

Evaluation of simultaneous MS and MS/MS method for detection and identification of pesticides residues in fruit and vegetables using LC-QToF

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INTRODUCTION

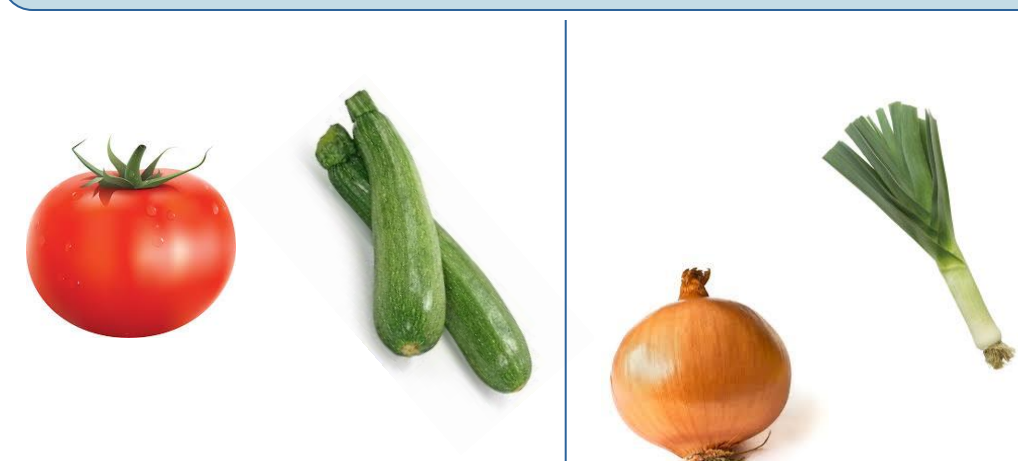
Nowadays, a growth in the applications of accurate mass instruments is observed. The predominant type of mass spectrometer applied in pesticide analysis in fruits and vegetables is triple quadrupole. However, during last decade a great improvement has been made in the field of accurate mass spectrometry, today this kind of analyzer can be considered not only as a complementary technique but also as real alternative to triple quadrupole mass spectrometers. The application of tandem accurate mass spectrometers operated simultaneously in full scan and MS/MS could give solutions when the identification approach applied full scan mode is not able to distinguish targeted pesticide from isobaric matrix compound.

This work presents application of LC-QTOF-MS/MS for detection, identification and quantitation of pesticides in fruits and vegetables. Two different simultaneous MS-MS/MS workflows were used **information dependent acquisition** method (IDA) and **data independent acquisition** method (SWATH).

