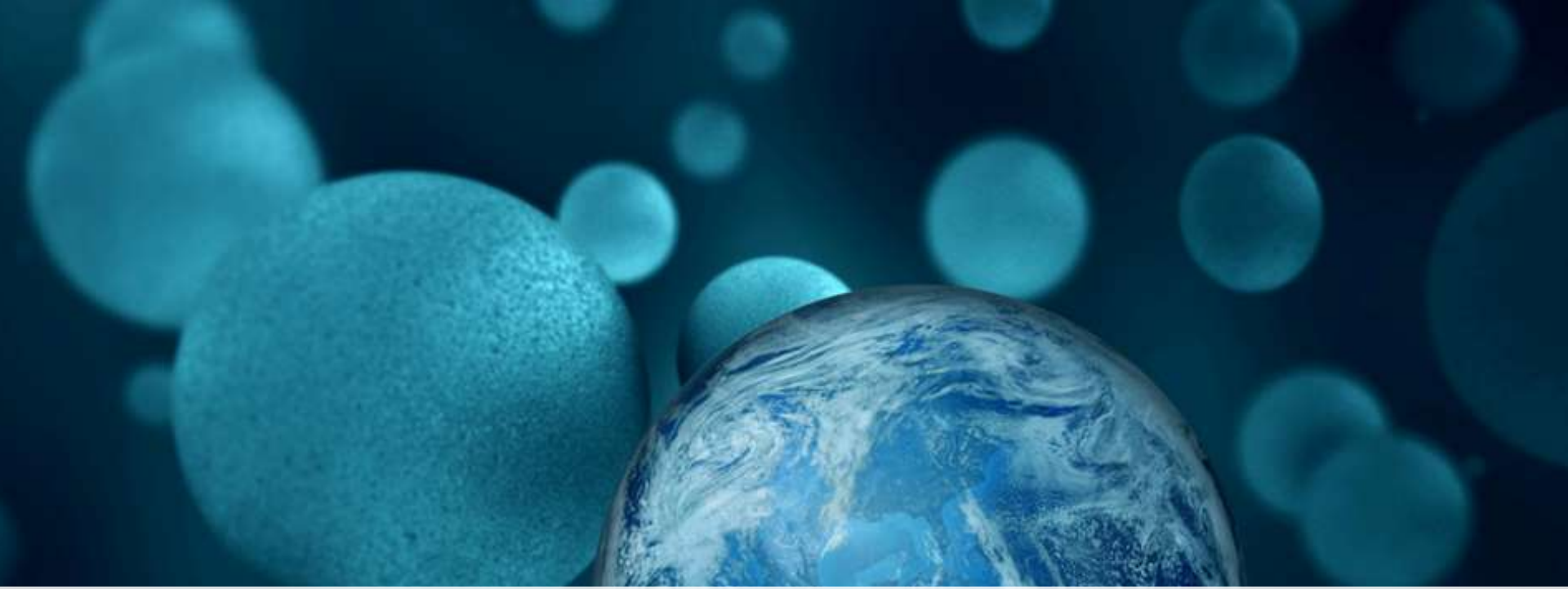

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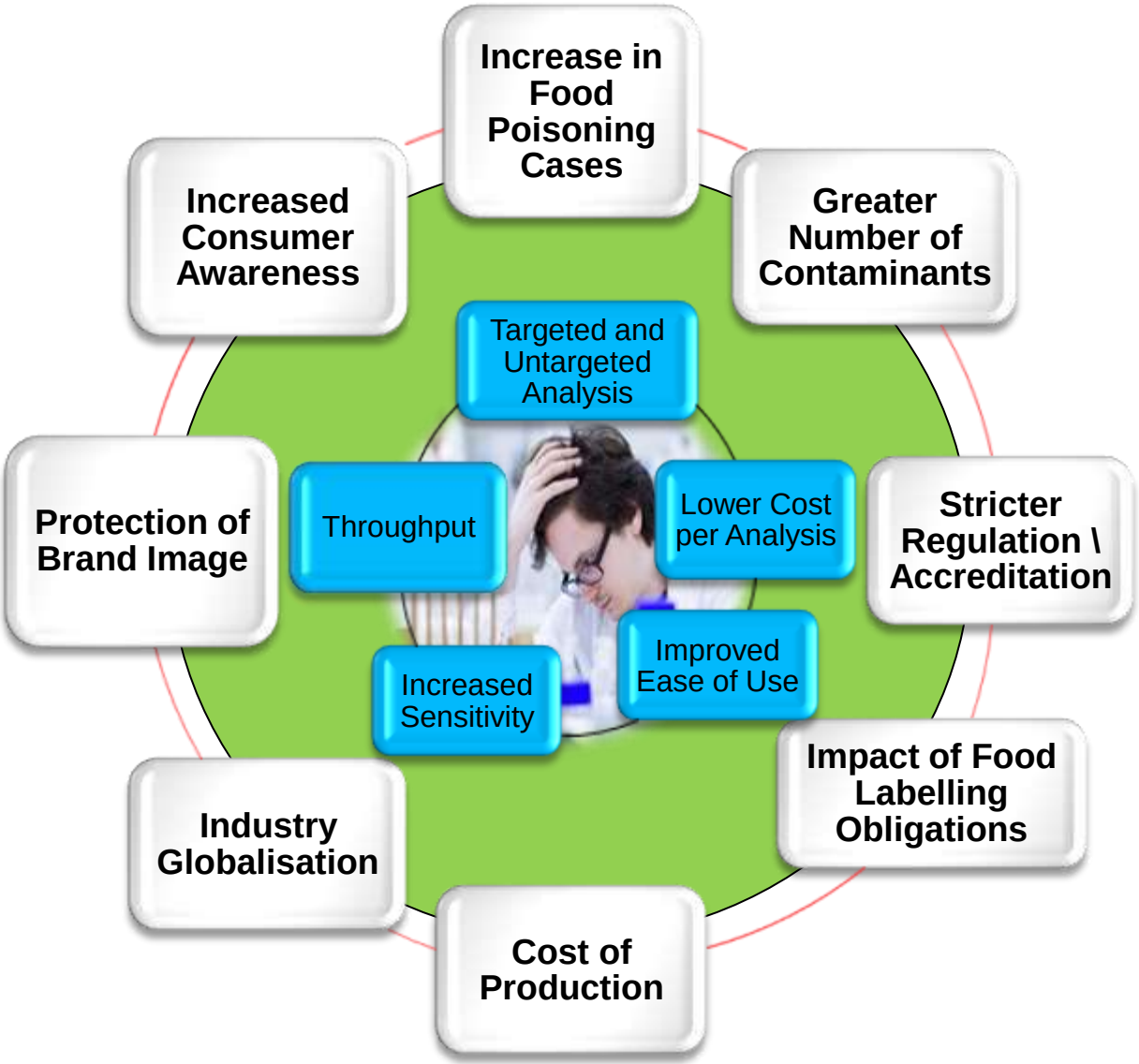
Food Hazards Screening and Food Fraud Analysis by Orbitrap HRAM MS

Zheng Jiang
LSMS Application Manager
Sep. 13th, Shanghai

Safety and Authentication Challenges in Food Industry



Laboratory Challenges

Industry Challenges

Key Requests from Food Manufacturers

Food supply chain from source to consumer

Chemical *Biological* *Physical*

- Produce safe food
- Prevent food fraud, adulteration
- Produce high quality products and monitor product variability
- Produce new products
- Meet legislative requirements for food safety, Labeling and GMP
- Produce and market healthier products

SANCO/12571/2013

- Method Validation & Quality Control Procedures for Pesticide Residues Analysis in Food & Feed
- Implemented 1/1/2014

HRAM criteria

≥2 ions (pref. including quasi molecular ion)
< 5 ppm mass accuracy
At least one fragment ion
Resolution typically >20000FWHM

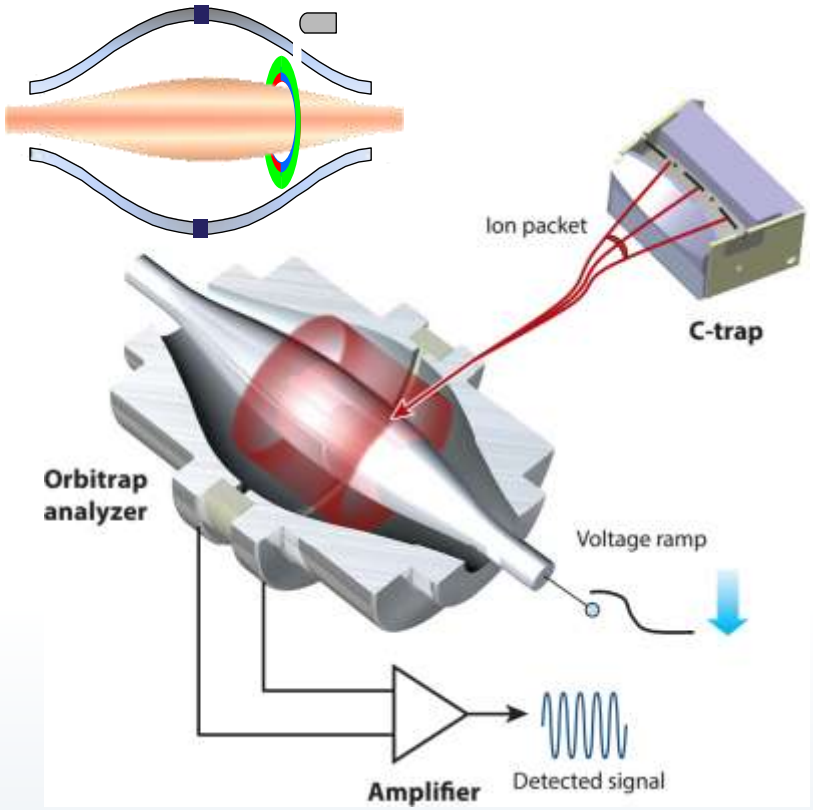
MS mode:	Single-stage MS (unit mass resolution)	Single-stage MS (high resolution/high mass accuracy)	MS/MS
Typical systems (examples):	Quadrupole, ion trap, time-of-flight (TOF)	TOF, Orbitrap, FTMS, magnetic sector	Triple quadrupole, ion trap, hybrid MS (e.g. Q-TOF, Q-trap)
Acquisition mode:	Full scan, 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		

Identification Criteria - Other Examples

P. Lucci and C.P.B. Martins in Fast Liquid Chromatography – Mass Spectrometry Methods in Food and Environmental Analysis - World Scientific Publishing Company (March 2015)

	EU 2002/657/EC	SANCO 12571/2013	**EU-RL-MB SOP**	**Gerssen (2010)**	**Mol (2012)**	**Domènech (2014)**	**Kumar (2014)**	**Pitarch (2007)**
Analytes	-	Pesticides	Lipophilic Toxins	Lipophilic Toxins	Pesticides	Lipophilic Toxins	Ronidazole Nitroimidazoles	Priority organic micropollutants
Matrix	Food	Food and Feed	Molluscs	Shellfish	Vegetables &Fruits	Mussels	Muscle	Water
Technique	HRMS	HRMS	LC-MS/MS	LC-MS/MS	LC-HRMS/MS	LC-HRMS/MS	LC-HRMS/MS	GC-MS/MS
Mass Accuracy	-	< 5ppm	-	-	< 5ppm	< 5ppm	< 5ppm	-
Mass Resolving Power (FWHM)	-	≥20,000	-	-	≥20,000	≥20,000	≥70,000	-
Retention Time (RT) Tolerance	2.5%	2.5%	Not exceed 3%	5%	1%	Mean ±3SD (not relative to time)	±1%	Agreement - RT samples & standards
Diagnostic Ions	≥ 2	≥ 2	1 precursor	1 precursor	≥ 2	1	2	1 or 2 precursors
Fragment Ions	-	At least one	At least 2 precursor-product transitions	2 products	At least one	1	At least 1 >20,000FWHM	At least 2 precursor-product transitions
Isotope Ions	-	-	-	-	M+1 M+2	M+1	-	-
Ion Ratio	Relative intensity (% at base peak)	Relative intensity (% at base peak)	Must be recorded	As described 2002/657/EC	Fragment Ion Ratio: Diagnostic/Fragment Isotope Ion Ratio: Diagnostic/M+1 (M+2)	Fragment Ion Ratio: Diagnostic/Fragment Isotope Ion Ratio: Diagnostic/M+1	At least one	Ratio between quantitative and confirmation transition
Fragment-Isotope Ion Ratio Tolerance	2 IPs for precursor ion 2.5 IPs for a product	As described 2002/657/EC	-	As described 2002/657/EC	Independent of relative intensity between ions: ±50%	As described 2002/657/EC	-	As described 2002/657/EC

Orbitrap HRAM MS with Unmatched Performance



Unmatched ultrahigh resolution, accurate mass performance

What Orbitrap provides

- Ultra-high resolution
- Long-term mass accuracy
- Uncompromised sensitivity
- Scan speed and dynamic range
- High-quality MS/MS fragmentation
- ***- at the same time***

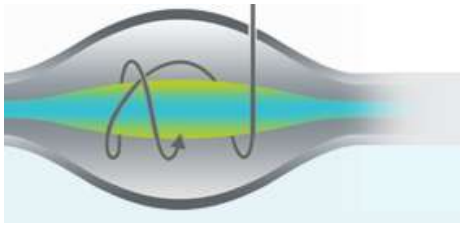
10 Years Development in Product

- LTQ Orbitrao
- Q Exactive LC/GC
- Orbitrap Fusion

Significantly superior analytical results for Multiple Omics metabolomics/lipidomics/proteomics In foodomics testing and research

Annual Review of Analytical Chemistry 2015.8:61-80

Typical LC-HRMS Workflow for Pesticide Residue Analysis



QuEChERS

LC-HRMS

Compound Inclusion List

Generic Instrument Method

Retention Time
Exact Mass (± 5 ppm)
Product ions
Ion ratios
Isotopic Pattern
Library Matching

Identification

Screening

Quantification

Identification

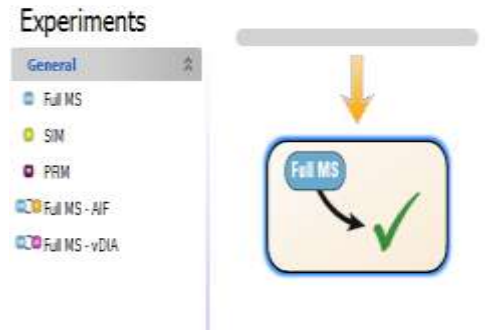
Reporting

Reporting

3 ways of Screening/Quantitation for Routine Work

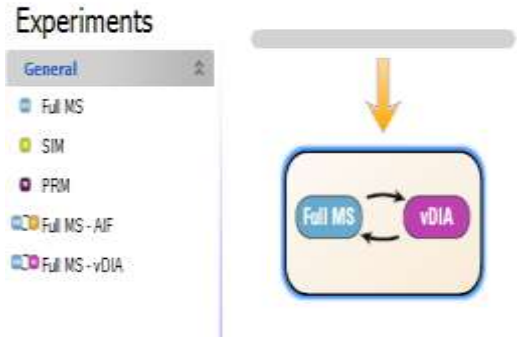
Full MS or targeted SIM/ddMS2

- Post-acquisition - extracted ion chromatograms of parent ions of interest
- Relies on high resolution for selectivity
- Useful for less complex background
- No method development/preparation needed



