm Atlantis T3; T=35°C
Gradient: water/methanol, 2 mM NH_4HCOO
Flow: 0.30 mL/min

HRMS: Q Exactive MS with H-ESI-II source

Heated capillary: 320°C

FS+vDIA
Cycle time 978 ms

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

HCD: 30 and 80 NCE, ACG: 10^6

Data handling: Thermo Scientific™ TraceFinder™ 3.2 software

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Quantitative validation

Frequently found + others to widen range of phys/chem properties

Abamectin	Carbofuran	DNOC	Fluroxypyr	Mesotrione	Pirimicarb	Spiroxamine
Acephate	Carfentrazone-ethyl	Dodemorph	Flutolanil	Metalaxyl	Pirimiphos-methyl	Sulcotrione
Acequinocyl	Chlorantraniliprole	Dodine	Foramsulfuron	Metamitron	Prochloraz	Tebuconazole
Acetamiprid	Chlorbromuron	Emamectin B1a	Fosthiazate	Metazachlor	Profenofos	Tebufenpyrad
Aclonifen	Chloridazon	Epoxiconazole	Haloxyfop	Metconazole	Propamocarb	Tepraloxydim
Aldicarb	Clodinafop-propargyl	Ethirimol	Haloxyfop-etotyl	Methabenzthiazuron	Propiconazole	Terbuthylazine
Ametoctradin	Clofentezine	Ethoprophos	Hexythiazox	Methamidophos	Propyzamide	Terbutryn
Aminopyralid	Clomazone	Etoxazole	Imazalil	Methiocarb	Prosulfocarb	Tetraconazole
Amisulbrom	Clopyralid	Famoxadone	Imidacloprid	Methomyl	Pymetrozine	Thiabendazole
Asulam	Clothianidin	Fenamidone	Indoxacarb	Methoxyfenozide	Pyraclostrobin	Thiacloprid
Azadirachtin	Cyazofamid	Fenamiphos	Iodosulfuron-methyl	Metolachlor	Pyridaben	Thiamethoxam
Azamethiphos	Cybutryne	Fenhexamid	Ioxynil	Metoxuron	Pyridalyl	Thiophanate-methyl
Azoxystrobin	Cymoxanil	Fenoxaprop-p-ethyl	Iprovalicarb	Metrafenone	Pyridate	Tolylfluanid
Bendiocarb	Cyproconazole	Fenoxycarb	Isoproturon	Metribuzin	Pyrimethanil	Triallate
Bentazone	Cyprodinil	Fenpropidin	Isopyrazam	Metsulfuron-methyl	Pyriproxyfen	Tribenuron-methyl
Bifenazate	Cyromazine	Fenpropimorph	Isoxaben	Mevinphos	Pyroxsulam	Triclopyr
Bifenthrin	Cythioate	Fipronil	Isoxaflutole	Myclobutanil	Quinmerac	Trifloxystrobin
Bixafen	D 2 4-	Flonicamid	Kresoxim-methyl	Nicosulfuron	Quinoclamine	Triflumizole
Boscalid	Dichlofluanid	Florasulam	Lenacil	Omethoate	Quinoxyfen	Triflumuron
Brodifacoum	Difenoconazole	Fluazinam	Linuron	Oxamyl	Quizalofop-ethyl	Triflusulfuron-methyl
Bromadiolone	Diflubenzuron	Flubendiamide	Lufenuron	Oxydemeton-methyl	Rimsulfuron	Triforine
Bromoxynil	Diflufenican	Flucycloxuron	Malathion	Paclobutrazol	Silthiofam	Trinexapac-ethyl
Bupirimate	Dimethenamid	Fludioxonil	Mandipropamid	Penconazole	Simazine	
Buprofezin	Dimethoate	Flufenacet	MCPA	Pencycuron	Spinosyn-A	
Carbaryl	Dimethomorph	Flufenoxuron	MCPP	Phenmedipham	Spinosyn-D	
Carbendazim	Dinoterb	Fluopicolide	Mepanipyrim	Picoxystrobin	Spirodiclofen	
Carbetamide	Diuron	Fluoxastrobin	Mesosulfuron-methyl	Pinoxaden	Spiromesifen	

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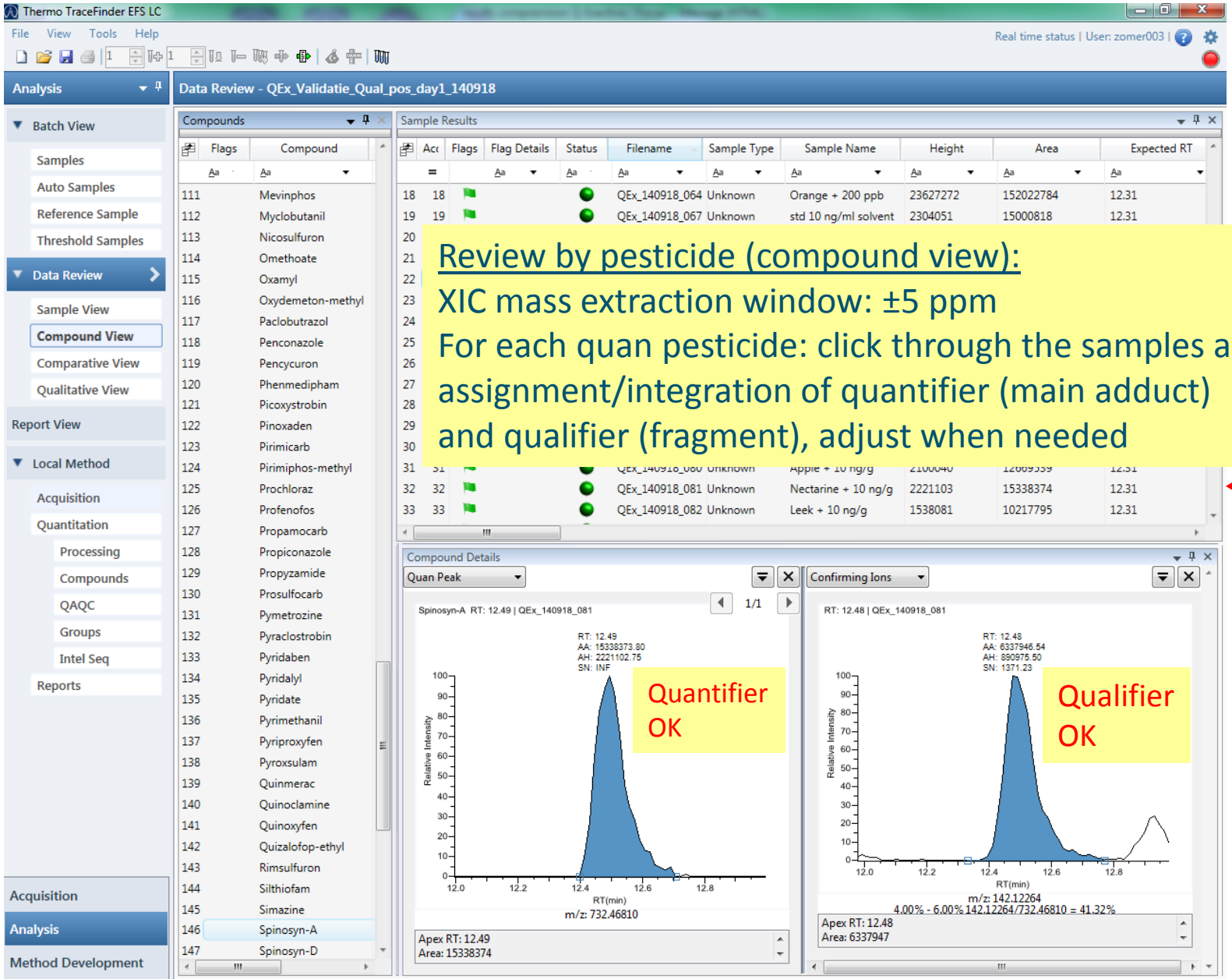
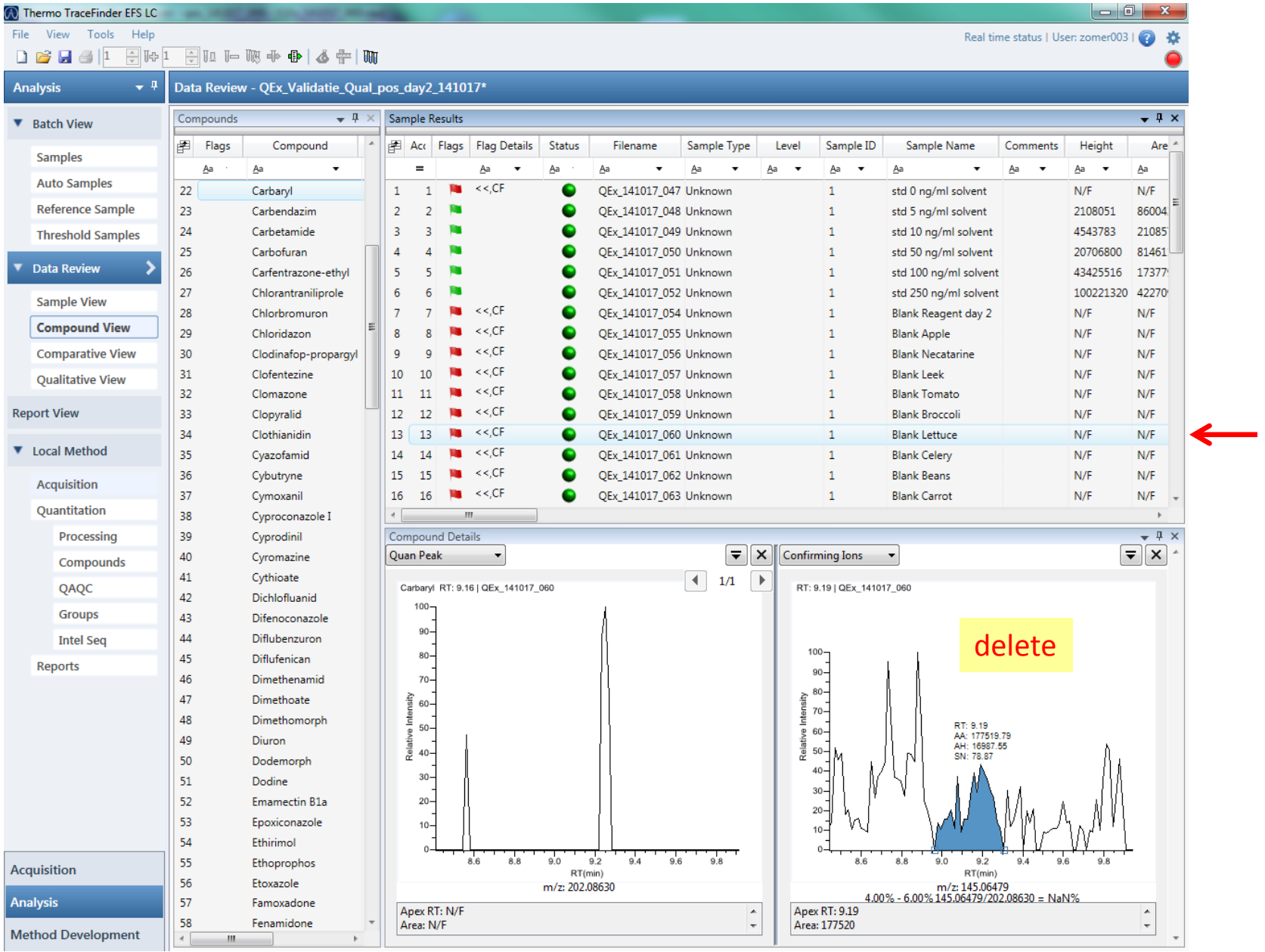
in red = ESI^-