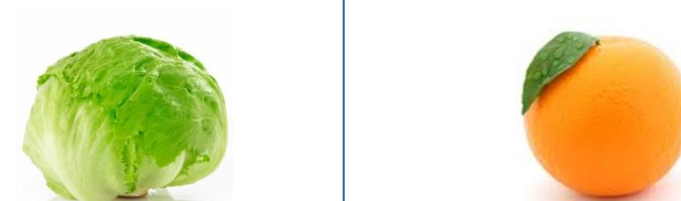
EXPERIMENTAL

Sample handling

QuEChERS protocol



Extracts spiked at different concentration levels



Extracts diluted 10 times



Chromatography

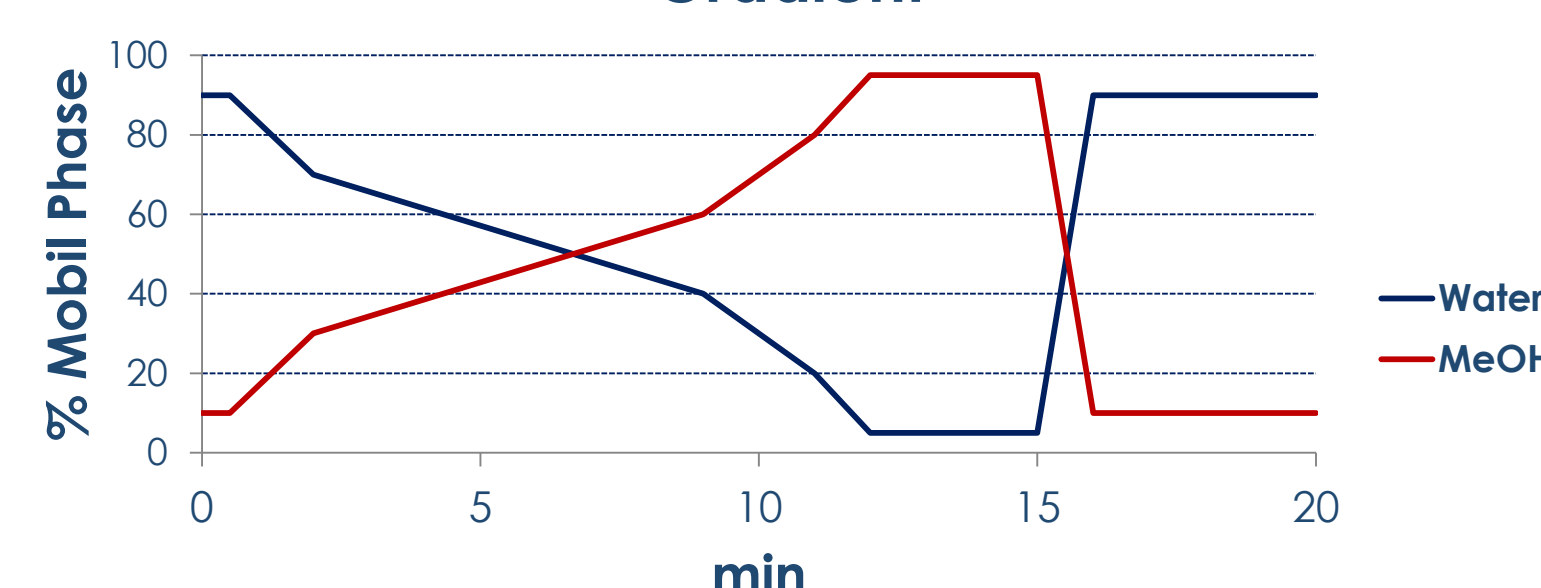
SCIEX ExionLC™ AC system

Column: Phenomenex Kinetex Biphenyl
2.6µm (50 x 2.1mm)

Mobile phase:

A: Water (5 mM ammonium formate buffer)
B: MeOH (5 mM ammonium formate buffer)

Gradient



SCIEX X500R QTOF system

Ion source

- Gas1 and Gas2: 60 psi
- Temperature: 450°C
- Curtain gas: 35psi
- Ion spray voltage: 5500V