Full MS/ All Ion Fragmentation – vDIA*

- Post-acquisition - extracted ion chromatograms of parent ions of interest
- Scheduled target (inclusion) list (Rt, *m/z*)
- Minimum method development (e.g., predefine parent ions, tr)
- Also for screening purposes

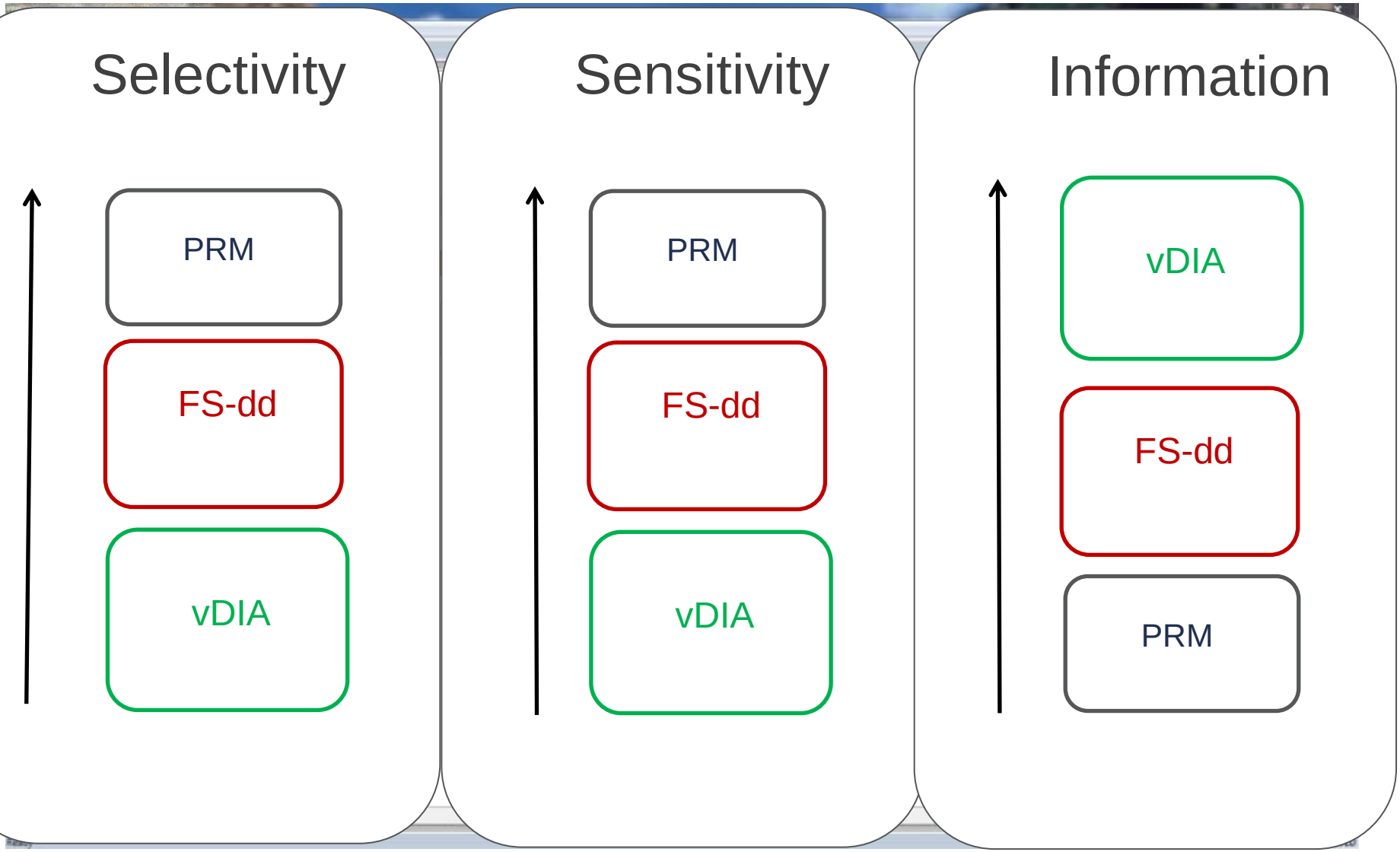


PRM (Parallel Reaction Monitoring)

- Post-acquisition – extracted ion chromatograms of parent -> fragment transitions acquired
- Scheduled target list (Rt, *m/z*, collision energy)
- Most sensitive and selective even in highly complex matrices

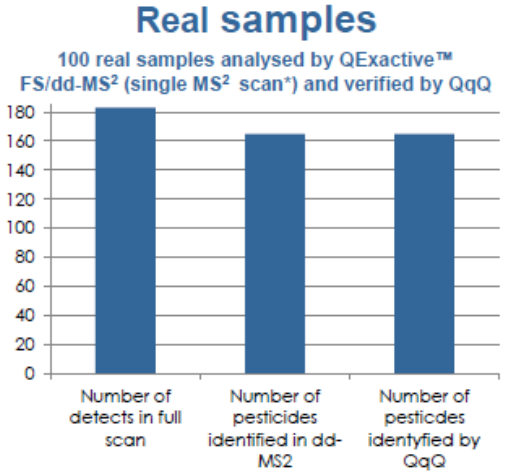
***vDIA method not available in the United States of America**

Q Exactive Focus Scan Methods



vDIA method not available in the United States of America

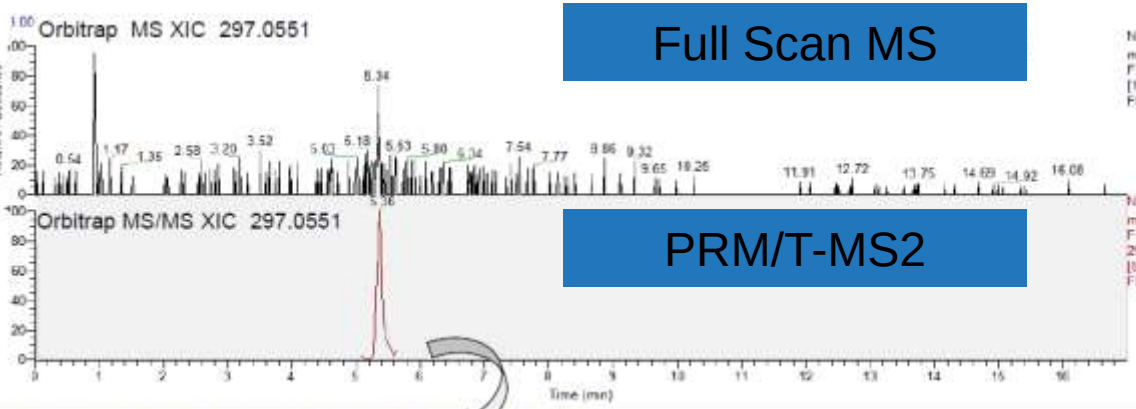
What Scan Mode is Right for Your Workflow?



Leek extract spiked with 0.1 ppb imazalil

Precursor ion @ R=70,000

Full Scan MS



PRM/T-MS2

Product ion @ R=70,000

M.M.Gomez-Ramos et al. *J Chrom A.,* **2013,** 1287, 24-37.

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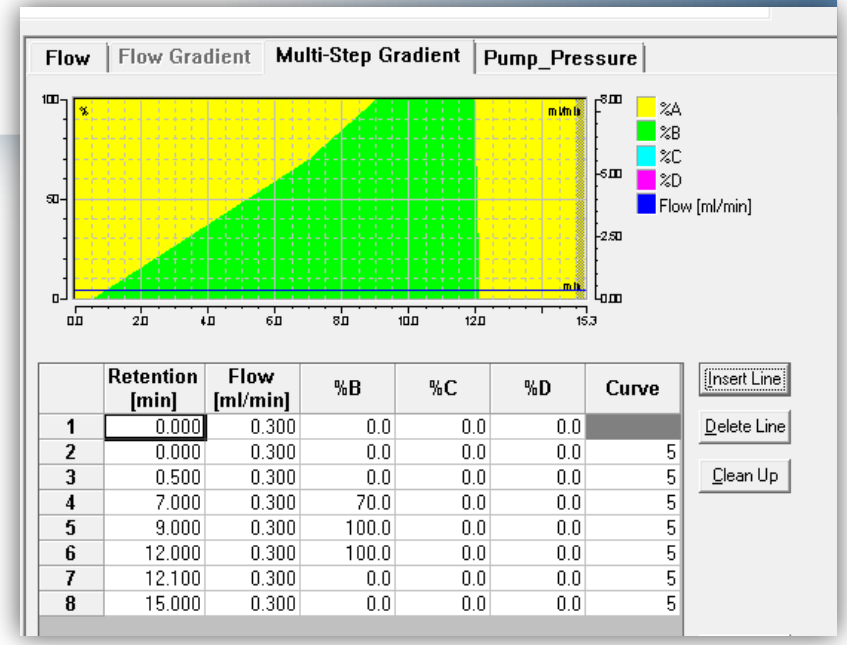
LC Instrumental Method

Thermo Scientific™ UltiMate™ XRS:

- Mobile phase:
  - A: Water:MeOH (98:2) + 5mM Ammonium formiate & 0.1% FA
  - B: MeOH:Water (98:2) + 5mM Ammonium formiate & 0.1% FA
- Injection volume: **1 µl**
- Column: Accucore aQ column 100 mm x 2.1 mm x 2.6 µm
- Column temperature: 25°C
- Flow rate: 300 µl/min
- Run time: 15 min
- Gradient:



	Retention [min]	Flow [ml/min]	%B	%C	%D	Curve
1	0.000	0.300	0.0	0.0	0.0	
2	0.000	0.300	0.0	0.0	0.0	5
3	0.500	0.300	0.0	0.0	0.0	5
4	7.000	0.300	70.0	0.0	0.0	5
5	9.000	0.300	100.0	0.0	0.0	5
6	12.000	0.300	100.0	0.0	0.0	5
7	12.100	0.300	0.0	0.0	0.0	5
8	15.000	0.300	0.0	0.0	0.0	5

Insert Line
Delete Line
Clean Up

Thermo Scientific™ UltiMate ™ XRS LC

ThermoFisher SCIENTIFIC

Recommended MS Tune Method Parameters

Q Exactive Focus:

- Source: HESI
- Detection mode: variable Data Independent Analysis (vDIA)

Scan parameters

History	
Scan type	Full MS
Scan range	70.0 to 900.0 m/z
Fragmentation	None
Resolution	70,000
Polarity	Positive
Microscans	1
Lock masses	Off
AGC target	1e6
Maximum inject time	50

Apply | Help | Hot link

HESI source

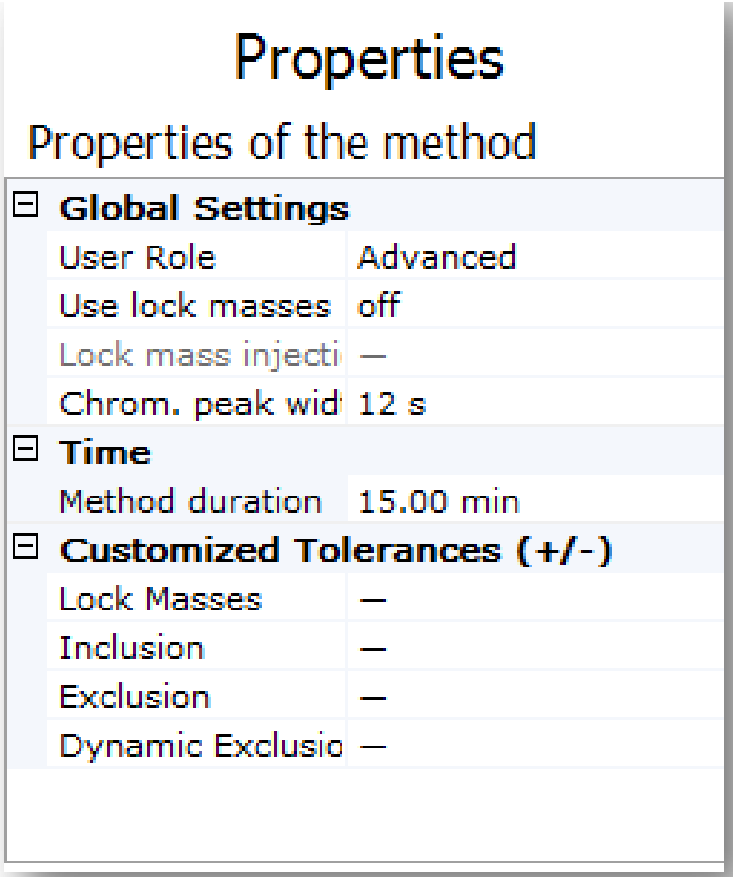
		actual
Sheath gas flow rate	40	40
Aux gas flow rate	10	10
Sweep gas flow rate	2	2
Spray voltage (|kV|)	3.50	3.47
Spray current (µA)		0.10
Capillary temp. (°C)	250	250
S-lens RF level	55.0	
Aux gas heater temp (°C)	270	272

Source Auto-Defaults...