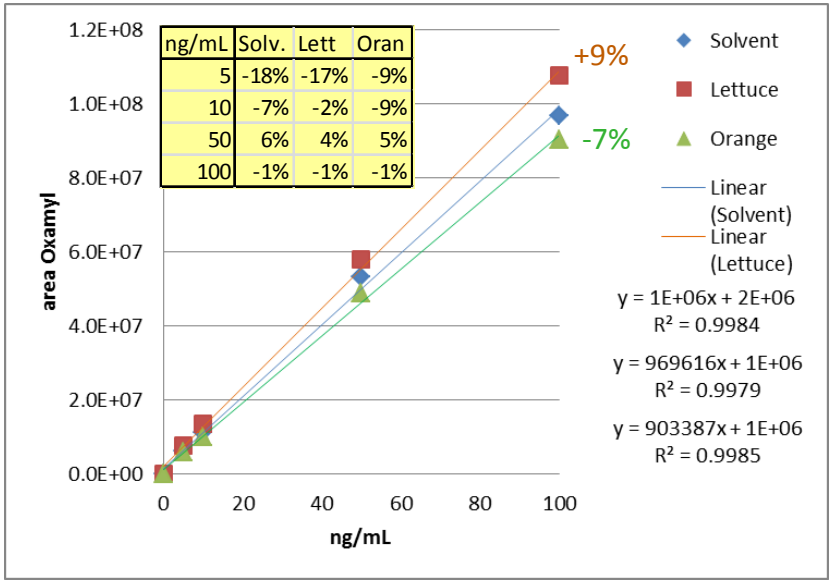
Quantitative data review

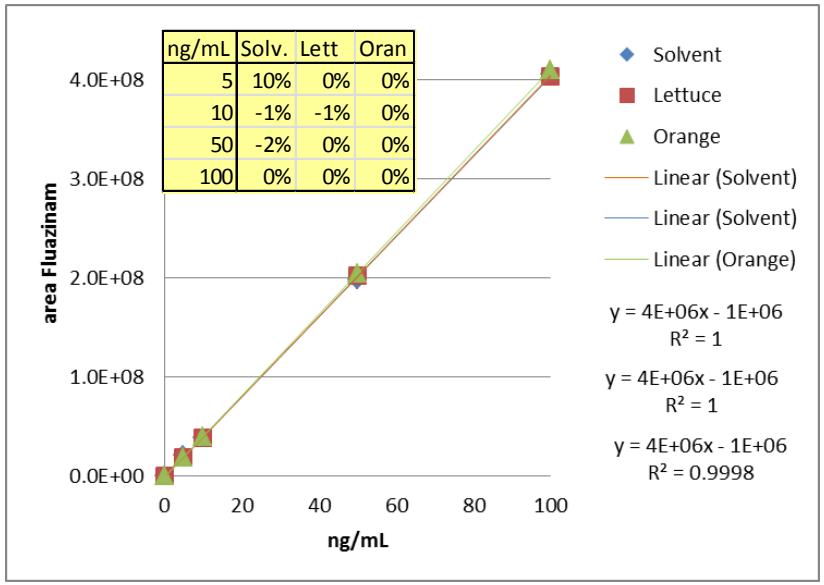


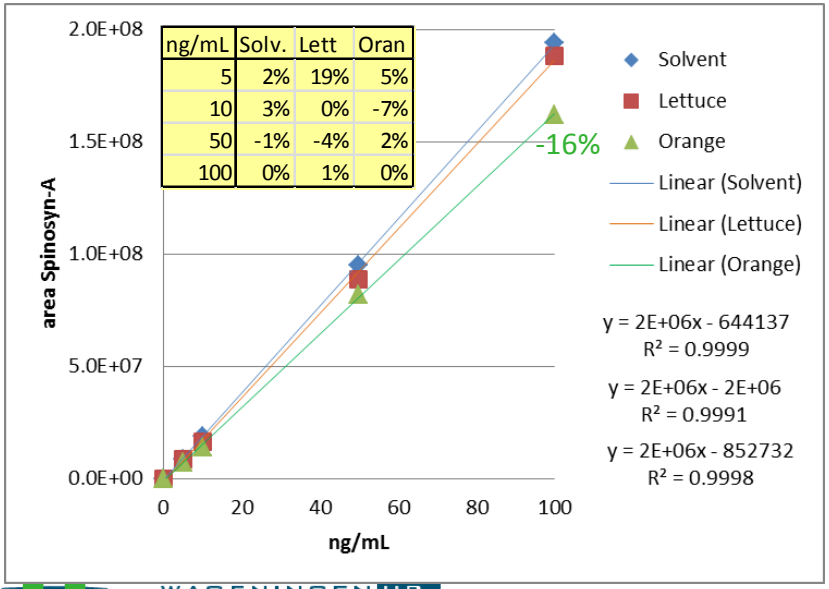
Quantitative data review

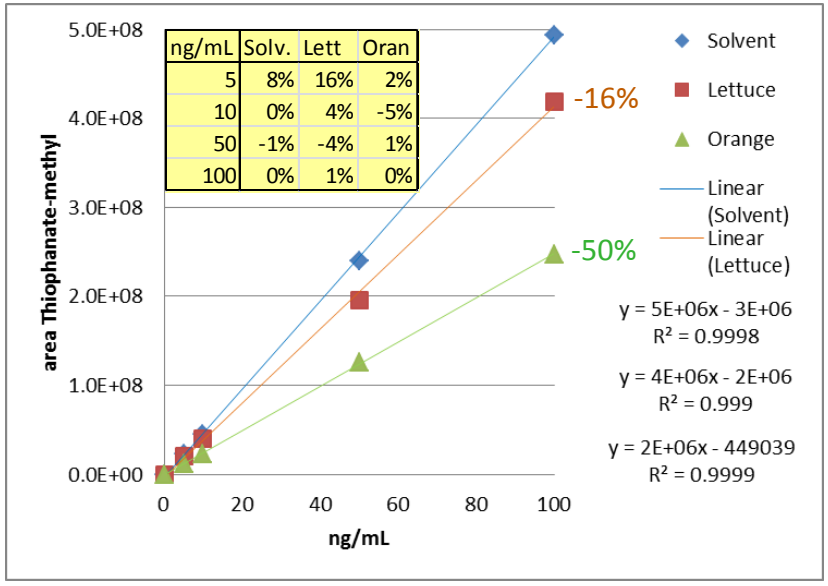


Verification of linearity

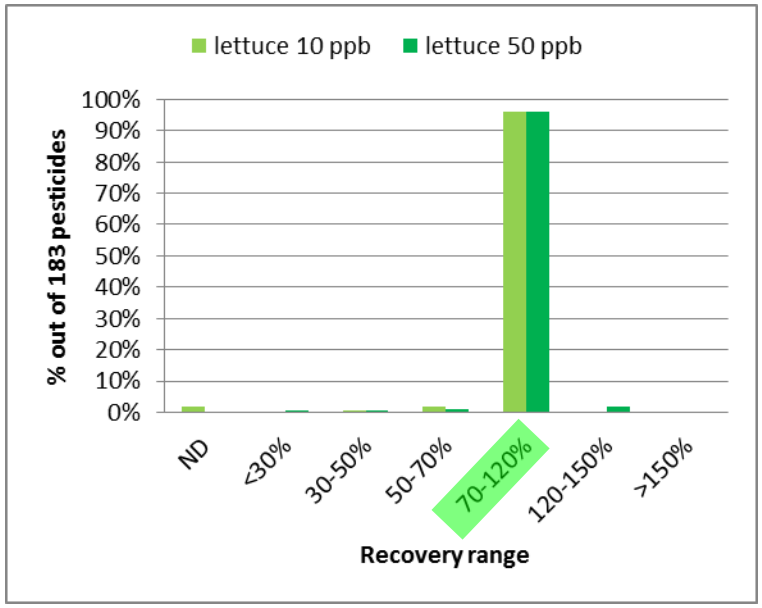


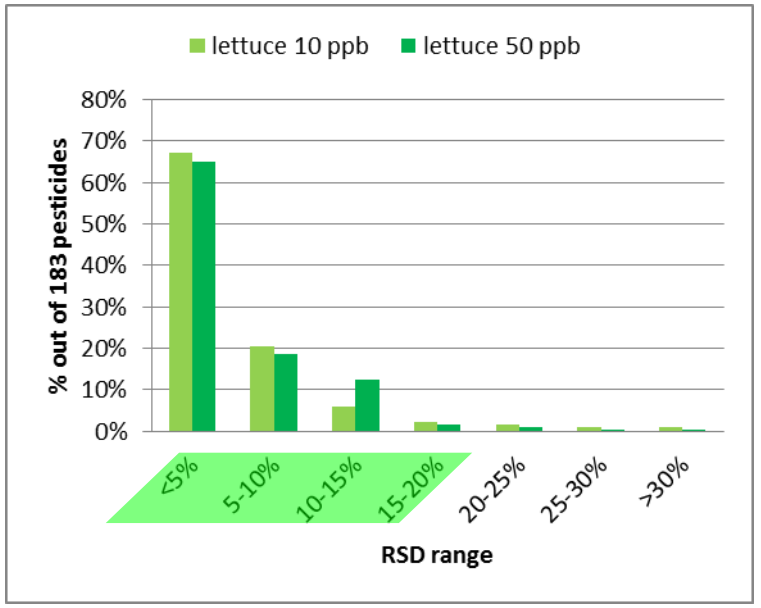


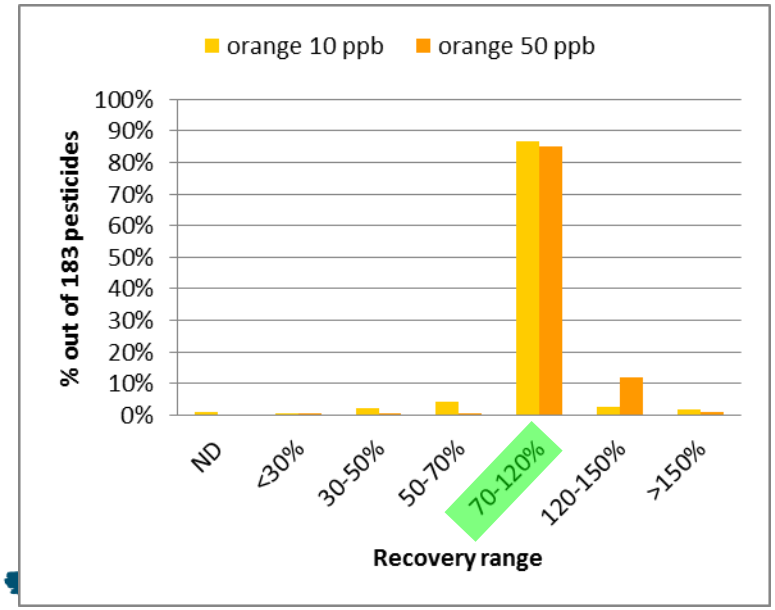


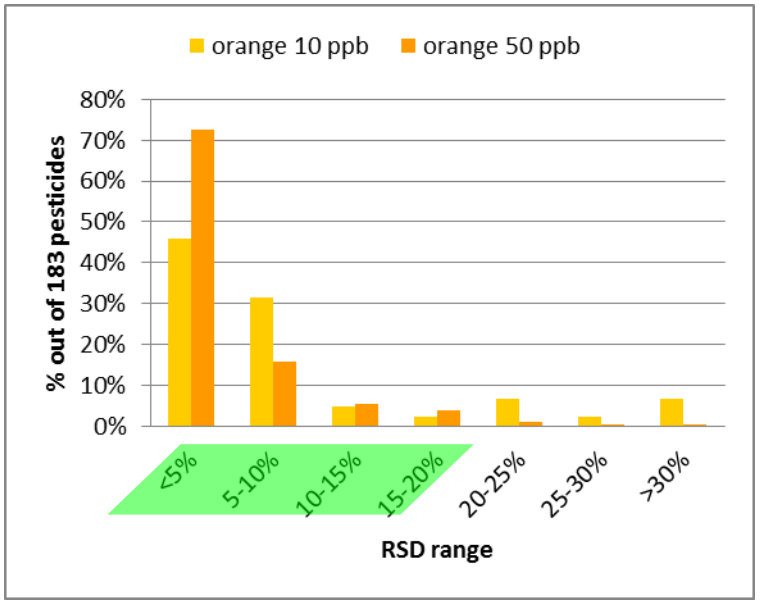


Recoveries and RSDs









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Guidance document: EU SANCO/12571/2013

Chromatography:

$t_r > 2t_0$; retention time deviation < ±0.2 min

Mass spectrometry

Table 4. Identification criteria for different MS techniques

MS mode:	Single-stage MS (unit mass resolution)	Single-stage MS (high resolution/high mass accuracy)	MS/MS
Typical systems (examples):	Quadrupole, ion trap, time-of-flight (TOF)	TOF, Orbitrap, FTMS, magnetic sector	Triple quadrupole, ion trap, hybrid MS (e.g. Q-TOF, Q-trap)
Acquisition mode:	Full scan, Limited *m/z* range, Selected ion monitoring (SIM)	Full scan, Limited *m/z* range, Selected ion monitoring (SIM)	Selected/multiple reaction monitoring (SRM/MRM),full scan product-ion spectra
Requirements for identification:	≥ 3 diagnostic ions, preferably including the (quasi) molecular ion	≥ 2 diagnostic ions, preferably including the (quasi) molecular ion; mass accuracy < 5 ppm; at least one fragment ion	≥ 2 product ions
	Ion ratio(s): according to Table 5	→ **±30% (relative)**	

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Identification

EU SANCO/12571/2013 under revision.....
Table below: under construction/discussion.....

Table 4. Identification requirements for different MS techniques[1)]