- Polarity mode: Positive

Swath Parameters

- Total scan time: 0.69s
- ToF MS accumulation time: 0.07
- ToF MS mass range: 110-750Da
- Number of mass windows:12
- ToF MS/MS accumulation time: 0.035s
- ToF MS/MS mass range: 50-750

IDA Parameters

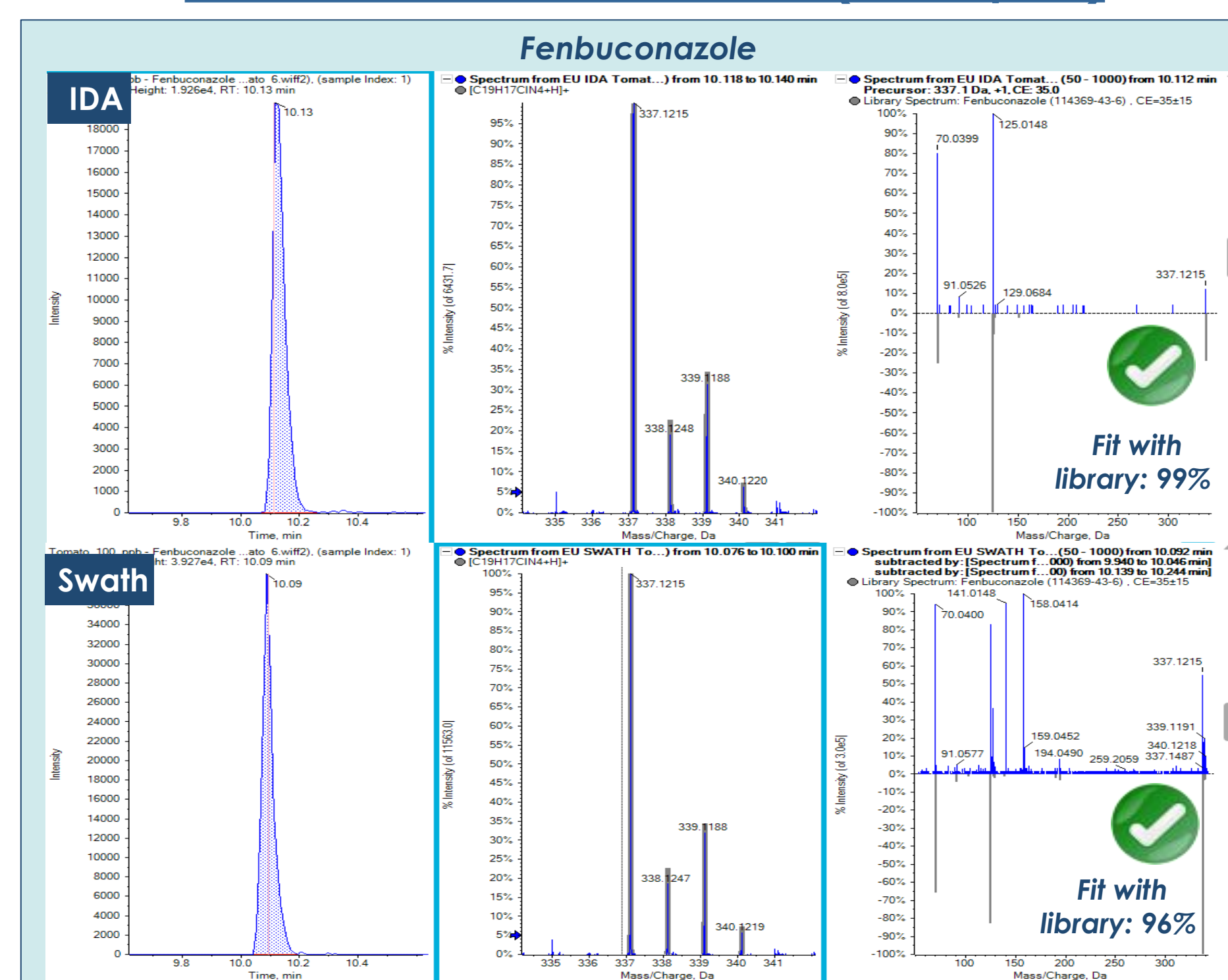
- Total scan time: 0.61s
- ToF MS accumulation time: 0.15
- ToF MS mass range: 110-750 Da
- Maximum candidate ions: **10 (most abundant)**
- ToF MS/MS accumulation time: 0.04s
- ToF MS/MS mass range: 50-750
- Non-inclusion list of targeted compounds (*)**