Apply | Help | Hot link

vDIA method not available in the United States of America

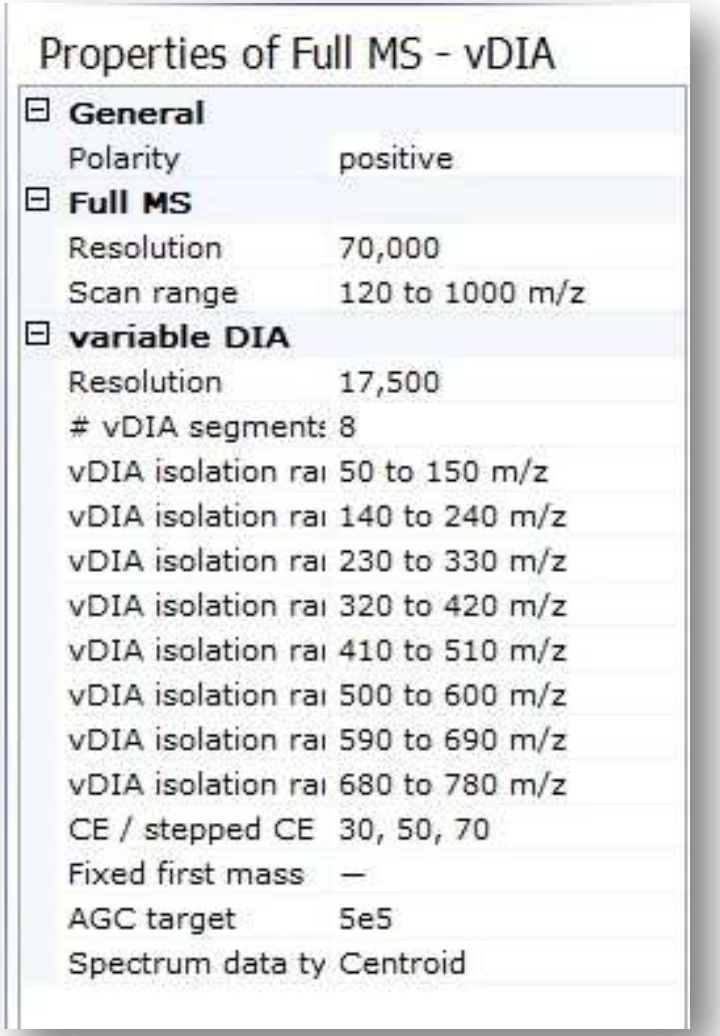
Recommended Method Parameters for Symmetric vDIA



Properties

Properties of the method

Global Settings	
User Role	Advanced
Use lock masses	off
Lock mass injecti	—
Chrom. peak wid	12 s
Time	
Method duration	15.00 min
Customized Tolerances (+/-)	
Lock Masses	—
Inclusion	—
Exclusion	—
Dynamic Exclusio	—

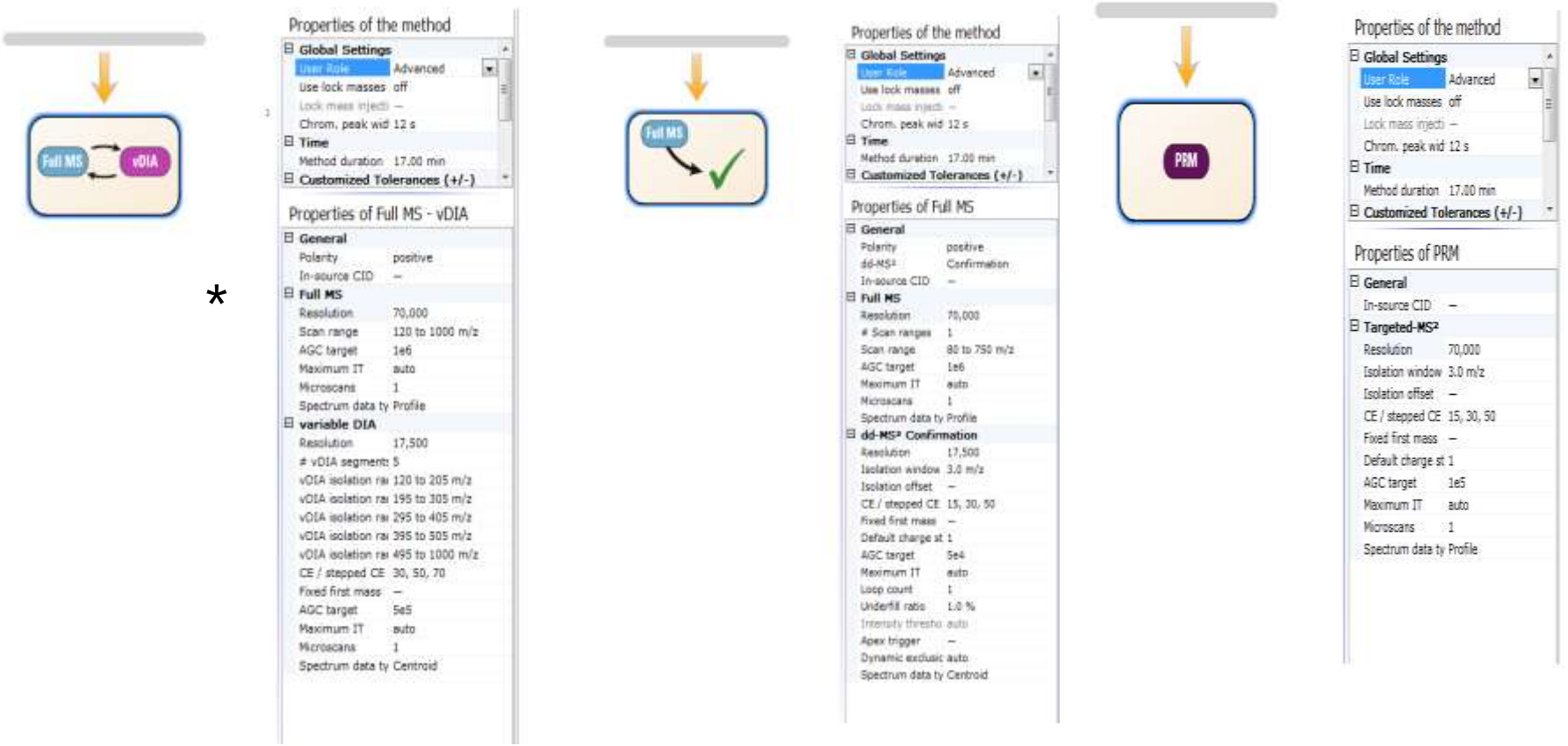


Properties of Full MS - vDIA

General	
Polarity	positive
Full MS	
Resolution	70,000
Scan range	120 to 1000 m/z
variable DIA	
Resolution	17,500
# vDIA segments	8
vDIA isolation rai	50 to 150 m/z
vDIA isolation rai	140 to 240 m/z
vDIA isolation rai	230 to 330 m/z
vDIA isolation rai	320 to 420 m/z
vDIA isolation rai	410 to 510 m/z
vDIA isolation rai	500 to 600 m/z
vDIA isolation rai	590 to 690 m/z
vDIA isolation rai	680 to 780 m/z
CE / stepped CE	30, 50, 70
Fixed first mass	—
AGC target	5e5
Spectrum data ty	Centroid

vDIA method not available in the United States of America

Alternative Recommended MS Method Settings



* Statistically identical results with symmetrical and asymmetrical vDIA settings

vDIA method not available in the United States of America

Targeted 330 Compounds – vDIA Screening Method

Acephate	Bromacil	Cumyluron	Dinotefuran	Fenthion-sulfone	Heptenophos	Methabenzthiazuron	Penconazole	Pyridaben	Thiacloprid
Acetamiprid	Bromuconazole	Cyanazine	Dioxacarb H	Fenthion-sulfoxide	Hexaconazole	Methamidophos	Pencycuron	Pyridate e	Thiamethoxam
Acibenzolar-S-methyl	Bupirimate	Cyazofamid	Disulfoton	Fenuron	Hexaflumuron	Methidathion	Permethrin	Pyrimethanil	Thiazopyr H
Aclonifen	Buprofezin T	Cycloate	Dithiopyr	Fipronil	Hexazinone	Methiocarb	Phenmedipham	Pyroquilon	Thidiazuron T
Alachlor	Butachlor	Cycluron	Diuron	Flazasulfuron	Hexythiazox T	Methiocarb sulfoxide	Phenthoate	Pyroxsulam	Thiobencarb
Alanycarb	Butafenacil	Cyflufenamid	Dodemorph	Flonicamid T	Imazalil	Methiocarb-sulfone	Phoxim	Quinoxyfen	Thiodicarb
Aldicarb	Butocarboxim	Cymoxanil	Epoxiconazole	Florasulam	Imazaquin	Metholcarb	Picoxystrobin	Quizalofop T	Thiofanox
Aldicarb sulfone	Butoxycarboxim	Cypermethrin T	Esprocarb	Fluazifop	Imazethapyr	Methomyl	Piperonyl butoxide	Quizalofop-p-ethyl	Thionazin
Aldicarb sulfoxide	Carbaryl	Cyproconazole	Etaconazole	Flufenacet	Imidacloprid	Methoprotryne	Piperophos	Resmethrin	Tolfenpyrad
Allethrin	Carbendazim	Cyprodinil	Ethiofencarb	Flufenoxuron	Indoxacarb	Methoxyfenozide	Pirimicarb	Rimsulfuron	Tralkoxydim
Ametryn	Carbetamide	Cyromazine	Ethiofencarb_sulfoxide	Flumetsulam	Iprovalicarb	Metobromuron	Pirimiphos-ethyl	Rotenone	Triadimefon
Aminocarb	Carbofuran	Deltamethrin	Ethiofencarb-sulfone	Flumioxazin	Isocarbophos	Metolachlor	Pirimiphos-methyl	Schradan	Triadimenol
Ancymidol	Carbofuran-3-hydroxy	Demeton-S-methylsulfone	Ethiprole	Fluometuron	Isofenphos	Metosulam	Pretilachlor	Sethoxydim	Triazophos
Anilofos	Carbosulfan	Desmedipham	Ethirimol	Fluopicolide	Isoprocarb	Metoxuron	Primisulfuron-methyl	Simeconazole T	Trichlorfon
Aramite H	Carboxin	Desmethyl-pirimicarb	Ethofumesate	Fluopyram	Isoprothiolane	Metrafenone	Prochloraz	Simetryn	Tricyclazole
Atrazine	Carfentrazone-ethyl	Desmetryn	Ethoxyquin	Fluoxastrobin	Isoproturon	Metribuzin	Profenofos	Spinosyn A	Tridemorph T
Azaconazole	Carpropamide	Dichlofenthion	Etofenprox	Fluquinconazole T	Isoxaben	Metsulfuron-methyl	Promecarb	Spiromesifen	Trietazine
Azamethiphos	Chlorantraniliprole	Dichlorvos	Etoxazole	Flurochloridone	Isoxadifen-ethyl	Mevinphos	Prometon	Spiroxamine	Trifloxystrobin
Azinphos-ethyl	Chlorbromuron	Diclobutrazol	Etrimfos	Fluroxypyr	Isoxaflutole	Mexacarbate	Prometryn	Sulfotep	Triflumizole
Azinphos-methyl	Chlorfenvinphos	Dicrotophos	Famoxadone	Flusilazole	Isoxathion	Monocrotophos	Propamocarb	Sulprofos HT	Triflumuron
Azoxystrobin	Chlorfluazuron	Diethofencarb	Fenamidone	Flutriafol	Kresoxim-methyl	Monolinuron	Propanil	Tebuconazole	Triforine
Barban	Chloridazon	Difenacoum	Fenamiphos	Fonofos	Lenacil	Napropamide	Propargite	Tebufenozide	Triticonazole
Bendiocarb	Chlorotoluron	Difenoconazole	Fenarimol	Forchlorfenuron	Malaoxon	Naptalam	Propazine	Tebufenpyrad	Vamidothion
Benfuracarb	Chloroxuron	Diflubenzuron	Fenazaquin	Formetanate	Malathion	Neburon	Propetamphos H	Tebuthiuron	Zoxamide
Benodanil	Chlorpyrifos	Dimefuron	Fenbuconazole	Formetanate hydrochlorid	Mandipropamide	Nicosulfuron	Propiconazole	Teflubenzuron	24D (neg)
Benoxacor	Cinosulfuron	Dimethachlor	Fenhexamid	Formothion	Mefenacet	Nitenpyram	Propoxur	Terbufos	Bentazone (neg)
Bensulfuron-methyl	Clethodim	Dimethametryn	Fenobucarb	Fosthiazate	Mepanipyrim	Nuarimol	Propyzamide	Terbumeton	Bromoxynil (neg)
Benzoximate	Clofentezine	Dimethenamide	Fenoxanil	Fuberidazole	Mepronil	Ofurace	Prosulfocarb	Terbuthylazine	DNOC (neg)
Benzoylprop-ethyl	Clomazone	Dimethoate	Fenoxycarb	Furathiocarb	Mesotrione	Omethoate	Pymetrozine	Terbutryn	Fluazinam (neg) H
Bifenazate	Clopyralid	Dimethomorph	Fenpiclonil	Griseofulvin	Metalaxyl	Oxadixyl	Pyraclostrobin	Tetrachlorvinphos H	Flubendiamide (neg)
Bitertanol	Clothianidin	Dimetilan	Fenpyroximate	Halofenozide	Metamitron	Oxamyl	Pyrazophos	Tetraconazole	MCPA (neg)
Boscalid	Coumaphos	Dimoxystrobin	Fensulfothion	Haloxyfop	Metazachlor	Oxyfluorfen	Pyrethrin I	Tetramethrin	Tepraloxydim (neg)
Brodifacoum	Crotoxyphos	Diniconazole	Fenthion	Haloxyfop-methyl	Metconazole	Paclobutrazol	Pyrethrin II	Thiabendazole	Terbacil (neg)

Constant peak area

No peak in tea at 10ppb

Peak neither in honey nor in tea at 10 ppb

Not found at all

Bad peak shape

No peak in honey at 10 ppb

Compound H or T Missing fragment ion confirmation in one of the matrices at 10 ppb

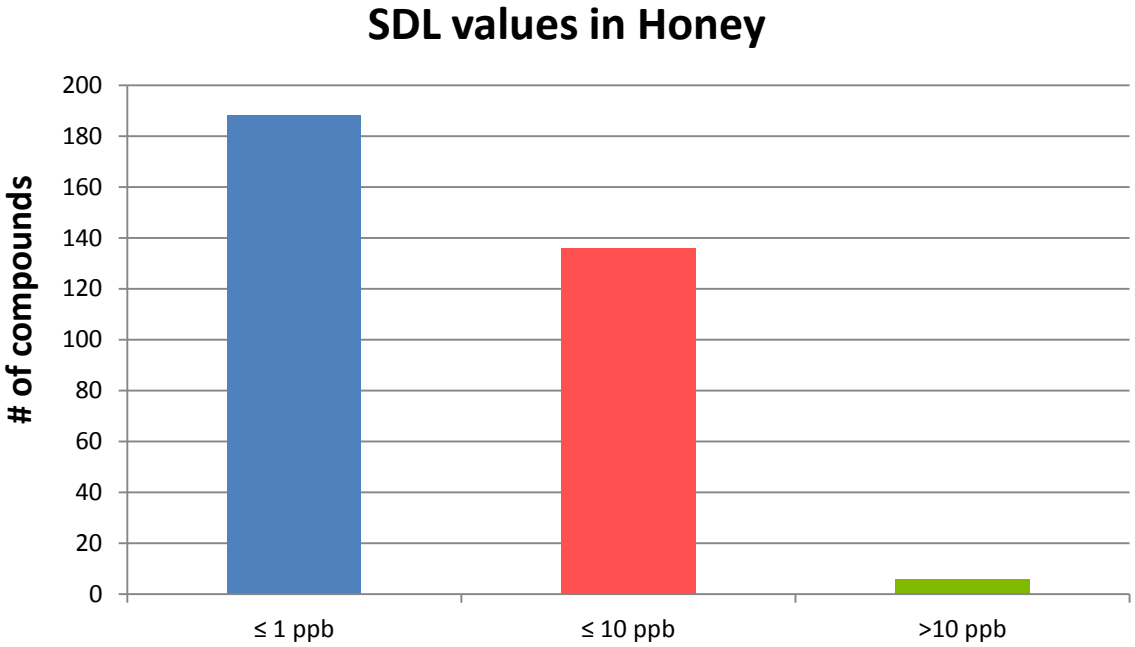
vDIA method not available in the United States of America

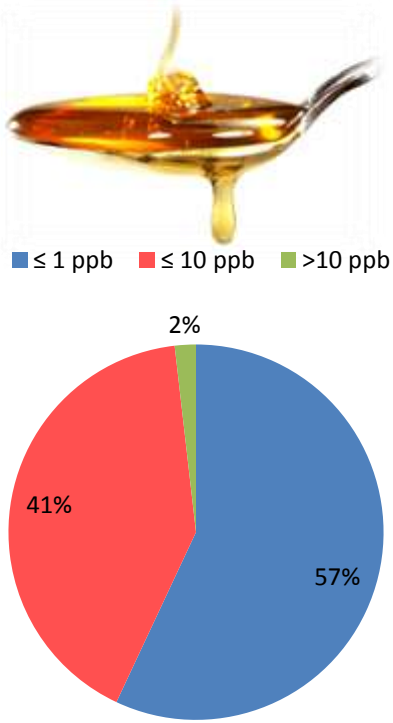
Validation Parameters

- Selectivity criteria: RT, min. detection of 1 HRAM quan and 1 HRAM qual ion with 5 ppm mass accuracy, ion ratio
- False negative and positive evaluation
- Recovery & repeatability at two concentration levels: 10 & 100 µg/kg
- Injection precision – 10 repeated injections of standard 100 µg/kg
- Screening detection limit (SDL), LOD/LOQ definition
- Linearity: 5 levels matrix matched calibration, duplicate measurement