MS detector / characteristics	Typical systems (examples)	Acquisition	Requirements for identification	
			minimum number of ions	other
Unit mass resolution	quadrupole, ion trap, TOF	full scan, limited m/z range, SIM	3 ions	S/N ≥ 3 Analyte peaks in the extracted ion chromatograms must coincide. Ion ratio within **±30% (relative)** of average of calibration standards from same sequence
MS/MS	triple quadrupole, ion trap, Q-trap, Q-TOF, Q-Orbitrap	selected or multiple reaction monitoring (SRM, MRM), mass resolution for precursor-ion isolation equal to or better than unit mass resolution	2 product ions	
Accurate mass measurement	High resolution MS: (Q-)TOF (Q-)Orbitrap FT-ICR-MS sector MS	full scan, limited m/z range, SIM, fragmentation with or without precursor-ion selection, or combinations thereof	2 ions with mass accuracy ≤ 5 ppm[2,3)]	
		combined single MS and MS/MS with mass resolution for precursor-ion isolation equal to or better than unit mass resolution	2 ions: 1 molecular ion or adduct ion with mass acc. ≤ 5 ppm 1 MS/MS product ion	

[1)] For definition of terms relating to mass spectrometry see Murray et al. (2013) Pure Appl. Chem., 85:1515–1609
[2)] preferably including the molecular ion or adduct ion ($[M-H]^-$, $[M+H]^+$, $[M+NH_4]^+$, $[M+Na]^+$, etc)
[3)] including at least one fragment or product ion

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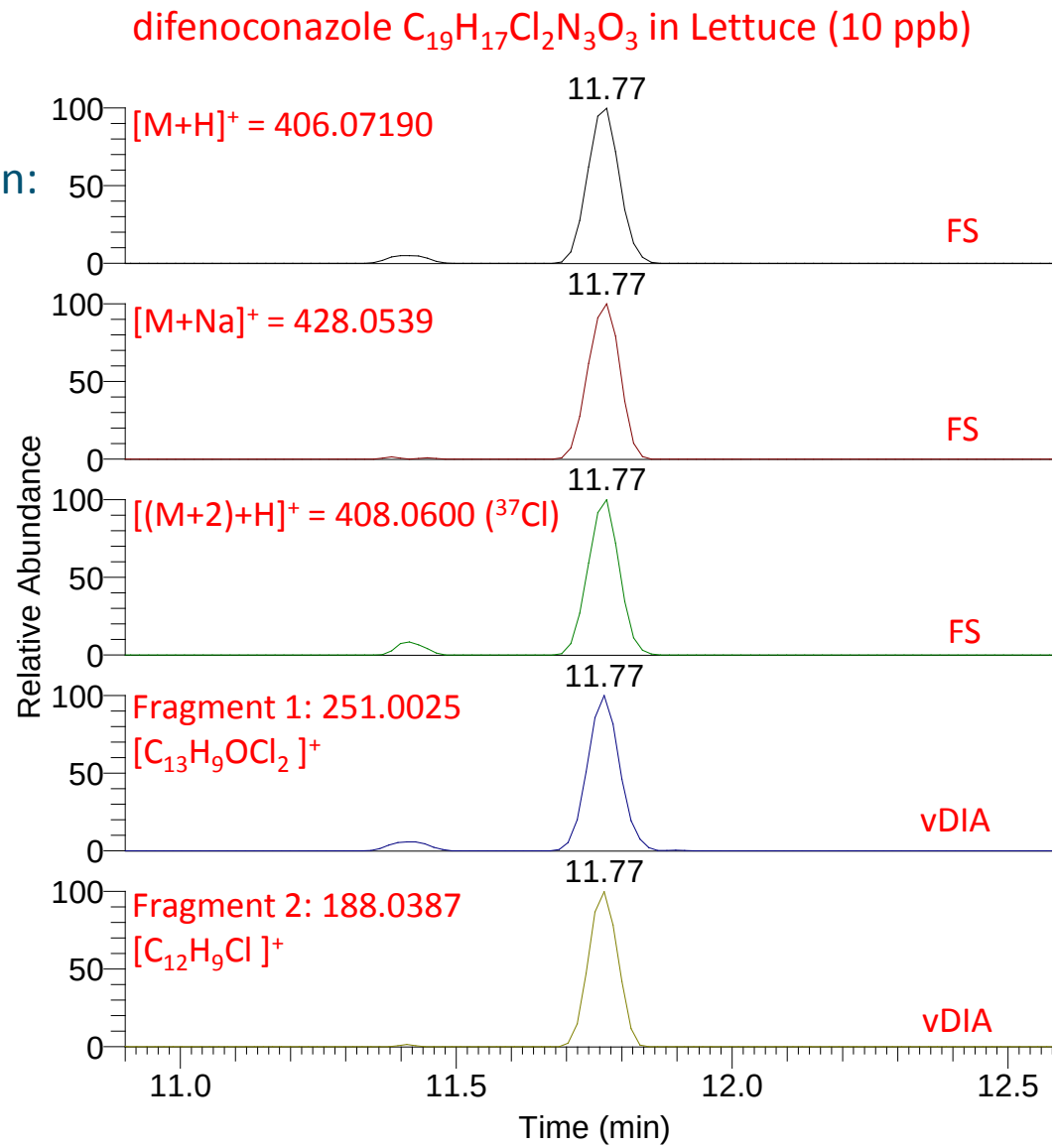
Ion ratio

Full scan acquisition
with/without fragmentation:
⇒ Various options for ratio determination:

$$\frac{\text{area F2}}{\text{area F1}} \qquad \frac{\text{area F1}}{\text{area [M+Na]}^+}$$

$$\frac{\text{area F1}}{\text{area [M+H]}^+}$$

$$\frac{\text{area F2}}{\text{area [M+H]}^+} \qquad \frac{\text{area F1}}{\text{area [(M+2)+H]}^+}$$