RESULTS

Compounds Evaluated (125)

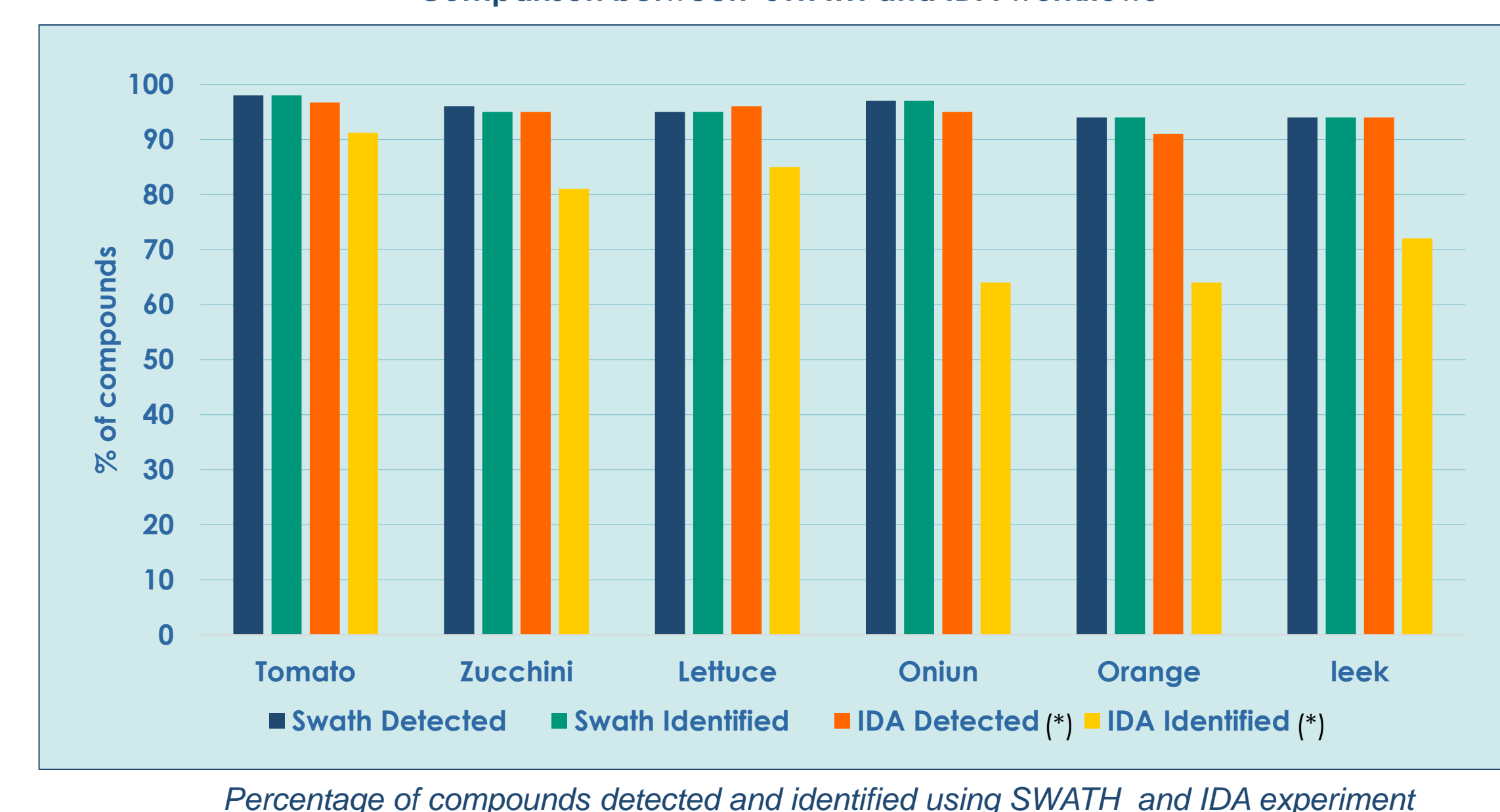
Compounds from Multiannual Control Programme for Pesticide Residues			
Acetamiprid	Epoxiconazole	Iprovalicarb	Profenofos
Aldicarb	Ethion	Isocarbofos	Propamocarb
Aldicarb sulfone	Ethionol	Isophenphos methyl	Propiconazole
Aldicarb sulfoxide	Ethoprophos	Kresoxim methyl	Propoxur
Azoxystrobin	Fenamidon	Linuron	Propyzamide
Bifenthrin	Fenamiphos	Malathion	Pyrethrin
Boscalid	Fenamiphos sulfone	Mandipropamid	Pyraclostrobin
Bromuconazole	Fenamiphos sulfoxide	Mepanpyrin	Pyridaben
Bupirimate	Fenarimol	Metaxyl	Pyrimethanil
Buprofezin	Fenazaquin	Metconazole	Pyriproxyfen
Carbaryl	Fenbuconazole	Methidathion	Quinoxifen
Carbendazim	Fenhexamid	Methiocarb	Rotenone
Carbofuran	Fenpropimorph	Methiocarb sulfone	Spinosyn A
Chlorantraniliprole	Fenpyroximate	Methiocarb sulfoxide	Spinosyn D
Chlorfenvinphos	Fenthion	Methoxyfenozide	Spirodiclofen
Clofentezine	Fenitrothion	Metobromuron	Spiramesifen
Clothianidin	Flonicamid	Monocrotophos	Spiroxamine
Cyproconazole	Fluazifop	Myclobutanil	Tebuconazole
Cyprodinil	Flufenoxuron	Nitenpyram	Tebufenozide
Cyromazine	Fluopyram	Ometoate	Tebufenpyrad
Demeton-S-methylsulfone	Fluquinconazole	Oxamyl	Terbutylazine
Diazinon	Flusulfazole	Paclobotrazol	Tetraconazole
Dichlorvos	Flutriafol	Penconazole	Thiabendazole
Dicofol	Formetanate	Pencycuron	Thiacloprid
Diethofencarb	Fosfiazate	Phenthoate	Thiamethoxam
Difenoconazole	Haloxifop	Phosalone	Thiodicarb
Diflubenzuron	Hexaconazole	Phosmet	Triazophos
Dimethoate	Hexythiazox	Pirimicarb	Trichlorfon
Dimethomorph	Imazalil	Pirimicarb desmethyl	Trifloxystrobin
Diniconazole	Imidacloprid	Pirimiphos-methyl	Triflumuron
Dodine	Indoxacarb	Prochloraz	Trifluralin
			Zoxamide

Identification-IDA vs Swath (examples)