Results vDIA – Sensitivity Overview Honey

- Screening Detection Limits (SDL) in honey matrix





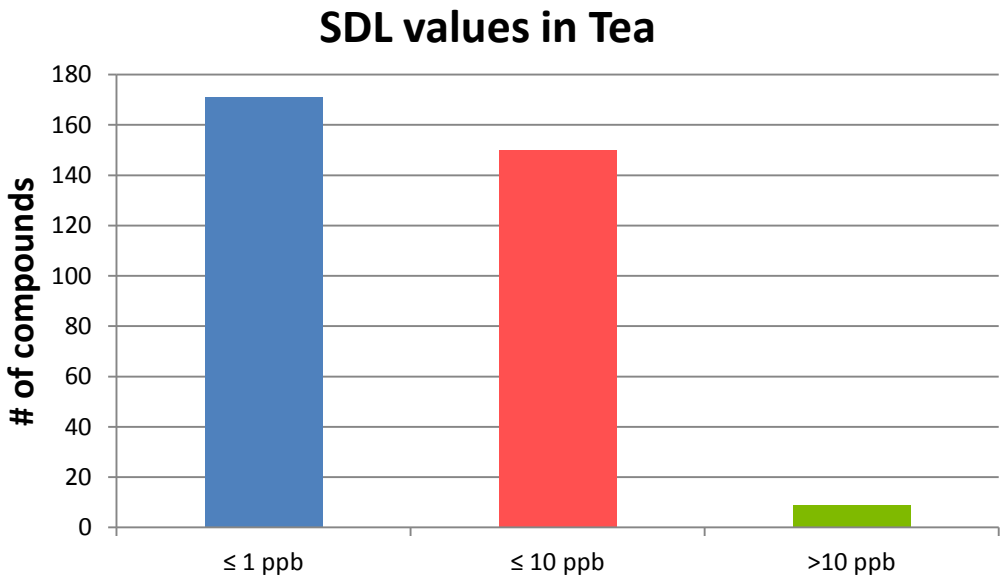
SUM = 330 compounds; 324 compounds SDL ≤ 10 µg/kg

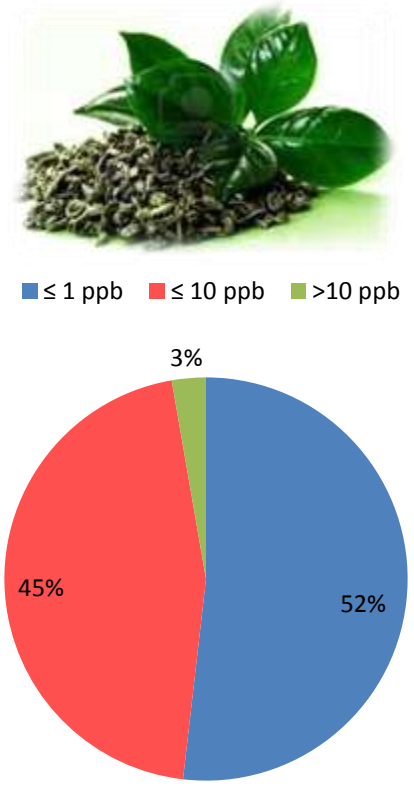
SDL determination according to SANCO12571/2013

vDIA method not available in the United States of America

Results vDIA – Sensitivity Overview Tea

- Screening Detection Limits – Tea matrix





SUM = 330 compounds; 321 compounds SDL ≤ 10 µg/kg

SDL determination according to SANCO12571/2013

vDIA method not available in the United States of America

Missing Compounds at 10 ppb

SDL and MRL values for compounds not seen at 10 ppb

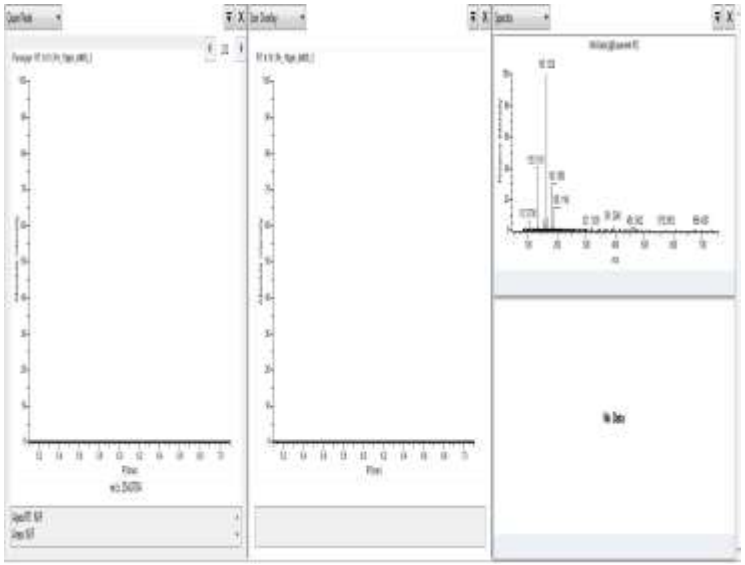
Compound name	SDL [ug/kg] in Honey	MRL for Honey [ug/kg]	SDL [ug/kg] in Tea	MRL for Tea [ug/kg]
Aramite	10	100	>100	n.d.
Bentazone	>100	50	0.5	100
Butafenacil	5	n.d.	60	n.d.
Dimethachlor	50	n.d.	40	20
Fenthion-sulfone	5	10	70	50
Hexaflumuron	3	n.d.	30	n.d.
Isoxathion	50	n.d.	50	n.d.
Mesotrione	>100	n.d.	>100	100
Pyridate	15	50	20	50
Sethoxym	40	50	50	100
Thiazopyr	10	n.d.	50	n.d.

n.d. - not defined

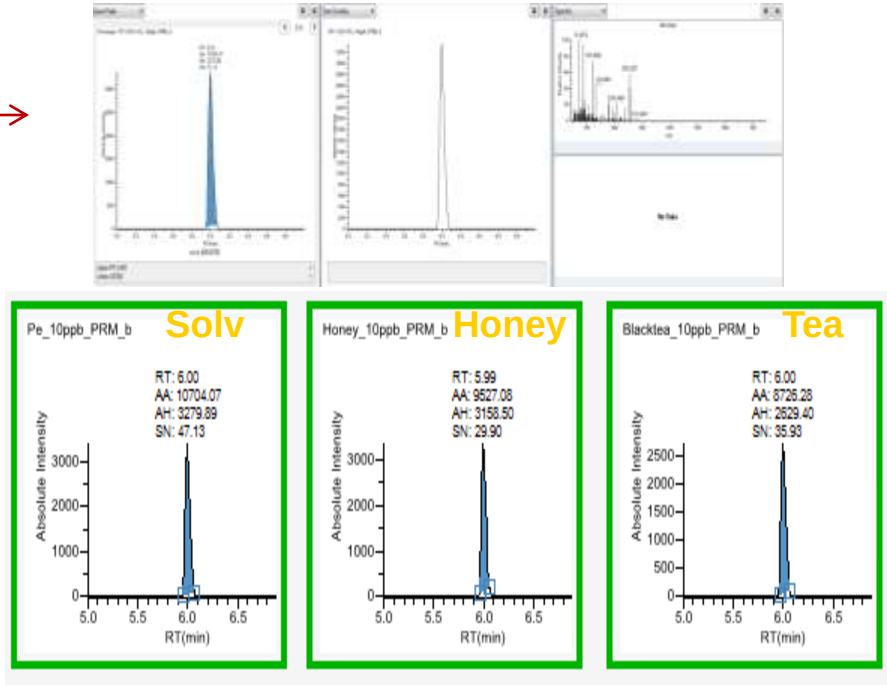
Sensitivity Improvement at MRL – ddMS vs PRM

Most of compounds fulfill EU MRL criteria, but in 16 cases not → PRM recommended

Fluroxypyr 10 ppb ddMS



Fluroxypyr 10 ppb PRM



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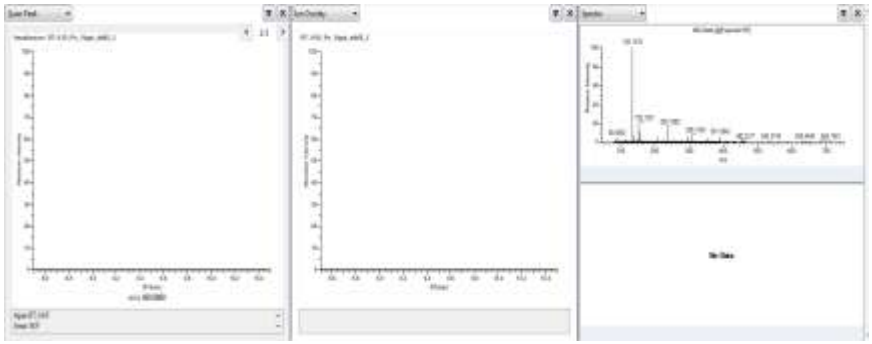
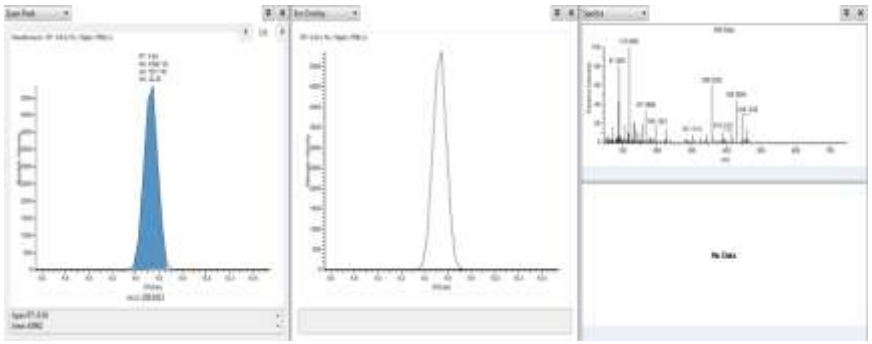
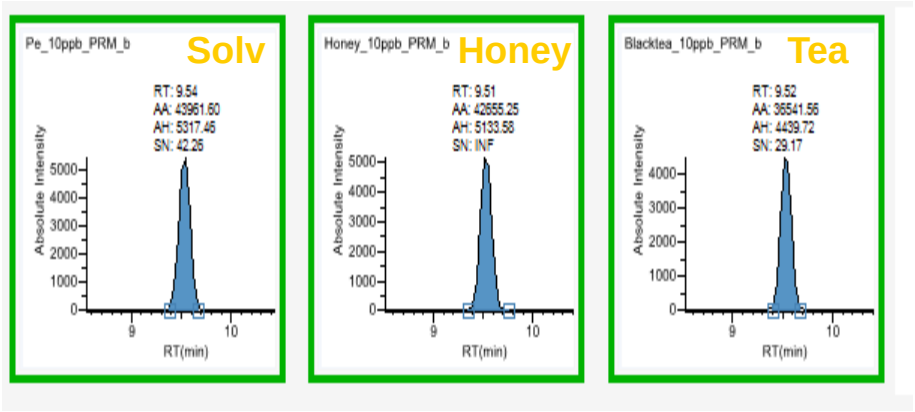
Sensitivity Improvement at MRL – ddMS vs PRM

Hexaflumuron 10 ppb ddMS



Hexaflumuron 10 ppb PRM





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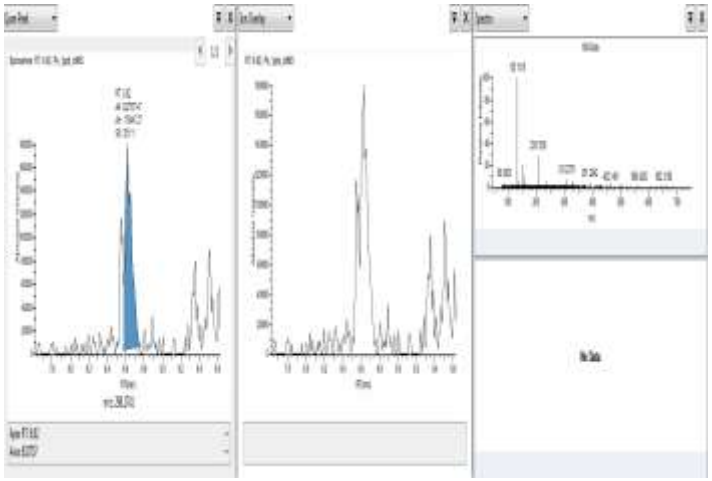
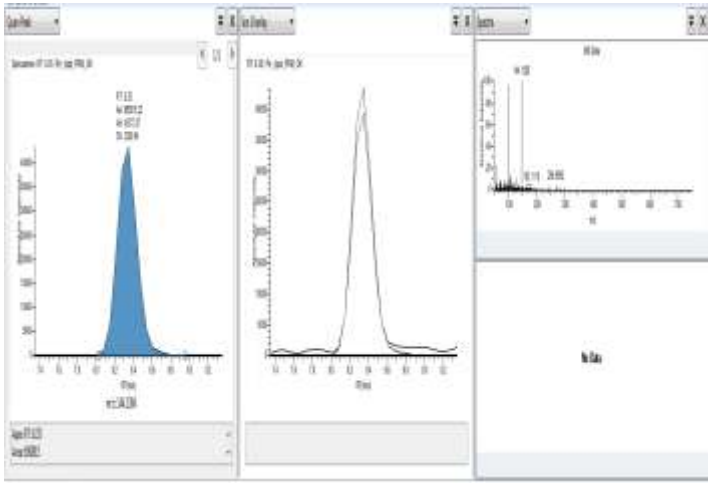
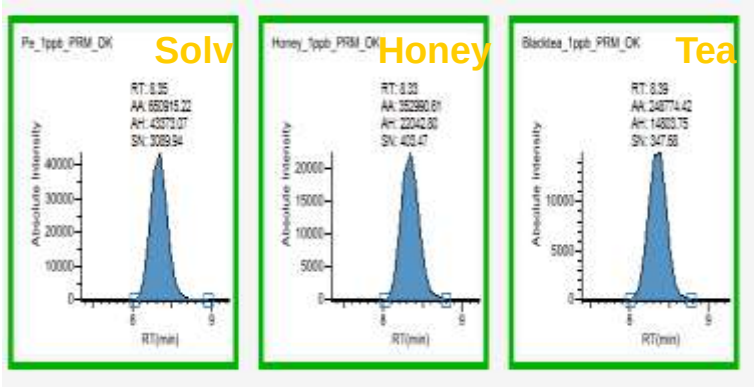
Sensitivity Improvement – With Parallel Reaction Monitoring