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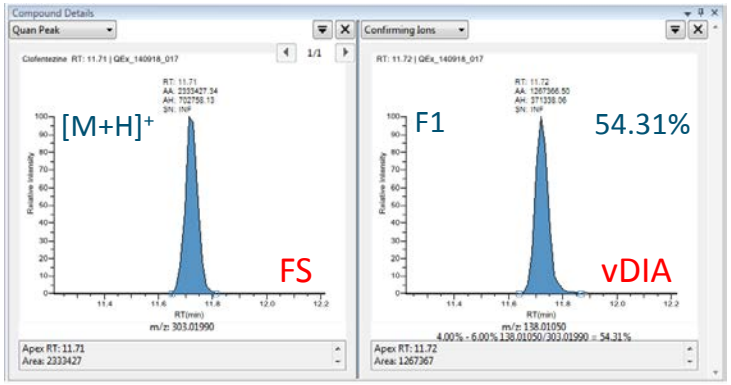
Identity confirmation

Examples: isopyrazam and clofentezine

Solvent standards isopyrazam	
ng/mL	ion ratio (%)
5	5.08
10	5.40
50	5.10
100	4.68
250	5.30
Reference ion ratio	5.11
tolerance -30%	**3.58**
tolerance +30%	**6.65**

Solvent standards clofentezine	
ng/mL	ion ratio (%)
5	54.31
10	54.62
50	55.79
100	46.78
250	48.00
Reference ion ratio	51.90
tolerance -30%	**36.33**
tolerance +30%	**67.47**



	Lettuce	Orange
µg/kg	ion ratio (%)	
10	**4.62**	**5.53**
50	**4.95**	**4.88**
200	**4.97**	**3.87**

	Lettuce	Orange
µg/kg	ion ratio (%)	
10	**53.28**	**50.05**
50	**52.16**	**50.08**
200	**49.77**	**51.10**

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Outcome Quantitative Method Validation

Selectivity: no significant response in blank lettuce and orange

Adequate linearity in most cases

Recovery and RSD_r meet requirements for majority of pesticides

exceptions included: acequinocyl, aminopyralid, clopyralid, quinmerac, fluroxypyr, triclopyr

Quantitative performance and identification capabilities
similar to triple quadrupole MS/MS / fit-for-purpose

=> Q Exactive suitable to replace triple quad

Outline

Introduction pesticide residue analysis

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Qualitative screening

What about GC?

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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

Various options:

TraceFinder SW (screening module), Thermo Scientific™ ToxFinder™ ID software, ...

Here: quan module (but without any quan)

Default settings for pesticide detection:

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

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

Data Review - QEx_Validatie_Qual_pos_day1_140918*

Samples

	Acq	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
☑			Prosulfocarb	153521	488041	12.13	12.17
☑			Terbuthylazine	49706	111306	10.64	10.67

<u>Review by sample (sample view):</u>

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 | 12.17 | 1/1 | Confirming Ions

Prosulfocarb RT: 12.17 | QEx_140918_073

RT: 12.17
AA: 488041.25
AH: 153520.84
SN: INF

Relative Intensity

RT(min)

m/z: 252.14170

Apex RT: 12.17
Area: 488041

Prosulfocarb?

⇒ Reject

RT: 12.31 | QEx_140918_073

RT: 12.31
AA: 11641639.72
AH: 2140913.01
SN: 1143.84

X

Relative Intensity

RT(min)

m/z: 91.05423

4.00% - 6.00% 91.05423/252.14170 = 2385.38%

Apex RT: 12.31
Area: 11641640

Screening: data review

Thermo TraceFinder EFS LC

File View Tools Help

Real time status | User: zomer003 |

Analysis

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Acquisition
Analysis
Method Development

Data Review - QEx_Validatie_Qual_pos_day1_140918*

Samples

	Acq	Flags	Status	Filename	Sample Type	Sample Name	Level
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	
25	25			QEx_140918_074	Unknown	Blank Broccoli	
26	26			QEx_140918_075	Unknown	Blank Celery	
27	27			QEx_140918_076	Unknown	Blank Fr. Beans	
28	28			QEx_140918_077	Unknown	Blank Carrot	
29	29			QEx_140918_078	Unknown	Blank Grape	
30	30			QEx_140918_079	Unknown	std 10 ng/ml solvent	
31	31			QEx_140918_080	Unknown	Apple + 10 ng/g	
32	32			QEx_140918_081	Unknown	Nectarine + 10 ng/g	
33	33			QEx_140918_082	Unknown	Leek + 10 ng/g	
34	34			QEx_140918_083	Unknown	Tomato + 10 ng/g	
35	35			QEx_140918_084	Unknown	Broccoli + 10 ng/g	
36	36			QEx_140918_085	Unknown	Celery + 10 ng/g	

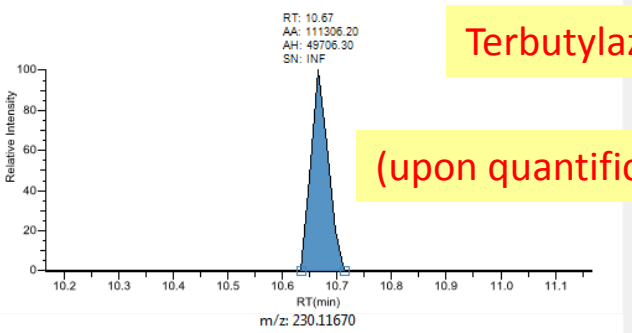
Compound Results

Active	Flags	Flag Details	Compound	Height	Area	Expected RT	Ac
☑			Prosulfocarb	153521	488041	12.13	12
☑			Terbuthylazine	49706	111306	10.64	10

Compound Details

Quan Peak — 1/1

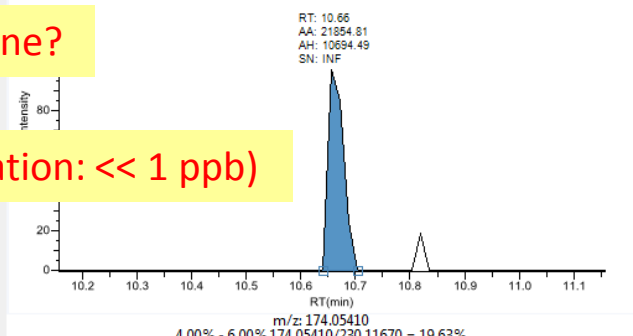
Terbuthylazine RT: 10.67 | QEx_140918_073



Apex RT: 10.67
Area: 111306

Confirming Ions

RT: 10.66 | QEx_140918_073



Apex RT: 10.66
Area: 21855

Terbutylazine?

(upon quantification: << 1 ppb)

Screening method: validation

Guidance document: EU SANCO/12571/2013*

Initial validation:
Required for each individual pesticide, for each commodity group
Establish SDL: screening detection limit = lowest concentration for which it has been demonstrated that a pesticide can be detected in ≥95% of the samples

≥20 samples (m matrices in n-fold, with n≥2) reflecting scope of laboratory
Spike each sample at anticipated SDL
Include a blank for each matrix

Supplemented by on-going validation (QC sample added to routine analysis):
Cover additional matrices
Demonstrate performance over time/routine conditions

Criteria:
False negative rate ≤ 5%
False positive rate: no requirement
(any detect triggers identification/quantification/confirmatory analysis)

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* http://ec.europa.eu/food/plant/pesticides/guidance_documents/docs/qualcontrol_en.pdf

Screening method: validation

Validation set:

11 matrices:

Non-fortified, 3 fortifications: 0.01, 0.05 and 0.20 mg/kg

Test set for fortification: 183 pesticides

Analysed on 2 different days (4 weeks in between) => 22 samples

Validation parameters:

Count # pesticides found in each sample

⇒ detection rate / false negatives

⇒ blank samples: false positives

Screening method: validation

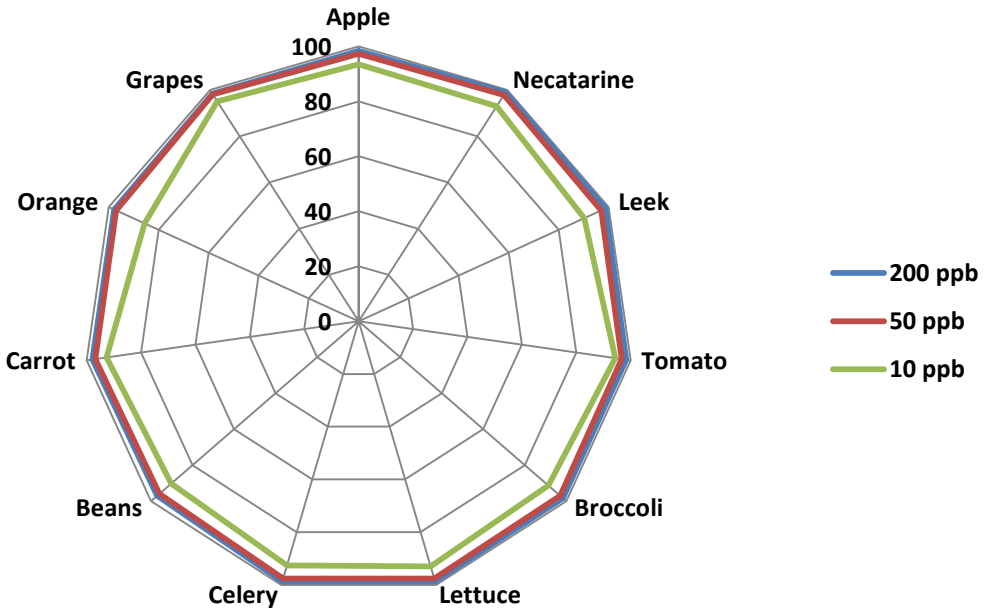
Overall detections in spiked samples (4026 pesticide/matrix combinations per level):

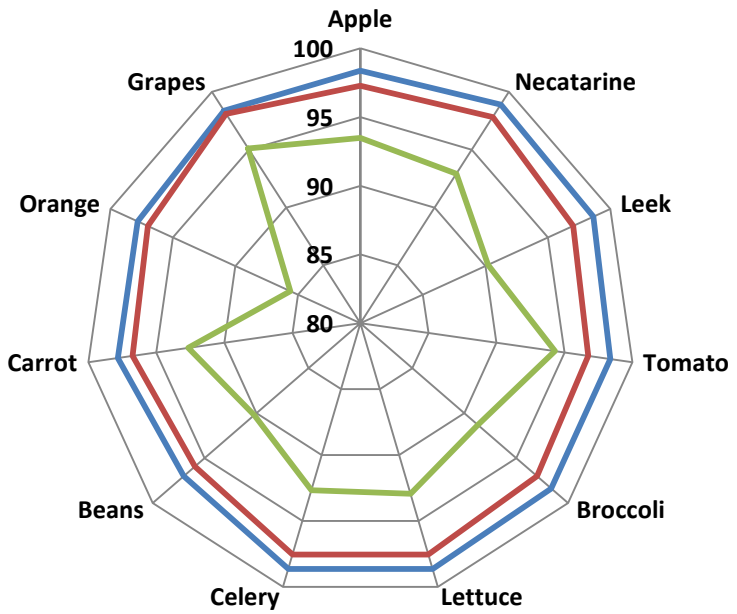
0.01 mg/kg: 91.9%

0.05 mg/kg: 97.2%

0.20 mg/kg: 98.3%

Detection rates in % of spiked pesticides / sample:





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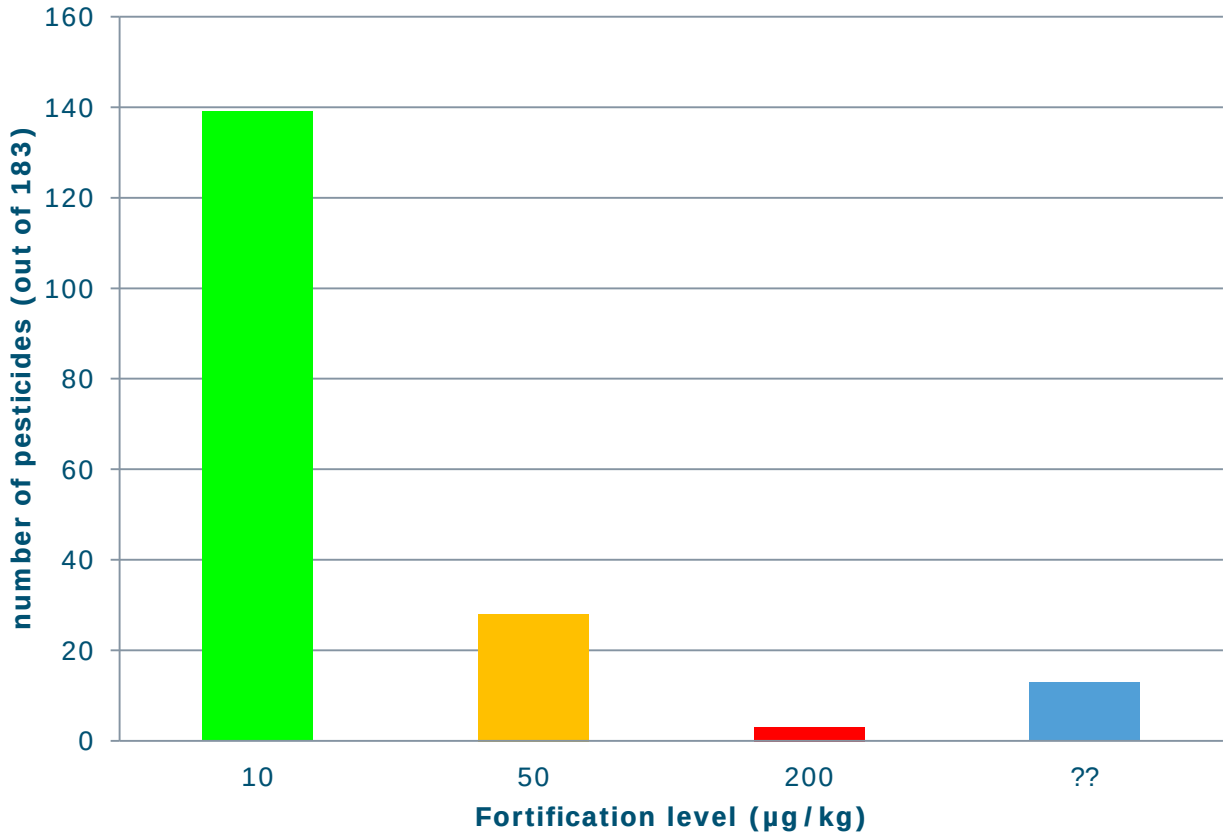
Screening method: validation

Screening detection limits:



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Outline

Introduction pesticide residue analysis

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What about GC?

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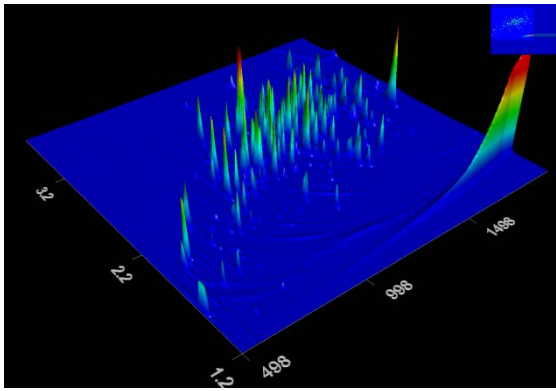
GC-full scan MS

Required for further coverage + highly useful complementary technique



> 1990s:	GC-EI-single quad / GC-ion trap / TOF	
> mid 2000s	GCxGC-EI-hs-TOF-MS	
> mid 2000s	GC-EI-hr-TOF-MS (RP 5-10K)	
> 2010	GC-EI-hr-TOF-MS and GC-EI-Q-TOF-MS	(RP 15-25K)
	GC-APCI-Q-TOF-MS	(RP > 20K)

APCI:
- con: can't use EI-MS libraries
- pro: molecular ion or adduct ion
- generation of fragment ions, same approach as in LC-ESI-HRMS

EI:
- pro: simple, one acquisition event to get multiple accurate mass ions
  - use of existing EI-MS libraries 100thousands of compounds
- con: molecular ion not always present

> 2015 GC-EI-Orbitrap MS (RP >60K @ m/z 200)

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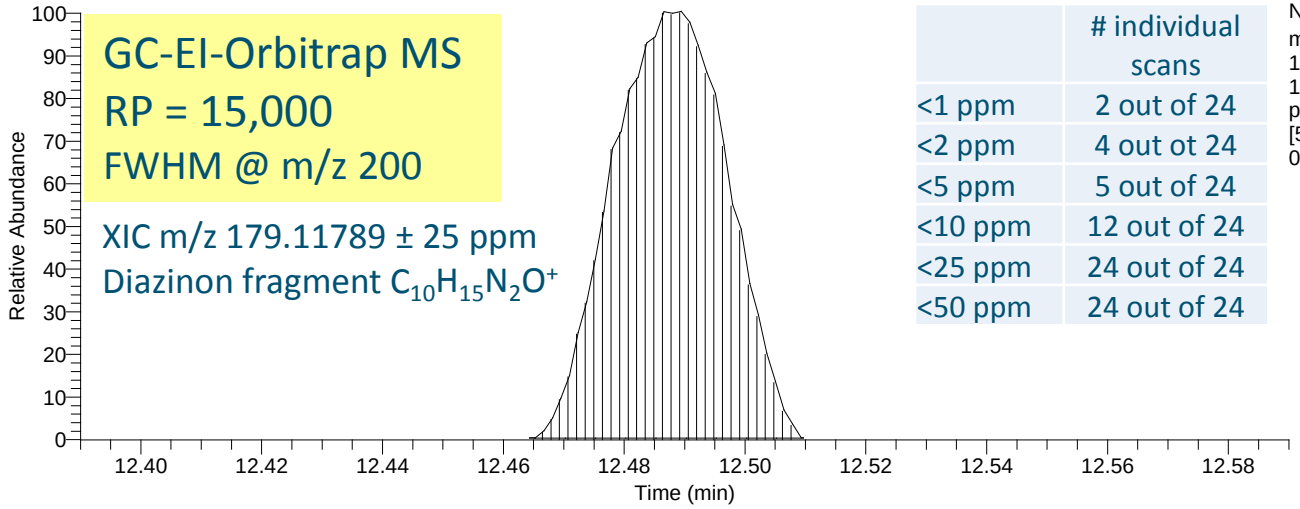
Mass accuracy in complex matrix RP 15,000

F:\GC-Orbitrap\...\02April15_15K_020 04/03/15 01:12:57 Spices 10

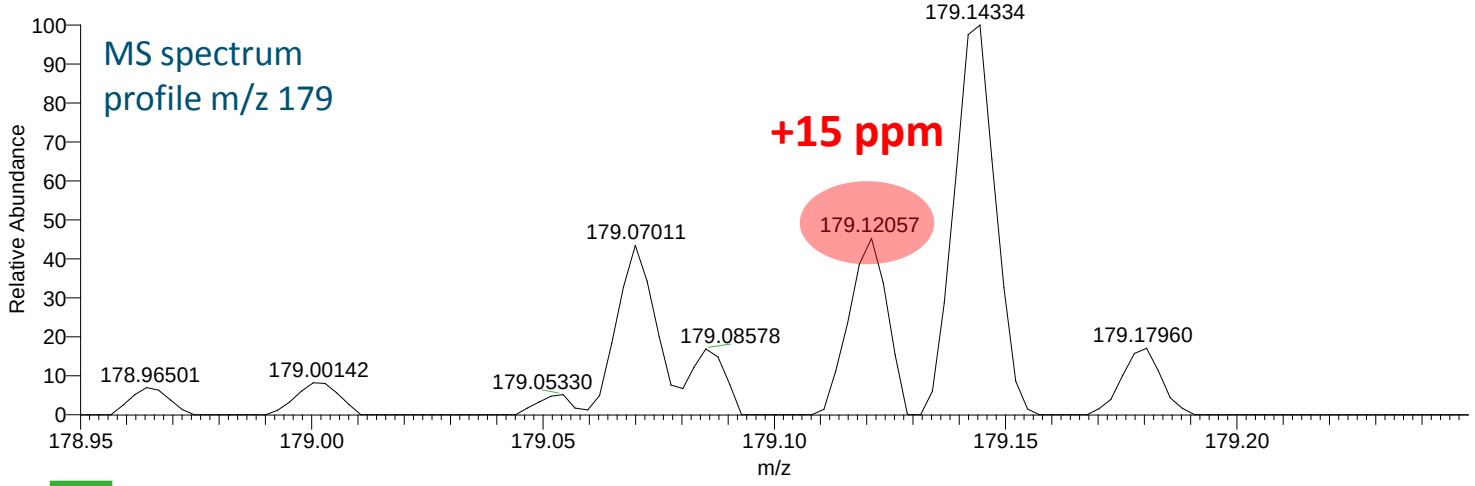
RT: 12.39 - 12.59 SM: 7B



	# individual scans
<1 ppm	2 out of 24
<2 ppm	4 out ot 24
<5 ppm	5 out of 24
<10 ppm	12 out of 24
<25 ppm	24 out of 24
<50 ppm	24 out of 24

NL: 3.84E5
m/z= 179.11341-179.12237 F: FTMS + p EI Full ms [50.00-500.00] MS 02April15_15K_020