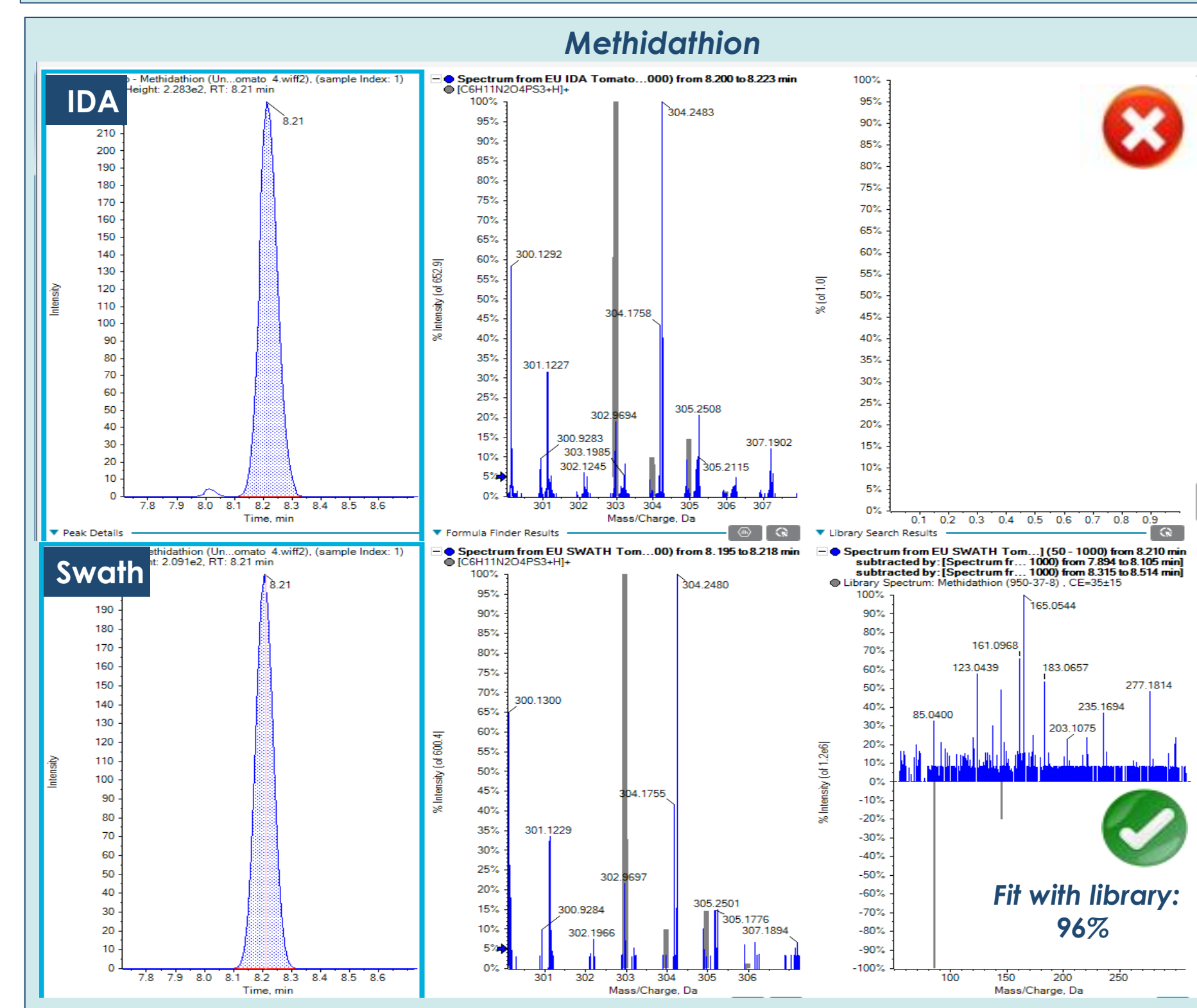