Spiroxamine 1ppb in ddMS



Spiroxamine 1ppb in PRM





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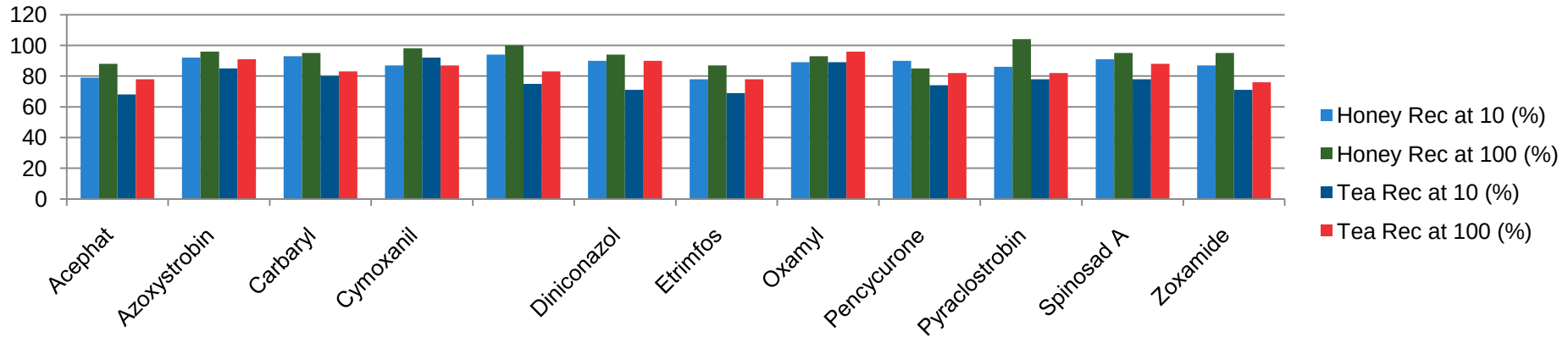
Method Sensitivity For 12 Representative Compounds - vDIA

Analyte	Solvent (µg/kg) LOQ	Honey (µg/kg) LOQ	Tea (µg/kg) LOQ	MRL's (µg/kg) Honey	MRL's (µg/kg) Tea
Acephate	2.5	10	10	20	50
Azoxystrobin	0.25	0.75	1.25	50	100
Carbaryl	0.25	2.5	3	50	50
Cymoxanil	0.25	1.25	5	50	50
Dimetomorph (sum of isomers)	12.5	12.5	25	50	50
Diniconazol	2	2.5	10	50	50
Etrimfos	1.25	1.25	2.5		
Oxamyl	1.25	2.5	5	50	50
Pencycurone	0.25	0.25	1.75	50	10
Pyraclostrobin	0.25	0.25	1.25	50	100
Spinosad A	12.5	12.5	25	50	100
Zoxamide	1.25	1.25	1.75	50	50

vDIA method not available in the United States of America

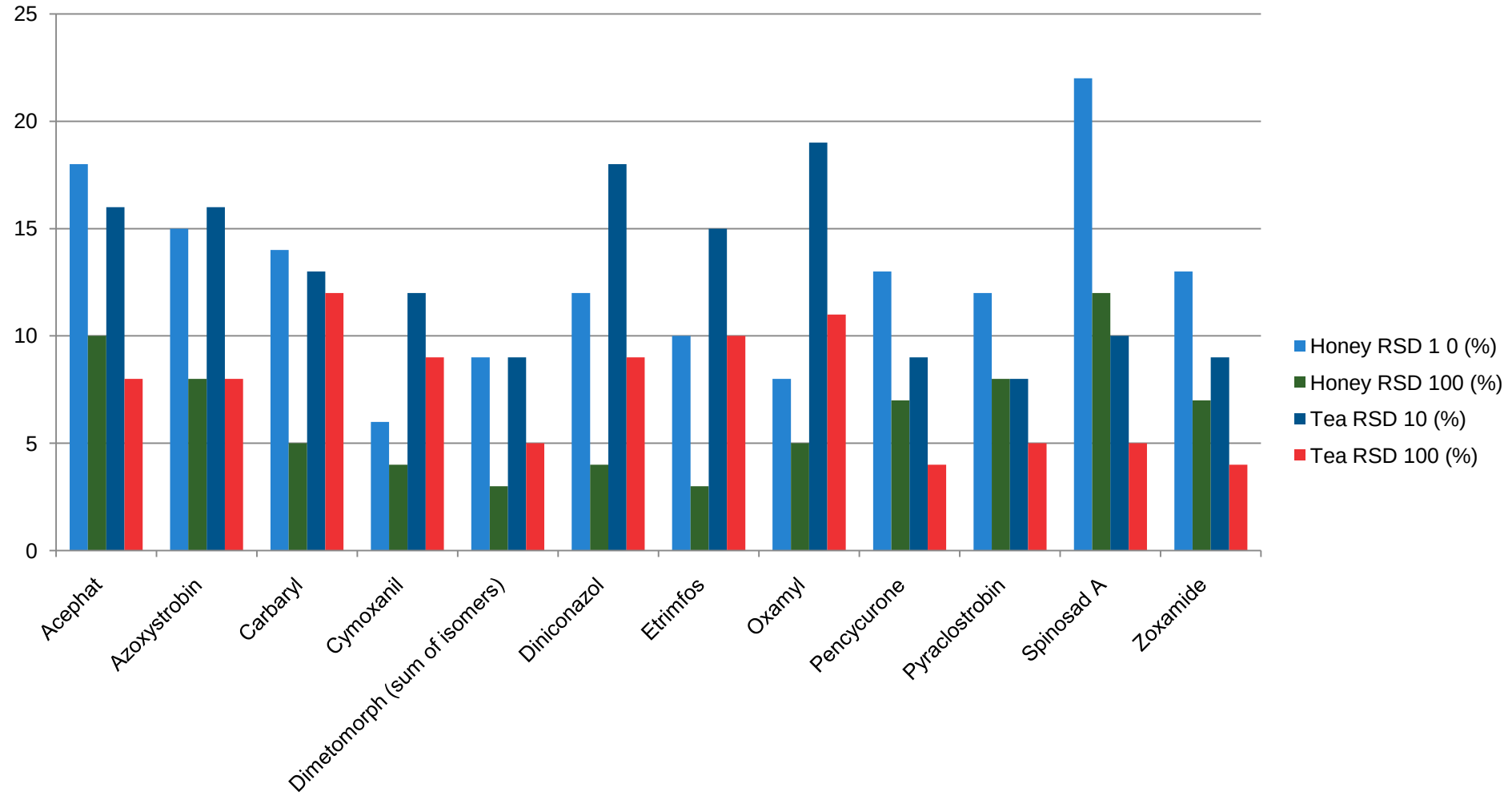
Method Recovery, Repeatability, Linearity - vDIA

Analyte	Sp. Level 1 (µg/kg)	Sp. Level 2 (µg/kg)	Honey RSD 1 (%)	Honey RSD 2 (%)	Honey Rec 1 (%)	Honey Rec 2 (%)	Tea RSD 1 (%)	Tea RSD 2 (%)	Tea Rec 1 (%)	Tea Rec 2 (%)	Linearity in solvent
Acephat	10	100	18	10	79	88	16	8	68	78	0.9902
Azoxystrobin	10	100	15	8	92	96	16	8	85	91	0.9879
Carbaryl	10	100	14	5	93	95	13	12	80	83	0.9906
Cymoxanil	10	100	6	4	87	98	12	9	92	87	0.9894
Dimetomorph (sum of isomers)	10	100	9	3	94	100	9	5	75	83	0.9855
Diniconazol	10	100	12	4	90	94	18	9	71	90	0.9872
Etrimfos	10	100	10	3	78	87	15	10	69	78	0.9992
Oxamyl	10	100	8	5	89	93	19	11	89	96	0.9875
Pencycurone	10	100	13	7	90	85	9	4	74	82	0.991
Pyraclostrobin	10	100	12	8	86	104	8	5	78	82	0.9896
Spinosad A	10	100	22	12	91	95	10	5	78	88	0.9899
Zoxamide	10	100	13	7	87	95	9	4	71	76	0.9913



vDIA method not available in the United States of America

vDIA - Repeatability – For 12 Representatives



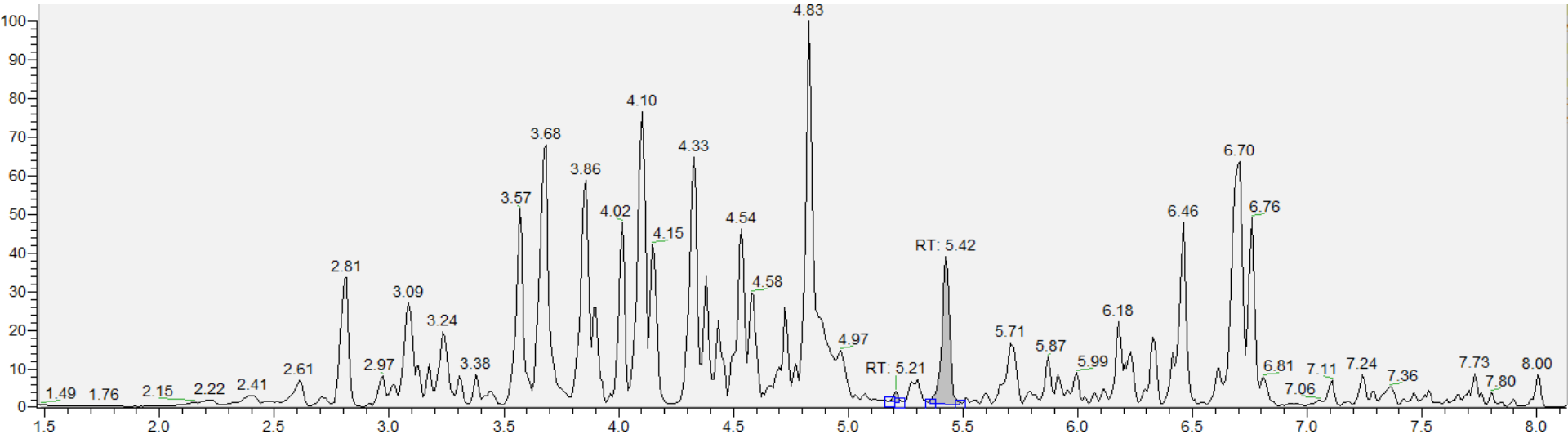
vDIA method not available in the United States of America

Non-target Screening of Food Contaminents

Targeted analysis has its limits… its targeted

How do we detect all the other compounds in a sample?

Do we want/need to detect all compounds in a sample?



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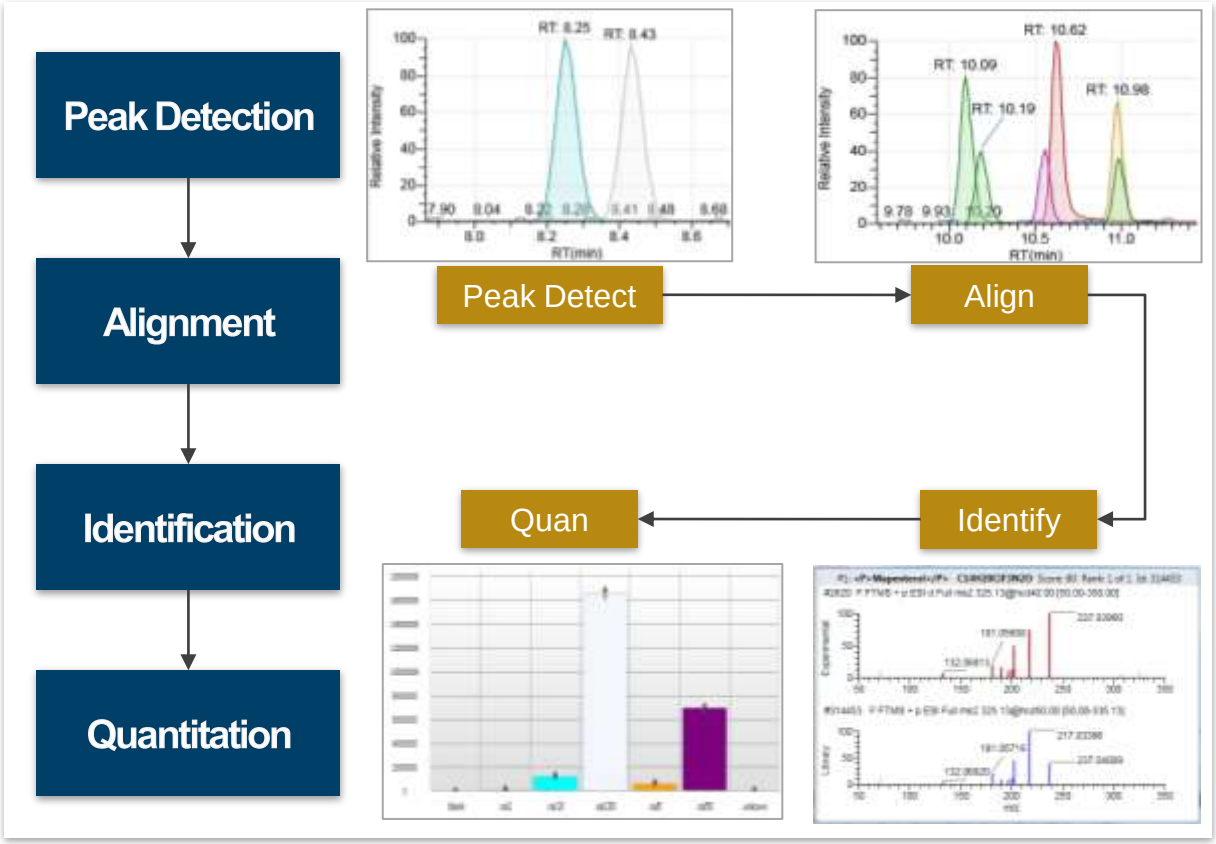
Unknown screening workflow

All-in-One solution

Trace Finder

- Targeted Quan
- Targeted Screening
- Unknown Screening
- Targeted Analysis with Unknown Screening

TraceFinder™
The Power to Know



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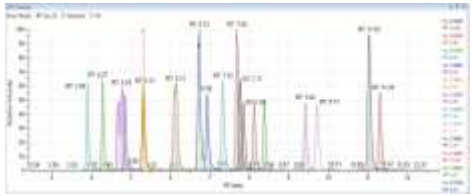
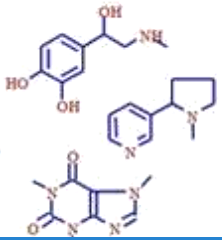
Orbitrap-based Unknown Screening and ID Workflow



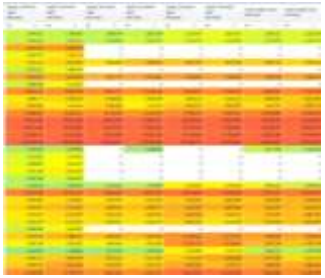
TraceFinder™
The Power to Know

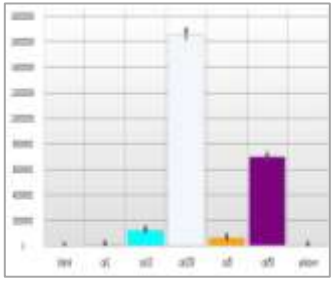
Chemspider: 高针对性的食品安全、环境污染、药物毒物数据库

mzCloud



mzVault: 契合离线mzcloud数据库的高准确性风险物质鉴定谱库





差异未知风险物质定量、半定量统计分析手段

HRAM MS/MS Library

Introducing The EFS HRAM MS/MS Spectral Libraries:

- OPTON-30386 EFS HRAM MS/MS Spectral Library 1.0

EFS	No. of Spectra
Pesticides	698
Veterinary Drugs	108
Emerging Contaminants	756
PFCs	21
Mycotoxins	44

Food authentication challenges

- Chemically identical foods or identical chemical entities
- Unique marker compounds rarely found - more often small analytical differences (isotopic patterns)
- Large natural variability based on climatic conditions, fertilizers used, variety, processing……
- Techniques must be able to distinguish small differences

- Protected Designation of Origin (PDO)
  covers agricultural products and foodstuffs which are produced, processed and prepared in a given geographical area using recognized know-how.