02April15_15K_020 #6616 RT: 12.49 AV: 1 NL: 9.00E5
T: FTMS + p EI Full lock ms [50.00-500.00]



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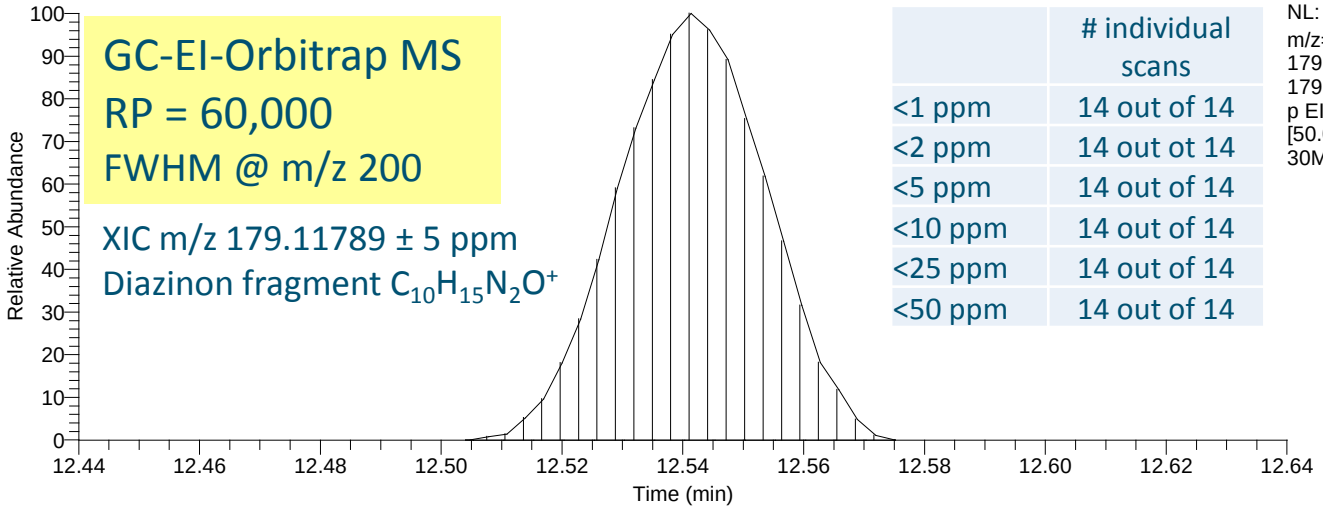
Mass accuracy in complex matrix RP 60,000

F:\GC-Orbitrap\...\30March15_60K_020 03/31/15 04:49:47 Spices 10

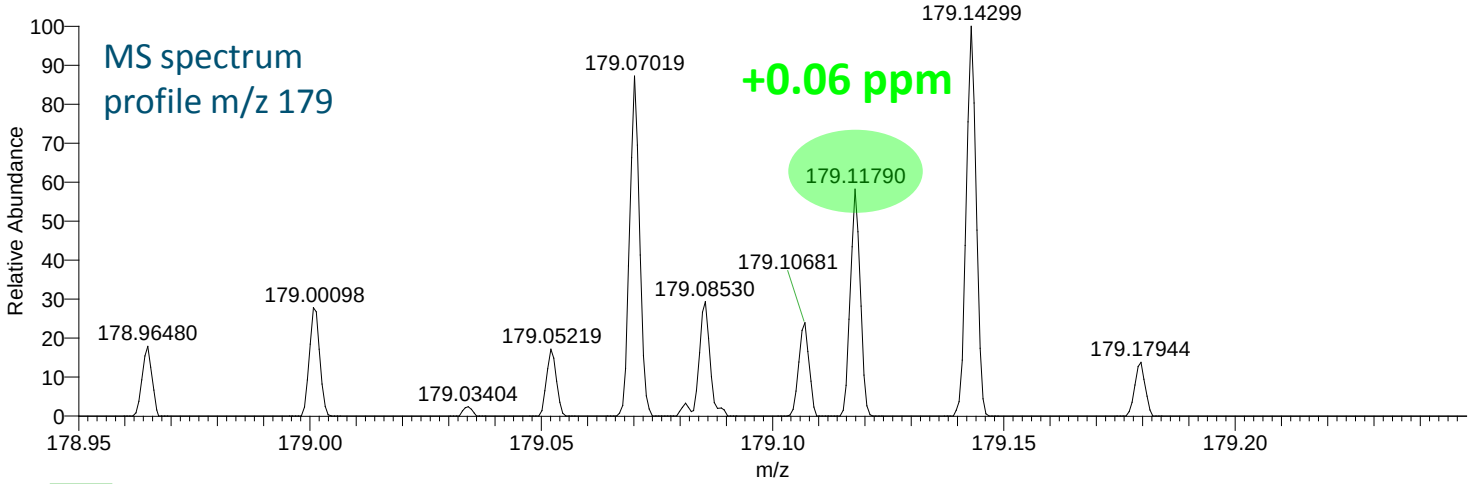
RT: 12.44 - 12.64 SM: 7B



	# individual scans
<1 ppm	14 out of 14
<2 ppm	14 out ot 14
<5 ppm	14 out of 14
<10 ppm	14 out of 14
<25 ppm	14 out of 14
<50 ppm	14 out of 14

NL: 3.25E5
m/z= 179.11341-179.12237 F: FTMS + p EI Full ms [50.00-500.00] MS 30March15_60K_020

30March15_60K_020 #3128 RT: 12.54 AV: 1 NL: 5.70E5
T: FTMS + p EI Full lock ms [50.00-500.00]



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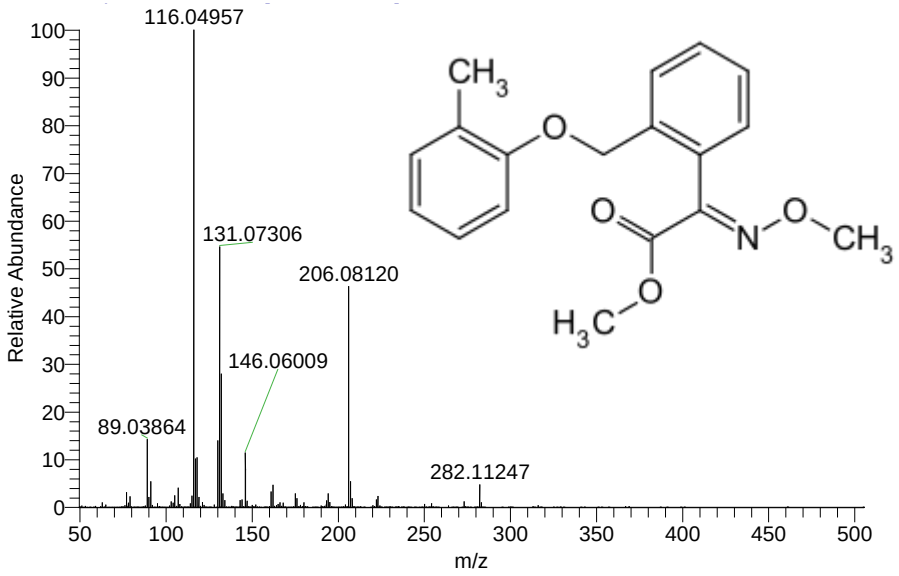
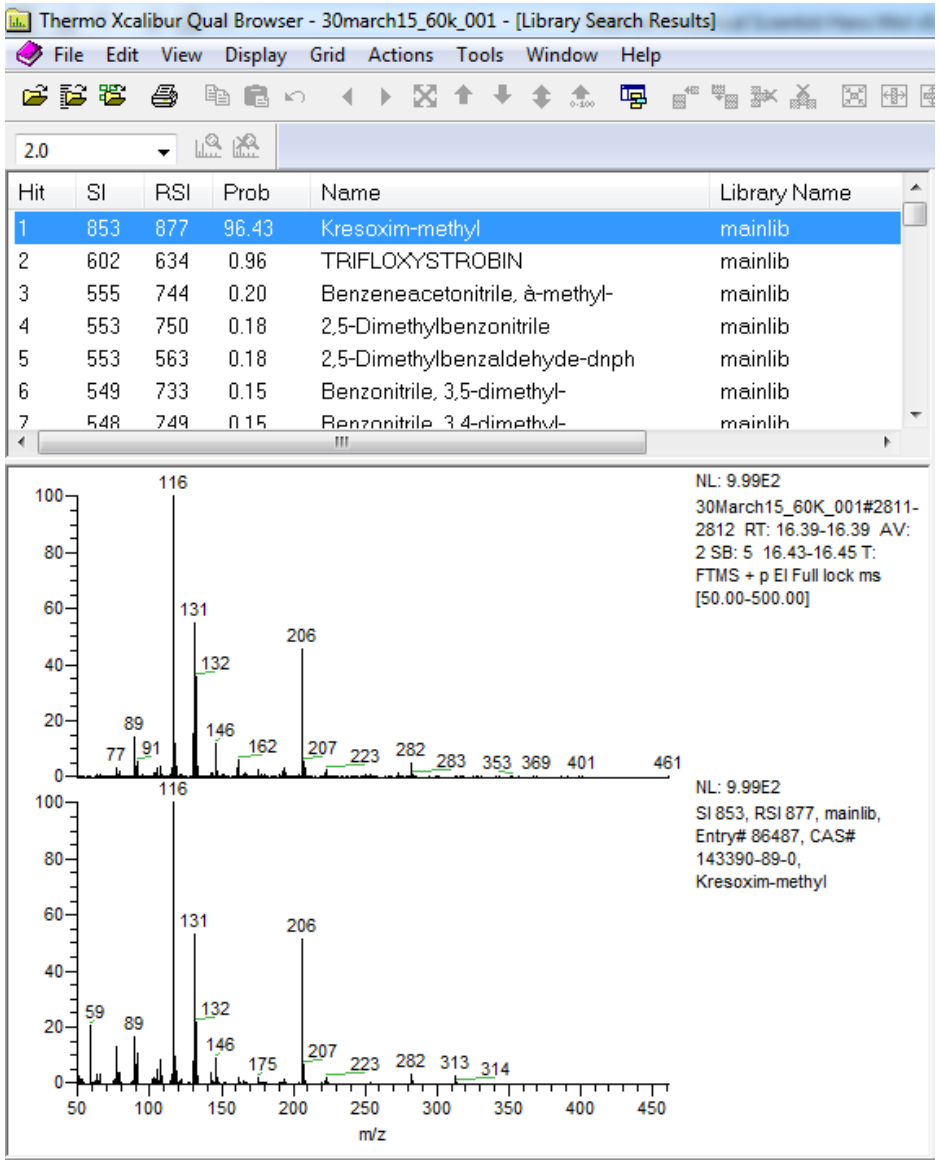
GC-Orbitrap MS: example kresoxim-methyl