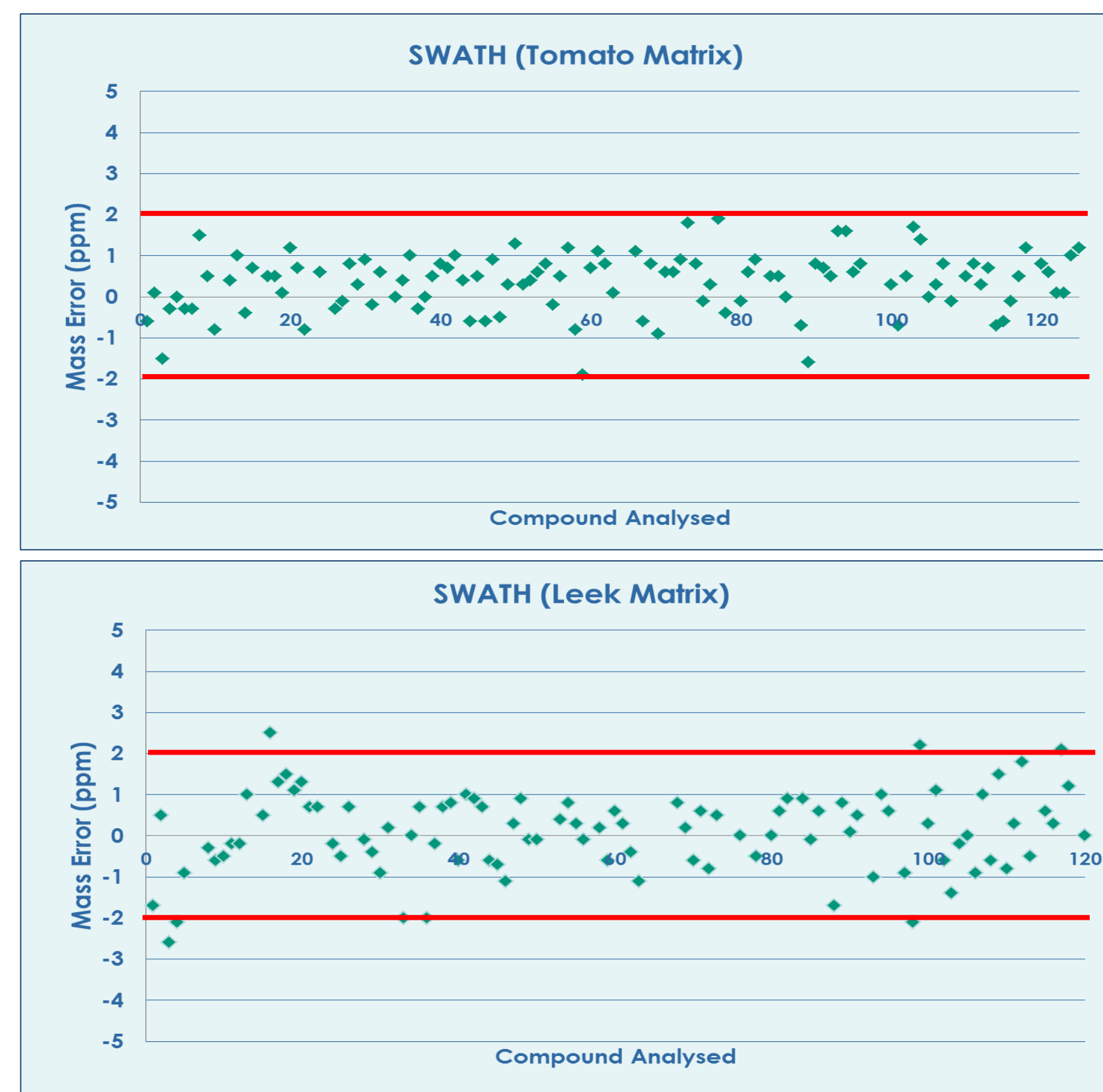
Detection and identification