- Protected Geographical Indication (PGI)
  covers agricultural products and foodstuffs closely linked to the geographical area. At least one of the stages of production, processing or preparation takes place in the area.

- Traditional Speciality Guaranteed (TSG)
  highlights traditional character

http://ec.europa.eu/agriculture/quality/

Council Regulation (EC) No 510/2006 of 20 March 2006

Council Regulation (EC) No 509/2006 of 20 March 2006

Food Fraud

Why Adulterate

- Mainly for financial gain
- Improve perceived quality attributes
- Brand / product substitution
- Reduce manufacturing cost

May also be malicious

- Reputation damage
- Terrorism

Top Adulterated Matrix:

Milk, Olive Oil, Honey, Orange Juice, Coffee, Seafood, Flour, Meat

High Profile Food Fraud

Olive Oil Authenticity

Determination of Olive Oil Adulteration by Principal Component Analysis with HPLC–Charged Aerosol Detector

Orange Juice Adulteration

Fruit Juice Adulteration Notebook

Melamine in Milk

- AN424:Simple and Rapid Screening of Melamine in Milk Products with LC-MS
- AN502:Determination of Melamine in Powdered Milk by LC-MS/MS Using a Core Enhanced Technology Solid Core HPLC Column

Honey

Isotope Ratio Mass Spectrometry: Authenticity Control, Fraud And Forensices In Food -

Food Fraud Analysis Solutions

Fingerprinting
- GC-MS,LC- QQQ, Exactive/QE, Orbitrap
- IC, LC, GC, LC

Authenticity
- IR-MS, IC, LC, GC with MS

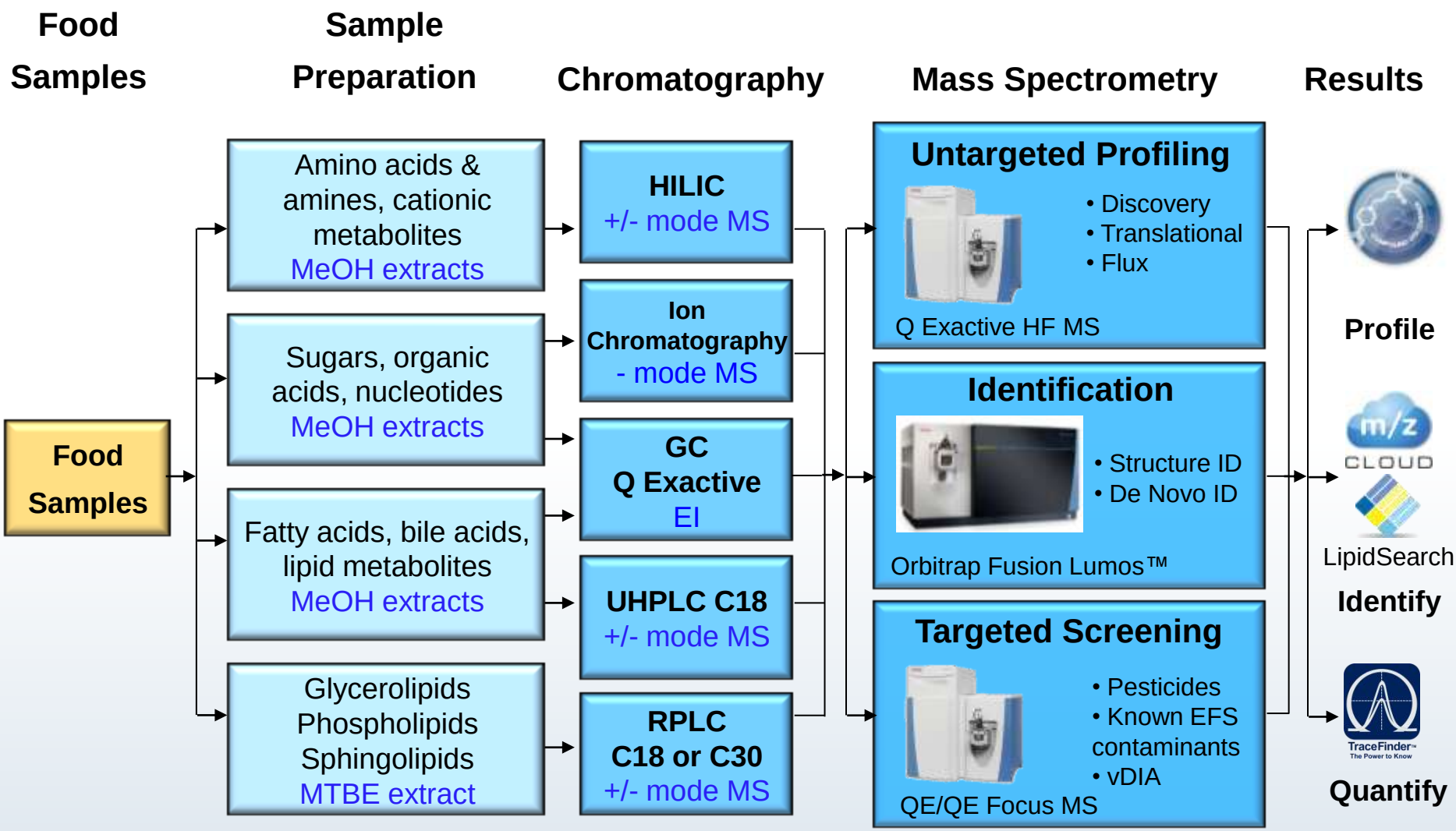
Targeted Analysis
- GC-MS,LC- QQQ, Exactive/QE, Orbitrap
- IC, LC, GC, LC

Omics Technology
- IC-MS, GC-MS,LC, Exactive/QE, Orbitrap

Non-Targeted Analysis
- GC-MS,LC- QQQ, Exactive/QE, Orbitrap

Elemental Analysis
AA and emission spectroscopy, ICP/MS

Comprehensive Workflow for Foodomics Analysis



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Hot Topics Food Fraud

- Olive oil
- Wine adulteration
- Halal food testing
- General untargeted screening for adulterants
- Country of origin (COO)
  - Isotope Ratio Mass Spectrometry: Authenticity Control, Fraud And Forensics In Food
- Honey
  - AN30177:Detection of Honey Adulteration with FlashEA Elemental Analyzer and DELTA V Isotope Ratio Mass Spectrometer

UHPLC-HRMS UNTARGETED METABOLOMICS APROACH APPLIED TO THE AUTHENTICATION OF ALCOHOLIC BEVERAGES

C. Martins; A. Checa; H. Gallart-Ayala; O. Núñez; X. Saurina; S. Hernández-Cassou

INTRODUCTION

E-Bacchus Database: http://ec.europa.eu/agriculture/markets/wine/e-bacchus/

As of May 2012

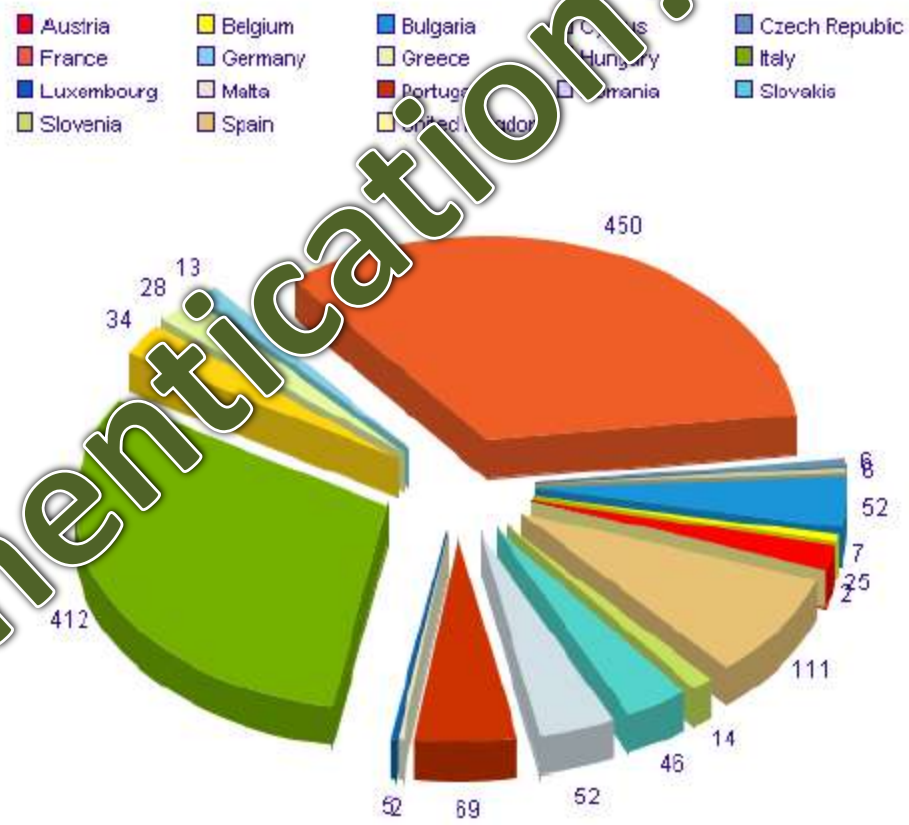
PROTECTED DESIGNATION OF ORIGIN – WINE

Statistics - Wine with a protected designation of origin (PDO)

Total of the geographical indications: 1334

Details

- Austria: 25
- Belgium: 7
- Bulgaria: 52
- Cyprus: 6
- Czech Republic: 6
- France: 450
- Germany: 13
- Greece: 28
- Hungary: 34
- Italy: 412
- Luxembourg: 5
- Malta: 2
- Portugal: 69
- Romania: 52
- Slovakia: 46
- Slovenia: 14
- Spain: 111
- United Kingdom: 2



Authentication?

INTRODUCTION

Analytical methodologies in food authentication

- LC (UV, FLD)
- LC-MS
- NMR
- CE-MS

METABOLOMIC

- ELECTRONIC NOSE
- AAS/ICP-MS (Mineral profile)
- IR
- UV-spectra
- Stable isotope analysis
- IMS….

INTRODUCTION

METABOLOMIC

Comprehensive analysis of low molecular weight compounds (< 1000 Da) in a biological sample

TARGETED METABOLOMIC

Measurement of defined groups of chemically characterized metabolites

Advantages: Sensitivity

Disadvantages: Discriminant compounds can remain undetected

UNTARGETED METABOLOMIC

Comprehensive analysis of all the measurable analytes in a sample including chemical unknowns

Advantages: Wider spectra of compounds detectable

Disadvantages: Sensitivity

EXPERIMENTAL CONDITIONS

Sample Treatment

Beer and wine samples were diluted with water 1:1

Liquid Chromatography

Column: Hypersil Gold aQ (100 mm x 2.1 mm ID, 1.9 µm)

Mobile Phase: ACN:0.1% Formic Acid

Flow: 600 µL min^{-1}

Mass Spectrometry

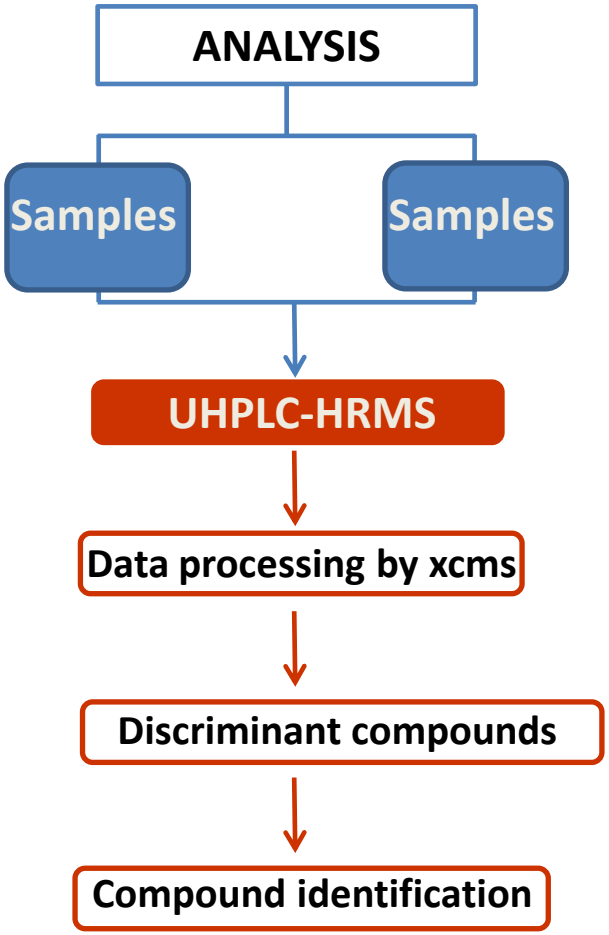
LTQ-Orbitrap Velos

ESI (+) and (-)

Mass Resolving Power: 60,000 FWHM

Acquisition mode: Scan event 1: Full scan

Scan event 2: MS/MS using CID



CASE STUDY

Spanish wines classification

Spanish wine classification

Wine composition

→ Water, Alcohols, Sugars, Polysaccharides, Aminoacids, Biogenic amines, Organic acids, Phenolic compounds, Metals

Factors that affect wine composition

→ Climate

→ Grape growing area

→ Grape variety

→ Winemaking process

Can we differentiate between PDO?