Exact mass most abundant fragment ions:

$C_{11}H_{12}NO_3^+$ 206.08117

$C_9H_9N^+$ 131.07295

$C_8H_6N^+$ 116.04948

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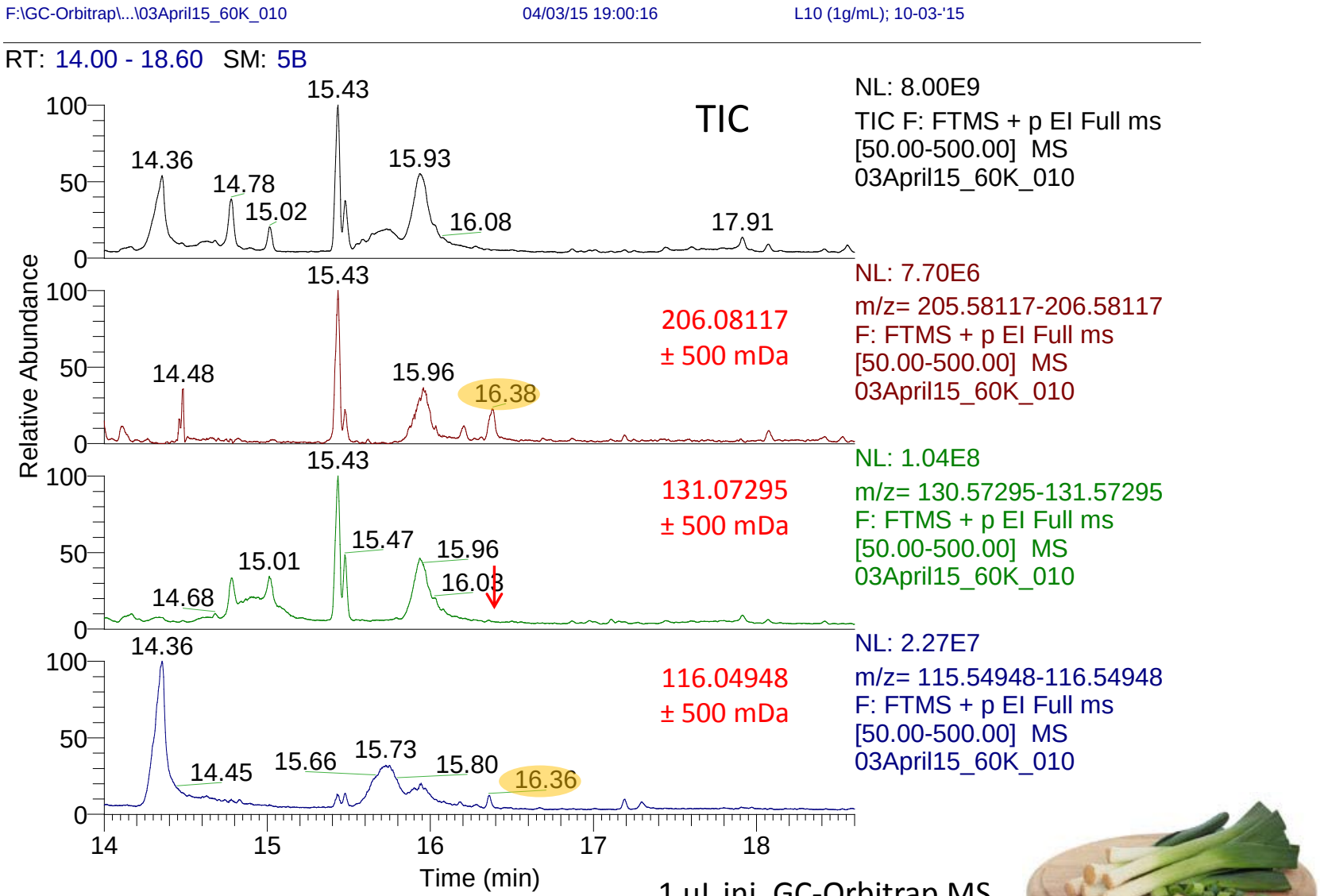
Simulated unit resolution MS: MEW: ± 500 mDa



1 µL inj. GC-Orbitrap MS
Leek spiked @ 10 ppb,
Full scan m/z 50-500; Res = 60,000

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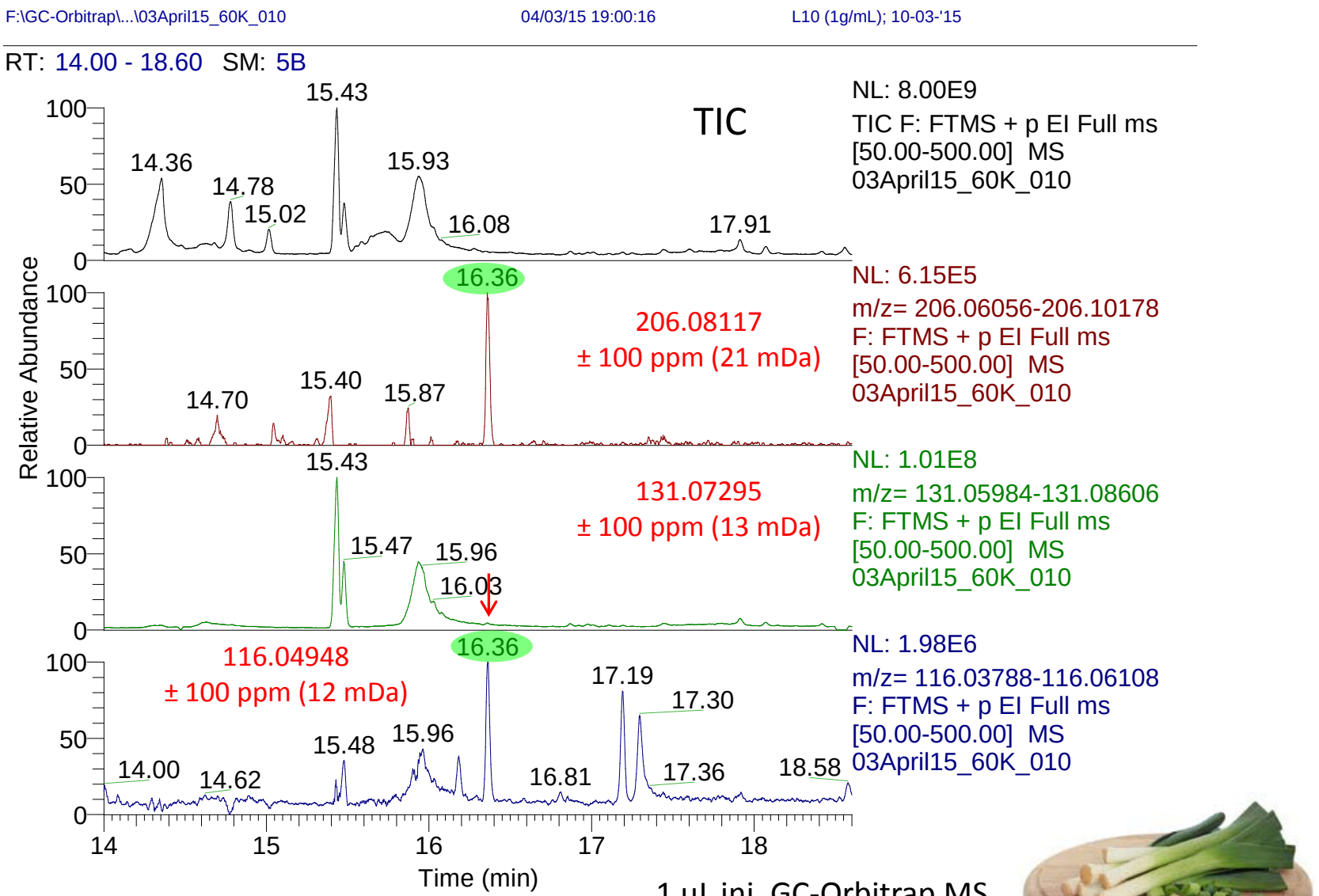
Narrowing down the MEW: ± 100 ppm



1 µL inj. GC-Orbitrap MS
Leek spiked @ 10 ppb,
Full scan m/z 50-500; Res = 60,000

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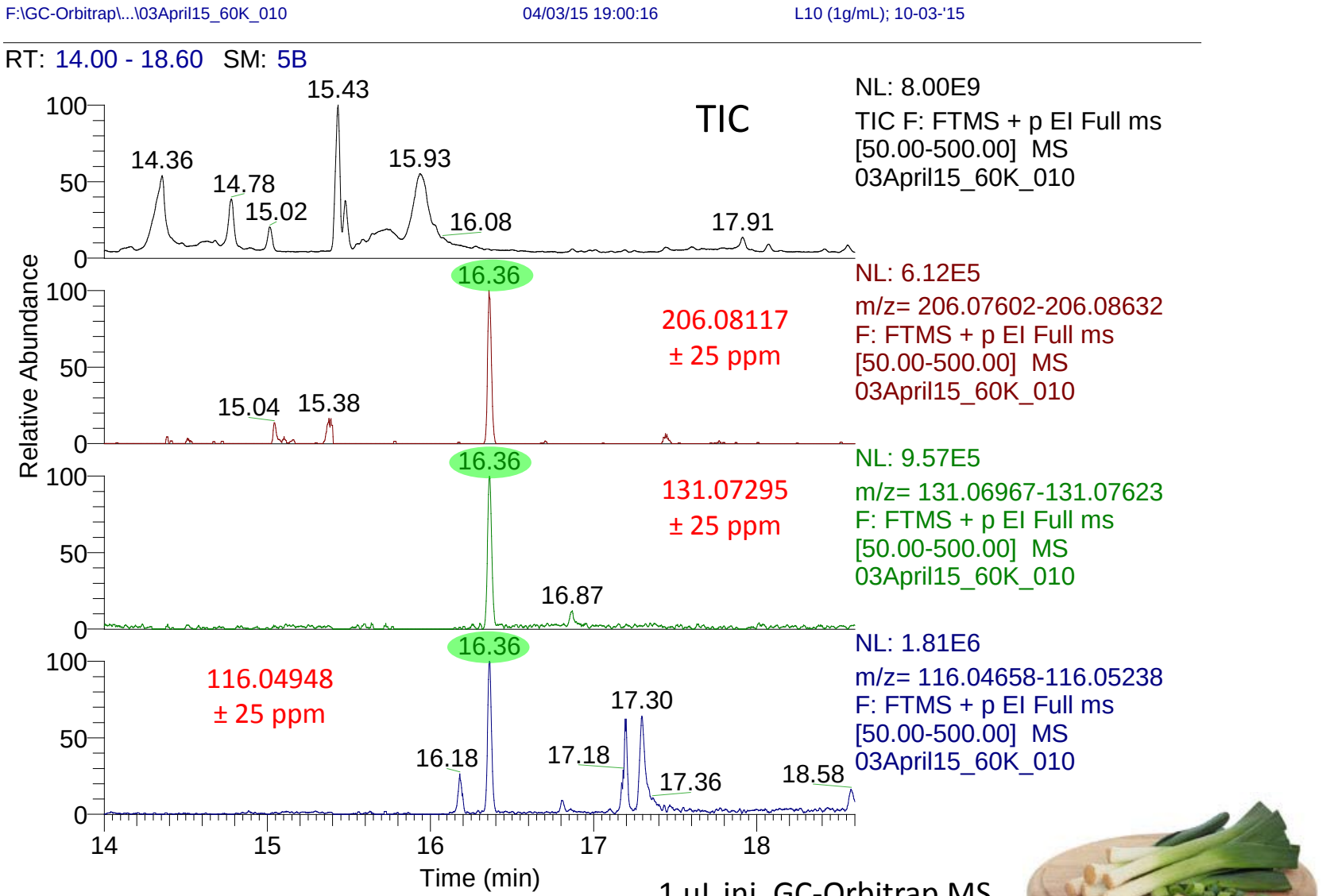
Narrowing down the MEW: ± 25 ppm