Comparison between SWATH and IDA workflows

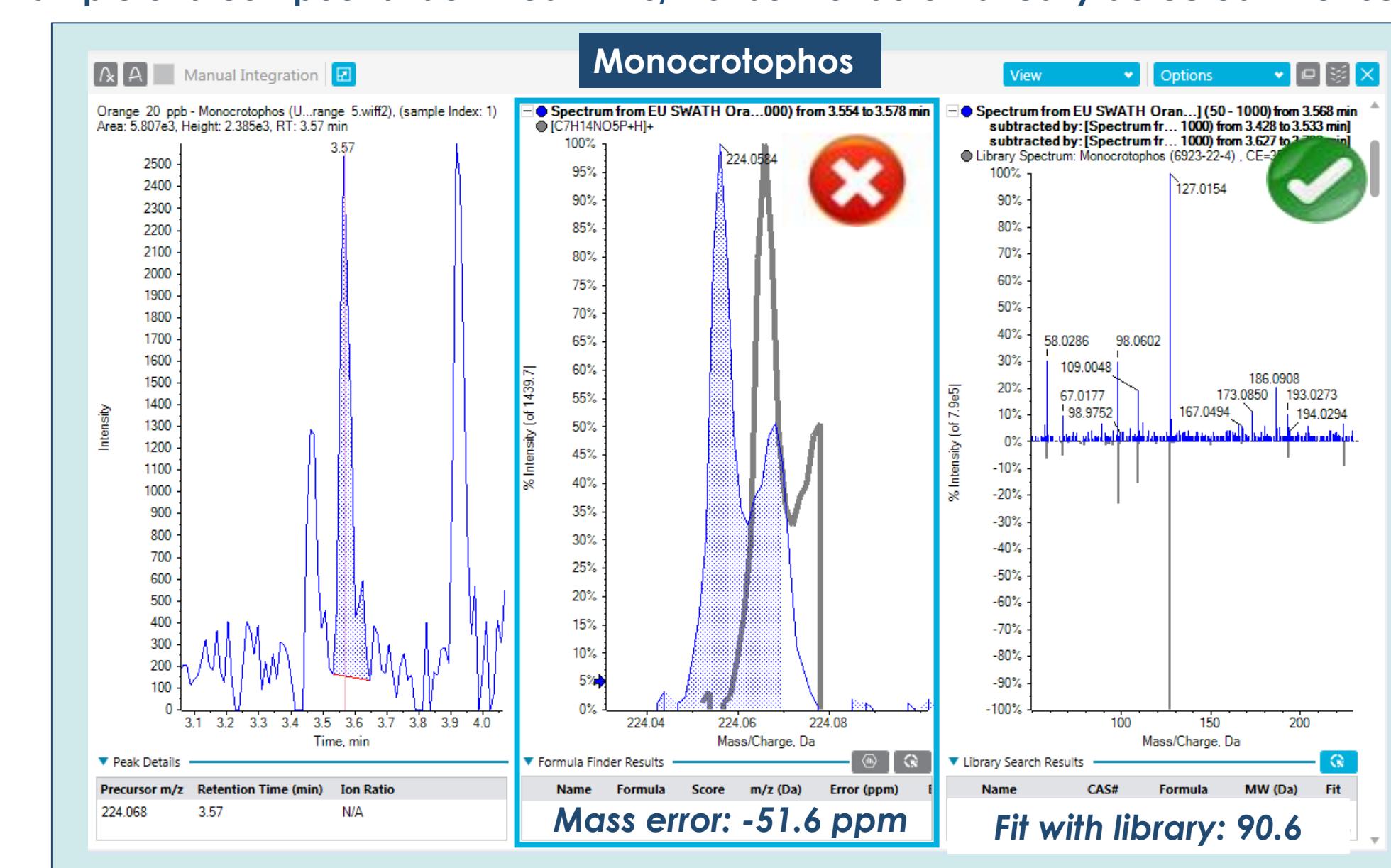


Percentage of compounds detected and identified using SWATH and IDA experiment

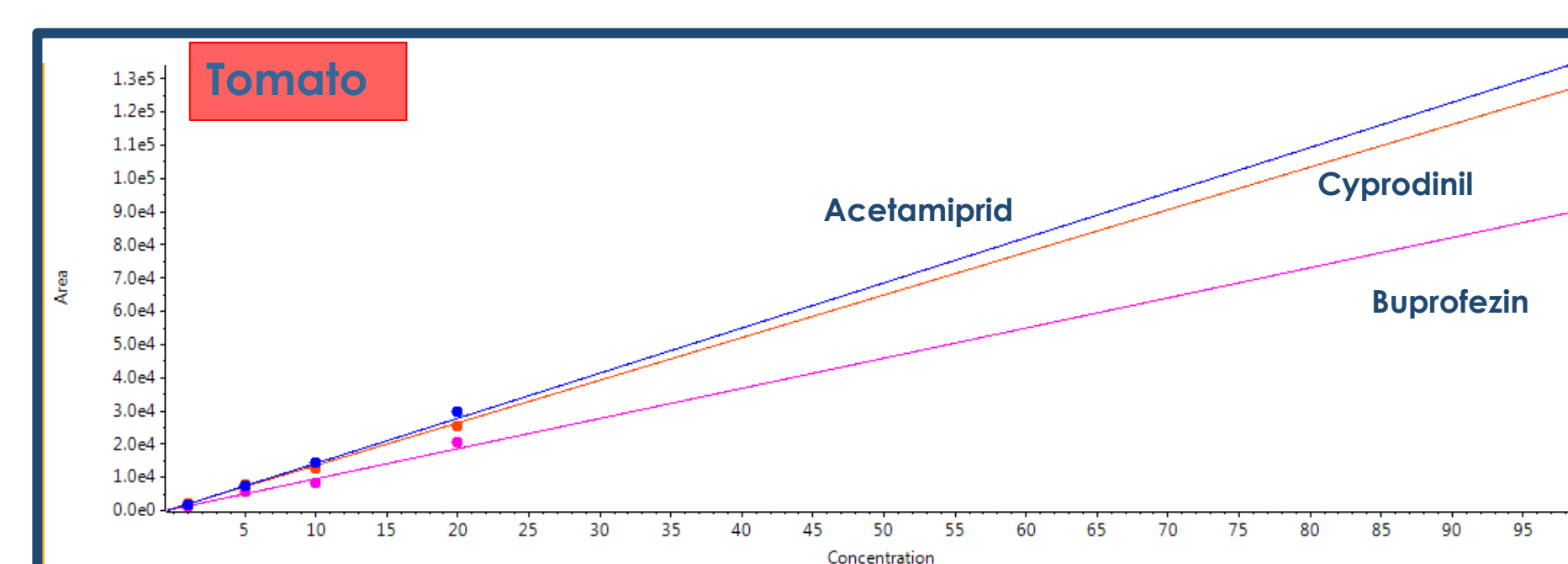
Mass Accuracy



Example of a compound identified in MS/MS but not automatically detected in full scan