2.a

Two class comparison
Somontano vs Rioja wines

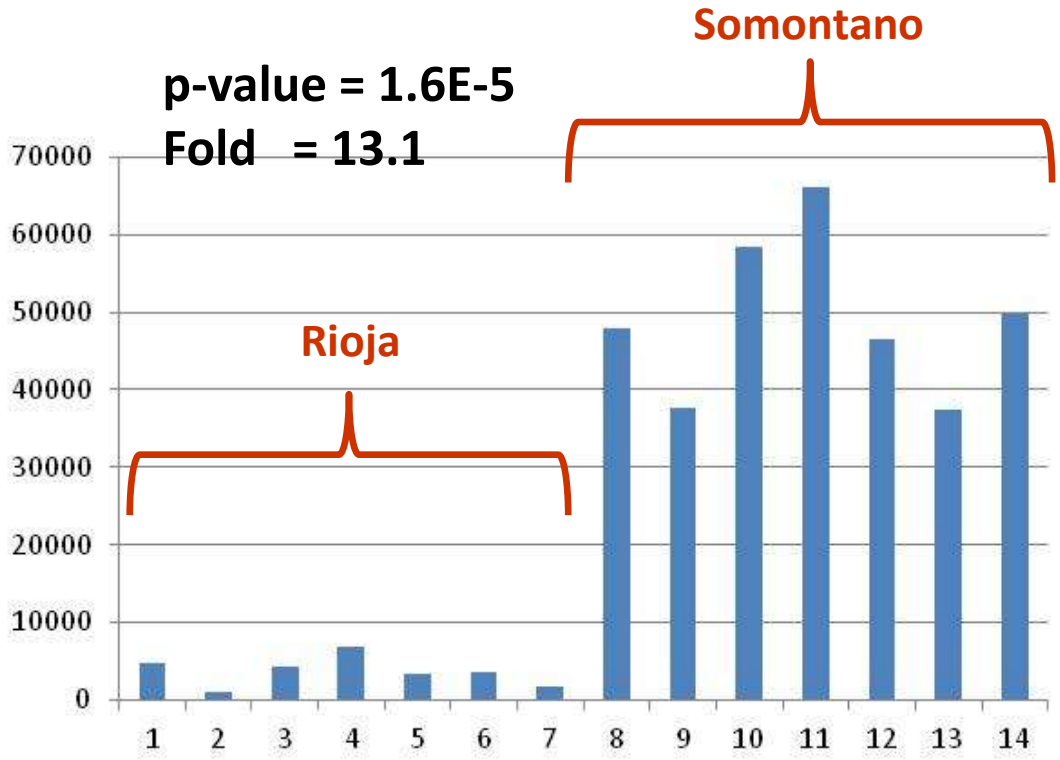
POTENTIAL DESCRIPTORS

ESI (-)

14 PEAKS DETECTED WITH XCMS

6 POTENTIAL DISCRIMINANT COMPOUNDS

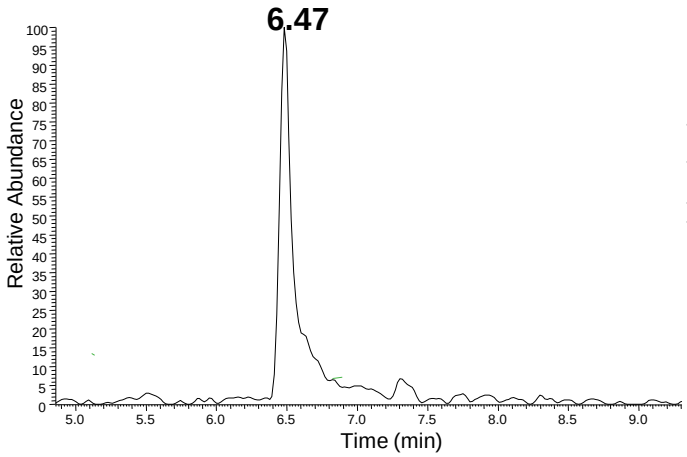
Name	*m/z* value	Retention time (sec)	Elemental composition	RDB value	Mass error (ppm)
M301T334	301.0343	334	C15H9O7	11.5	-3.71
M151T334	151.0030	334	C7H3O4	6.5	-4.12



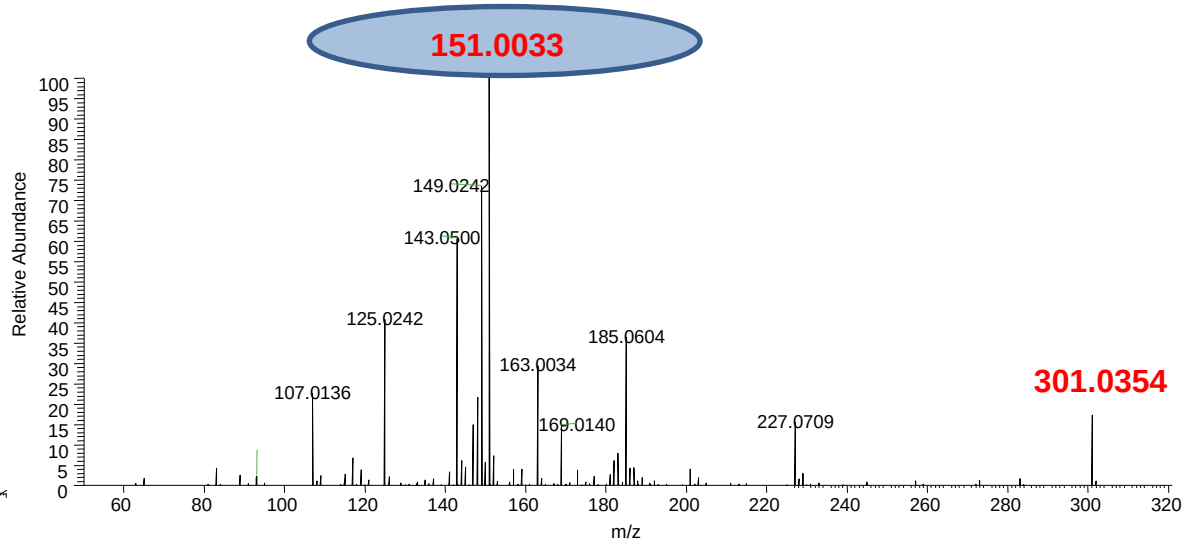
POTENTIAL DESCRIPTORS

ESI (-)

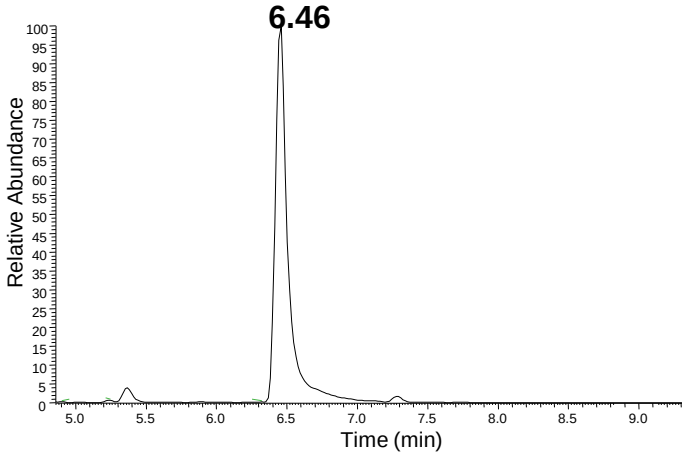
Somontano wine

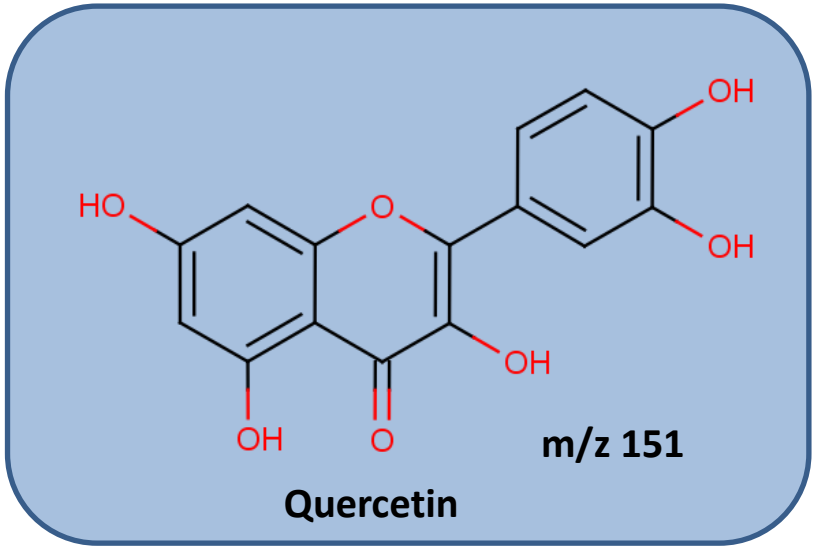


All Ion Fragmentation MS/MS



Quercetin standard





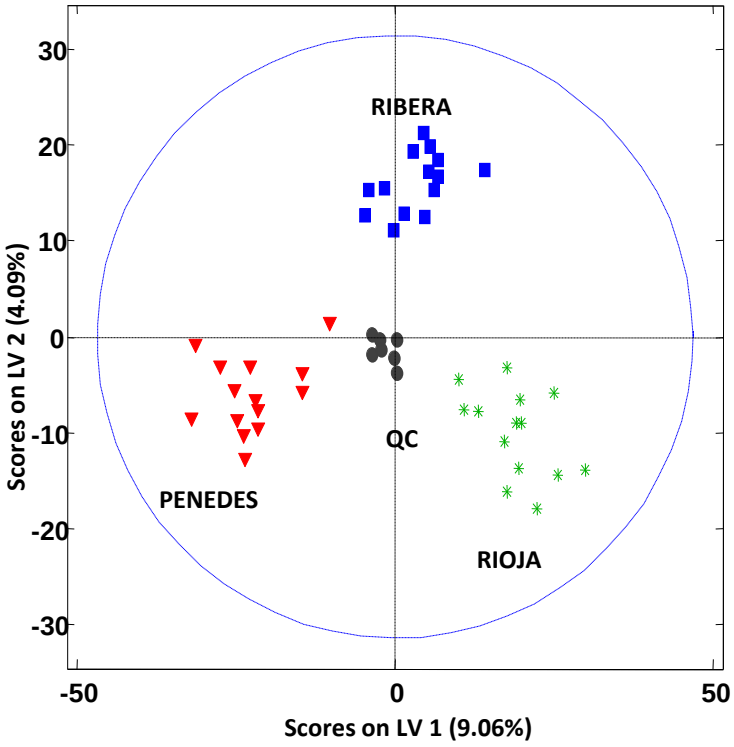
2.b

Multi-class comparison
Penedes vs Ribera vs Rioja wines

Spanish wines classification

Positive mode

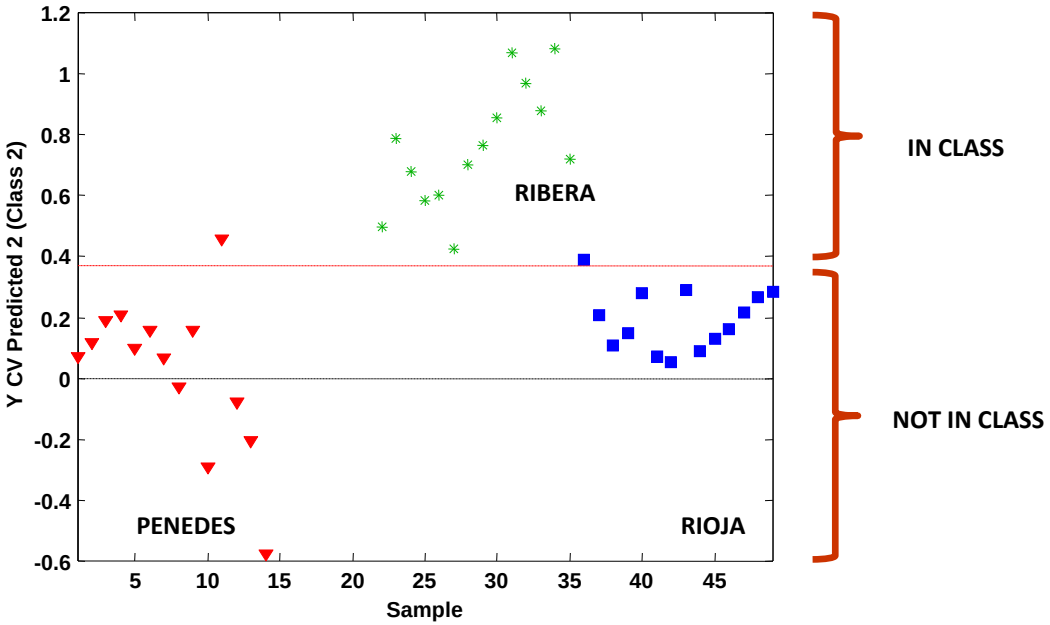
PLS-DA



3 Latent Variables

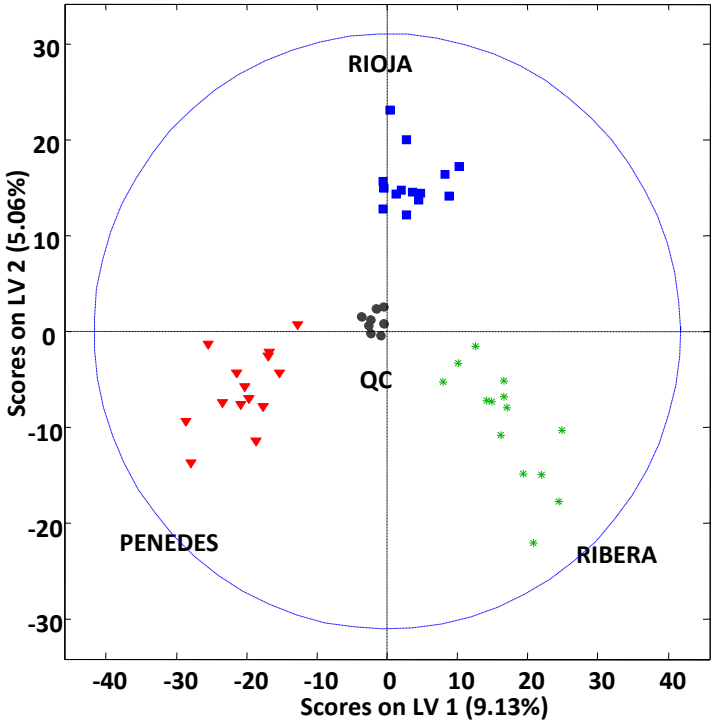
	PENEDES	RIBERA	RIOJA
R^2	0.95	0.91	0.94
Q^2	0.62	0.63	0.54
FP (CV)	0	2	0
FN (CV)	1	0	1