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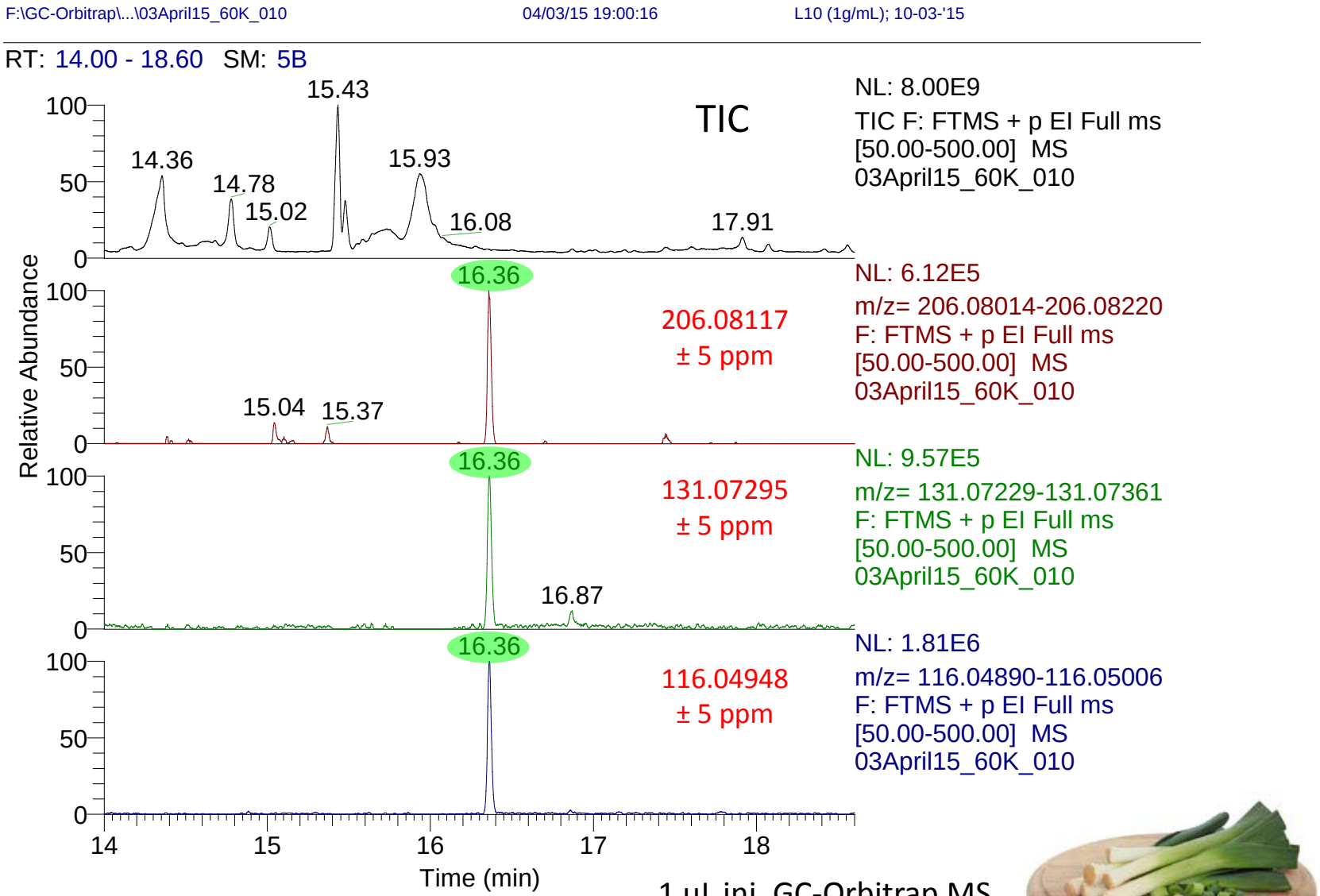
1 µL inj. GC-Orbitrap MS
Leek spiked @ 10 ppb,
Full scan m/z 50-500; Res = 60,000

Narrowing down the MEW: ± 5 ppm



1 µL inj. GC-Orbitrap MS
Leek spiked @ 10 ppb,
Full scan m/z 50-500; Res = 60,000

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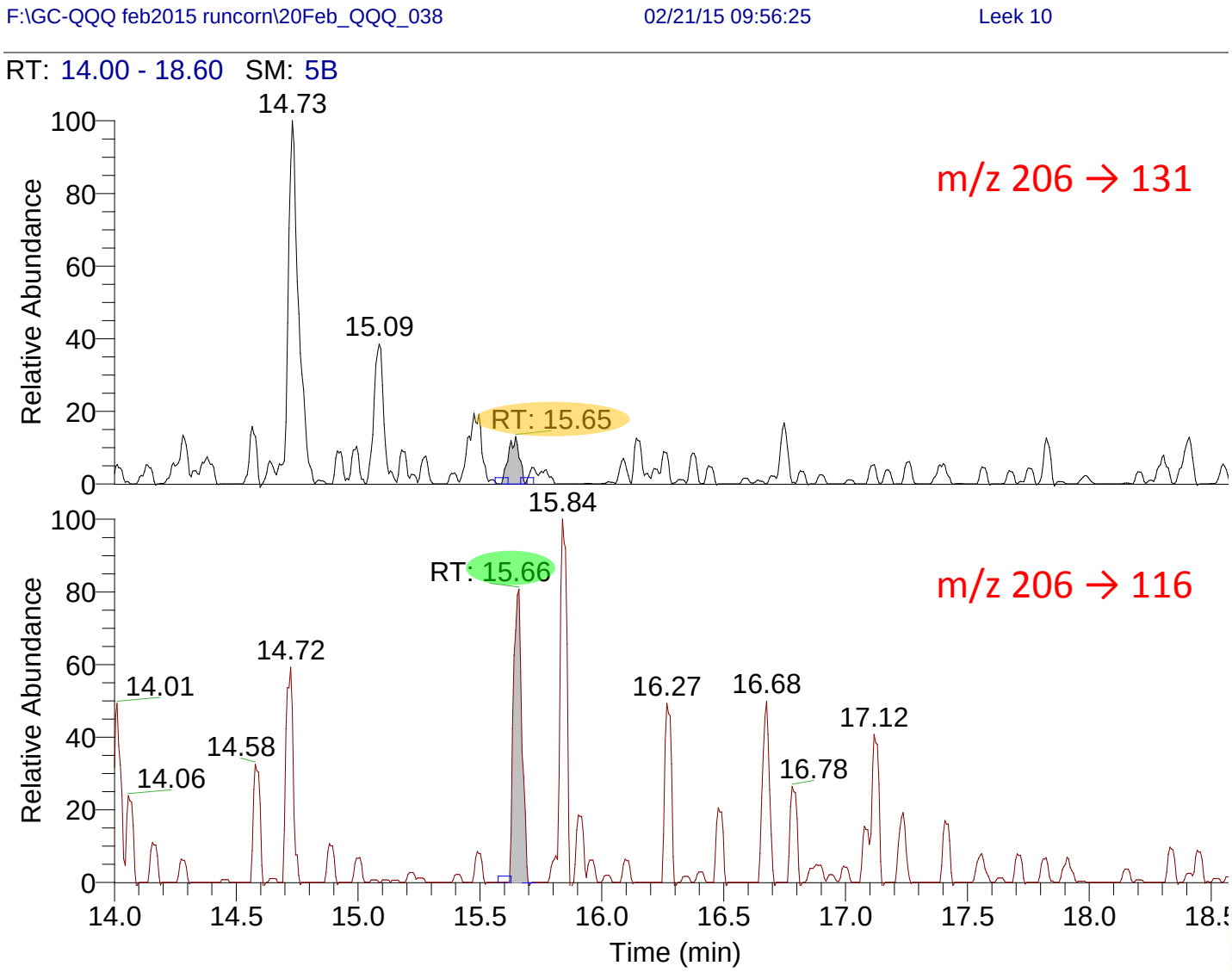
Comparison with GC-MS/MS (triple quad)



Kresoxim-methyl in leek @ 10 ppb
1 µL inj. GC-MS/MS (TSQ 8000 Evo)

Outline

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Conclusions

Acquisition:

Full scan combined with vDIA: optimum way of non-targeted measurement; provides best sensitivity, selectivity, fragments without sacrificing scope

Quantification [top 100-150 frequently found, with calibrants]:

Performance comparable with triple quadrupole instruments, sensitivity fit-for-purpose for pesticide residue analysis

Identification:

Meets EU requirements (SANCO/12571/2013)

Screening [for the other 100s, without calibrants]:

Fully automated output, low # false positives, easy manual accept/reject of hits
Overall detection rate 92% @ 10 ppb
SDLs 10 ppb for majority of pesticides tested

GC-Orbitrap MS highly promising to complement LC-based quan/qual analysis

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Thermo Fisher Scientific: Olaf Scheibner, Markus Kellmann, Dominic Roberts, Cristian Cojocariu, Paul Silcock

Thank you for your attention!

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