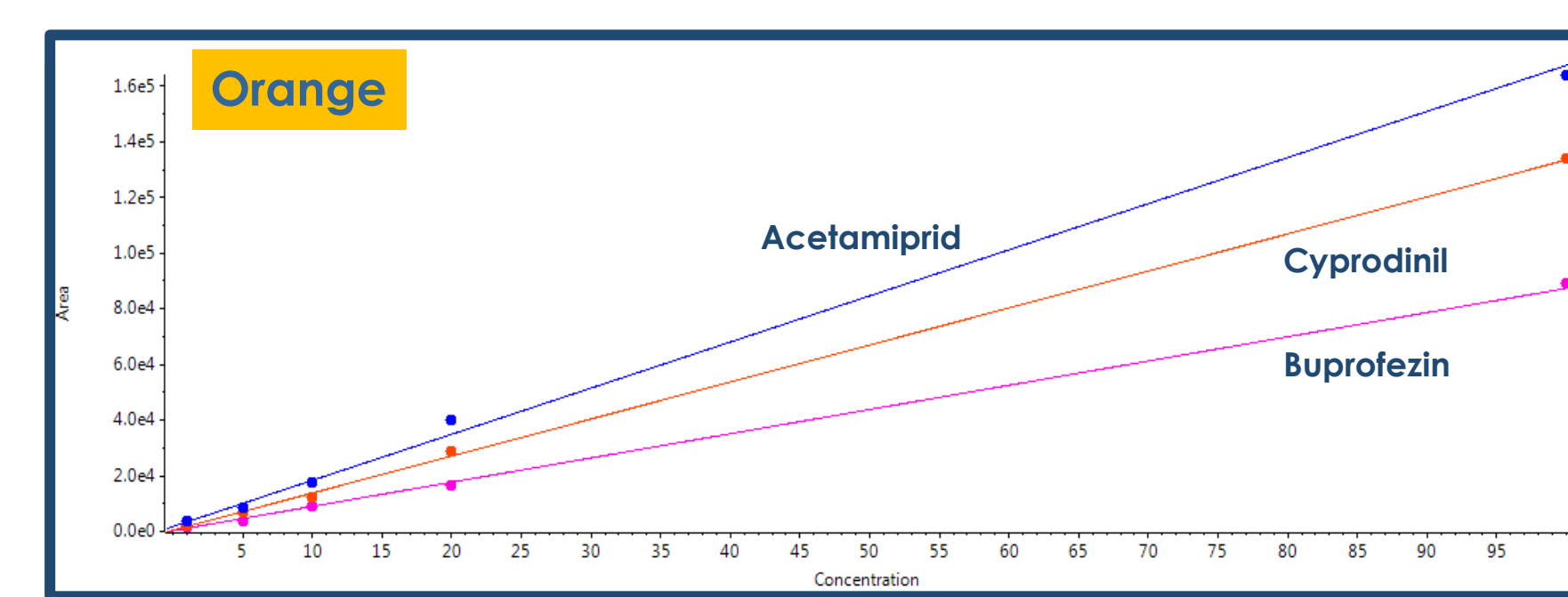


Monocrotophos is an example of a compound whose automatic detection in full scan mode is not possible due to matrix co-extractives but in MS/MS mode was identified.



Linearity

Calibration curve from 1µg/Kg to 100 µg/Kg in tomato and orange diluted 10 times



CONCLUSIONS

- Regarding mass accuracy, all evaluated compounds in all studied matrices (tomato, lettuce, leek, onion, orange and zucchini) presented mass error below 5 ppm and the majority of them, even below 2ppm.
- The results show good detection and identification capabilities for Swath acquisition method. The identification by IDA acquisition mode is less confident due to loss of information in MS/MS experiment when a targeted list is not considered. Therefore, swath method is the workflow recommended to work.
- In some cases the percentage of identified compounds is higher than the detected compounds. This is because the natural components present in the matrix can affect in the detection of the targeted compounds because a targeted list is not included in the acquisition method.
- Over 95% of the evaluated compounds present a lineal range between 1-100 µg/Kg.