LEAVE ONE OUT CROSS-VALIDATION

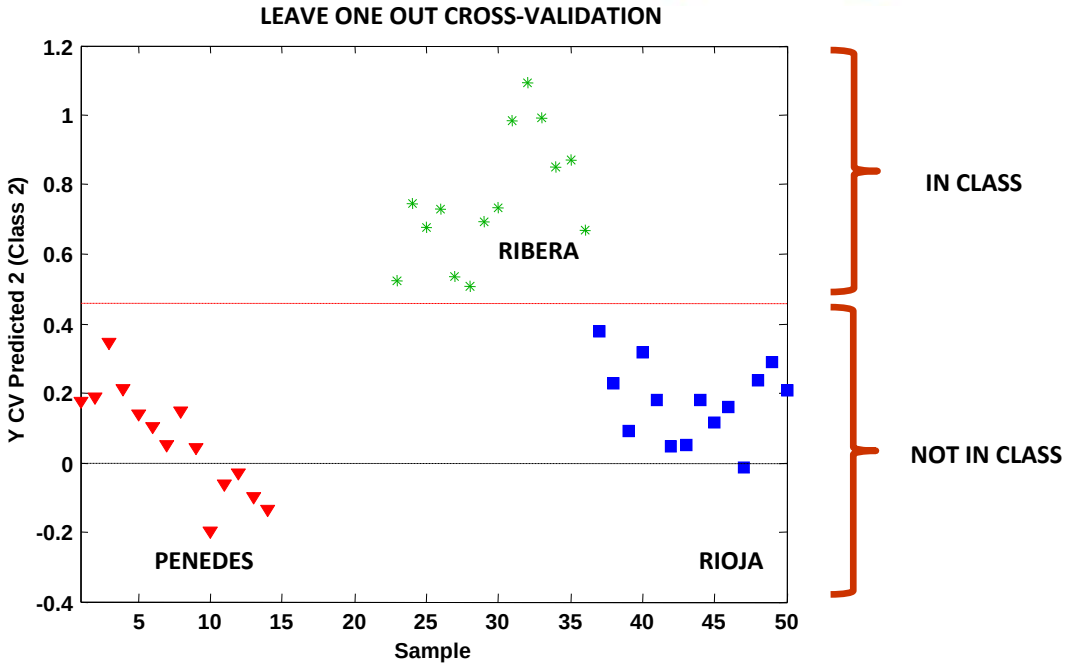


Spanish wines classification

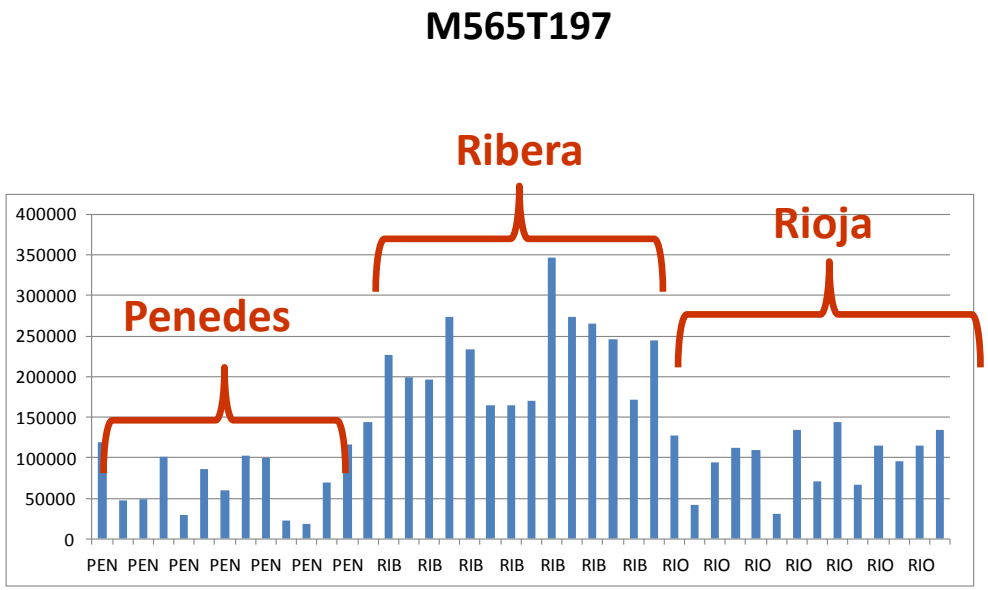
Negative mode 3 Latent Variables

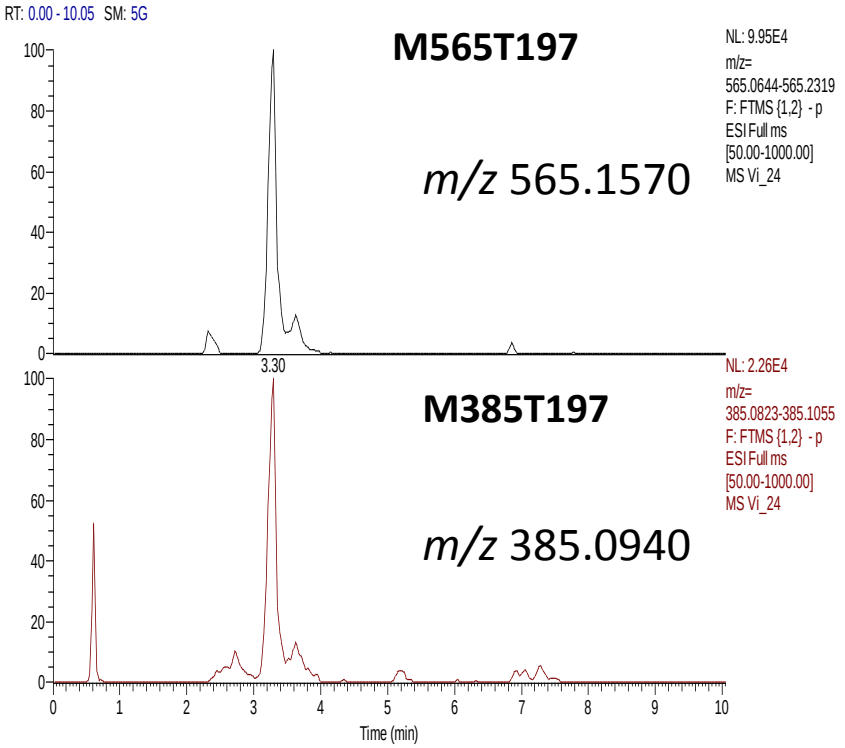


	PENEDES	RIBERA	RIOJA
R^2	0.93	0.92	0.93
Q^2	0.86	0.78	0.74
Specificity(CV)	1.00	1.00	1.00
Sensitivity (CV)	1.00	1.00	1.00



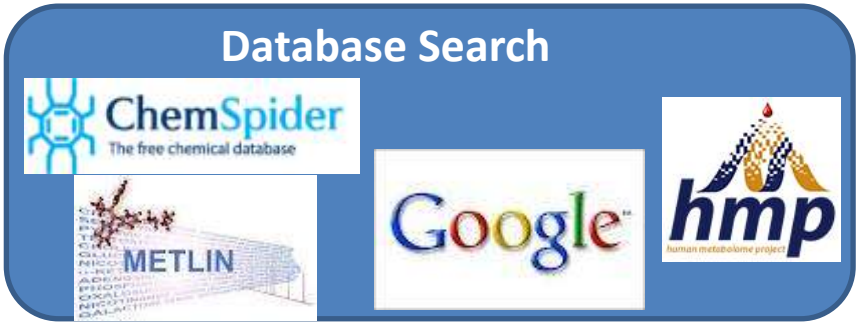
Spanish wines classification

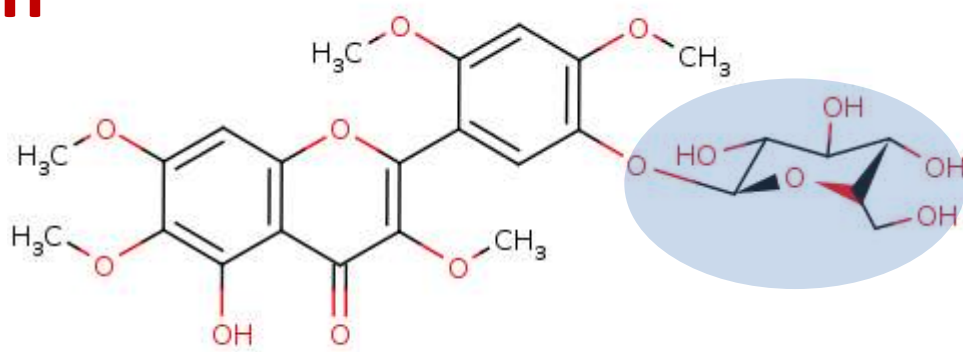




Spanish wines classification

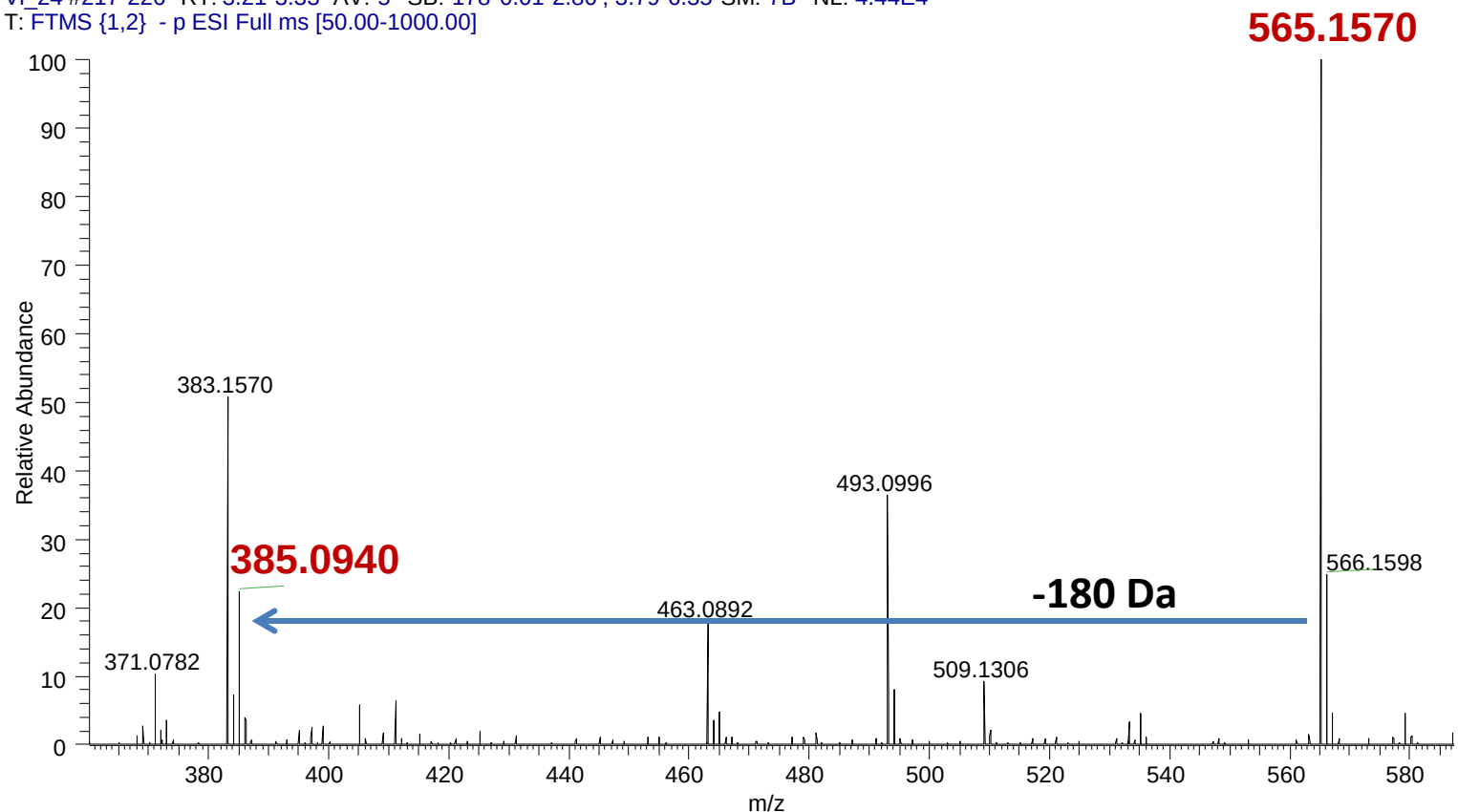
Compound identification



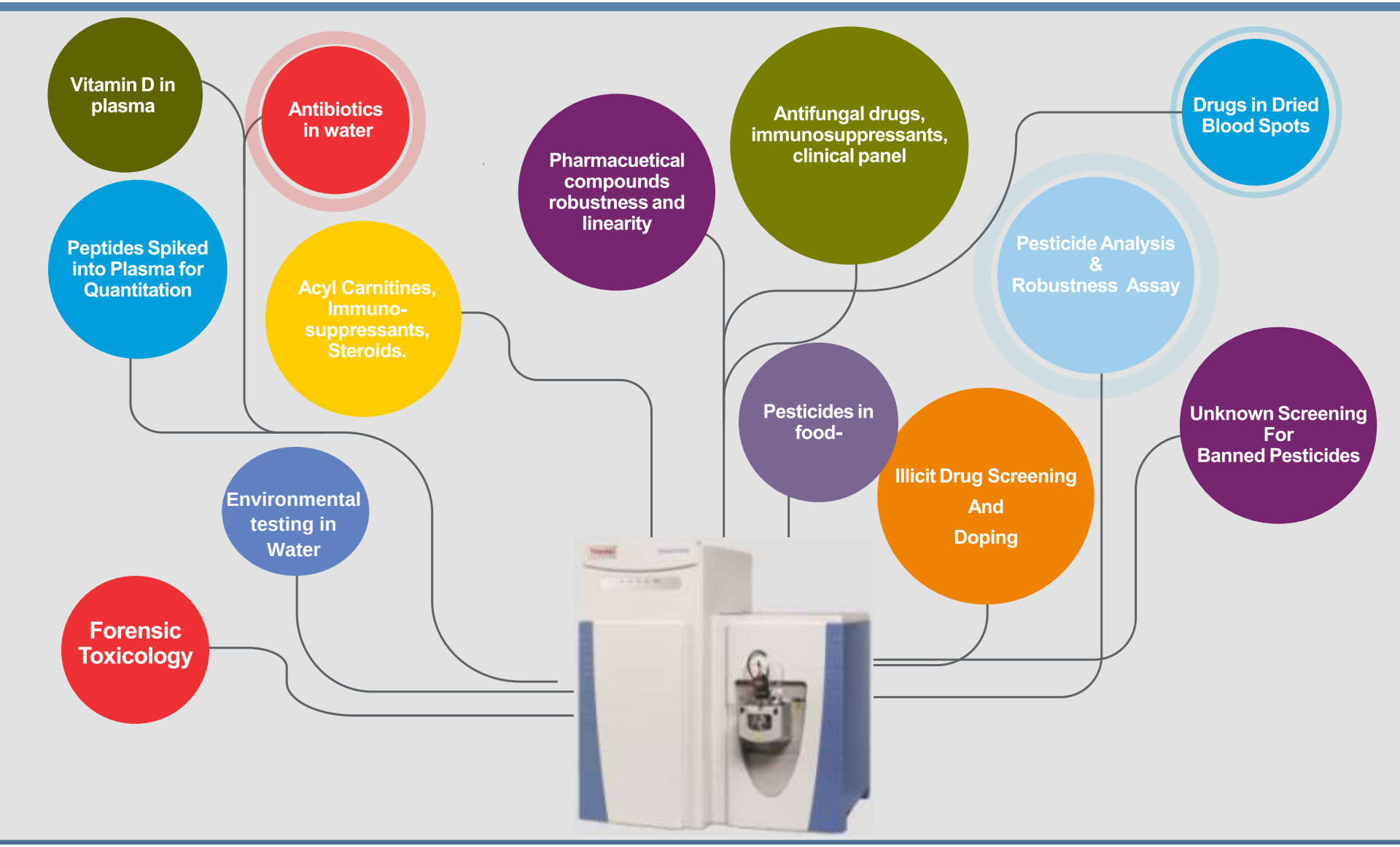


5,5'-Dihydroxy-3,6,7,2',4'-pentamethoxyflavone 5'-glucoside

Vi_24 #217-226 RT: 3.21-3.33 AV: 5 SB: 178 0.01-2.80 , 3.79-6.35 SM: 7B NL: 4.44E4
T: FTMS {1,2} - p ESI Full ms [50.00-1000.00]



Q Exactive Focus Applications Universe



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Transform Your Science