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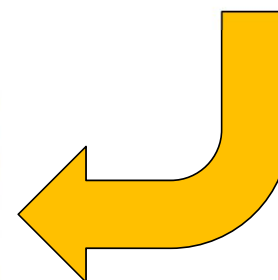
Routine Multi-Pesticide Residue Analysis by Orbitrap MS Technology

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CMD Sales Support Specialist
MECEC , Dubai

The world leader in serving science

Challenges of Pesticide-Residues Analysis

- Sample variability (matrix)
- Different compound characteristics
- Large number of samples
- Hundreds of analytes monitored
- Low levels controlled
 - Baby food
(MRL for all pesticides = 0.01 mg/kg)
- Fast response required



Former Pesticide Multi-Residue Method Setup



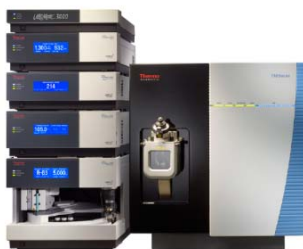
■ Extraction

Acetonitrile, Ethyl acetate, Methanol...



■ Clean-up

GPC, SPE, LLE, LC



■ Determination

GC, LC, GC-MS, LC-MS, GC-MS/MS, LC-MS/MS...

Mostly replaced
by **QuEChERS**
today



Thermo Scientific™ QuEChERS™
method

Simplified Extraction Procedure Applied



10 g of sample is weighed into Quechers extraction tube

+ 20 mL of water

+ 10 mL of ACN

shaking 10 min

Centrifugation 5 min @ 5000 rpm

Injection to LC-HRAM

Consumables Used

Consumables/Chemicals	Part Number
Acetonitrile	A/0638/17
QuEChERS extraction tube, 50 mL, 250 pack	60105-216
QuEChERS pouches, 50 pack	60105-344

Apparatus/Columns	Part Number
Horizontal shaker	1069-3391
Horizontal shaker plate	1053-0102
Thermo Scientific™ Barnstead™ EASYpure™II water	3125753
Thermo Scientific™ Heraeus™ Fresco™ 17 micro centrifuge	3208590
Thermo Scientific™ Accucore™ aQ column 100x2.1, 2.6 μm	17326-102130

www.thermoscientific.com/chromatography

Improving QuEChERS Extraction Tips & Tricks:

- **Dry food (cereals/dried food, < 25 % water content):**
 - Addition of water to enable adequate partitioning and reducing interaction of pesticides with matrix
- **Food containing fat/wax (avocado/oil):**
 - After extraction step add a freezing out step and transfer supernatant to clean-up tube
 - More clean-up might be needed of raw extract (PSA+C18)
- **Food containing complex matrix (tea/spices)**
 - Additional clean-up with GCB might be necessary (potential loss of planar structure pesticides like thiabendazole)
- **Acidic food (citrus):**
 - Adjust pH (5-5.5) to increase recovery (e.g. citrate buffering salts in QuEChERS extraction tube) and reduce coextraction of matrix interferences (Note: acid labile compounds require higher pH 8)



Improving QuEChERS Clean-up Tips & Tricks:

- **QuEChERS clean-up tube additives:**

Product Selection

Matrix Type	Examples	Sorbent Requirements
General Matrices	Apples Cucumber Melon	Magnesium Sulfate, PSA
Fatty Matrices	Milk Cereals Fish	Magnesium Sulfate, PSA, C18
Pigmented Matrices	Lettuce Carrot Wine	Magnesium Sulfate, PSA, C18, GCB
High Pigmented Matrices	Spinach Red Peppers	Magnesium Sulfate, PSA, C18, GCB

[Click here for more information](#)

How To Use QuEChERS ?

Productivity simplified

Video Library
Pesticide Analysis

Would you like to speak with an expert?

Yes, I would like to speak with an expert to learn how Thermo Scientific products can help maximize productivity in my laboratory.

Please Contact Me

Search:

Filter by:

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previous **1** next

Sample Preparation Tips to Improve Your Pesticide Anal...

Sample Preparation Tips To Improve Your Pesticide Analysis
Presented by Ebru Sarikaya

Link to video

Pesticide Analysis by HRMS



Start-to-finish
workflows for pesticide analysis

Configuration and complete start-up kit provides everything needed to perform robust, high resolution routine workflows for rapid screening and quantitation of pesticides, from the QuEChERS sample extraction kit to proven multi-class pesticide residue analysis methods.



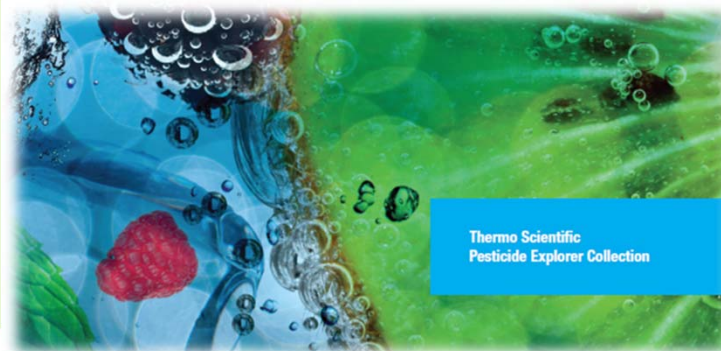
Thermo Scientific™ Q Exactive™ Focus MS



Pesticide Explorer Collection – Software Package

Quantitation Package

- Thermo Scientific™ TraceFinder™ 4.1 software
- EFS HRAM MS/MS Spectral Library 2.0
- USB (Methods and User guide)



- **Pesticide Explorer Collection comes with the software installation instructions as you open the box. It is an easy to follow guide that walks you through the process from installation to activation of the software.**
- **Pesticide Explorer Collection also comes with an usb drive which includes a Method Installation guide as well as methods and libraries. This document outlines the necessary steps that will be needed to install the Pesticide methods and it's library within TraceFinder software as well as using TraceFinder software.**

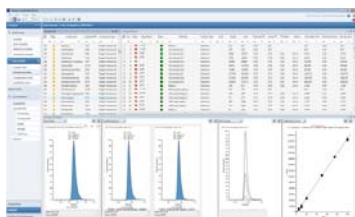
Total Pesticide Solution Workflow



QuEChERS sample preparation kits



Thermo Scientific™ Q Exactive™
Hybrid Quadrupole-Orbitrap Mass
Spectrometer

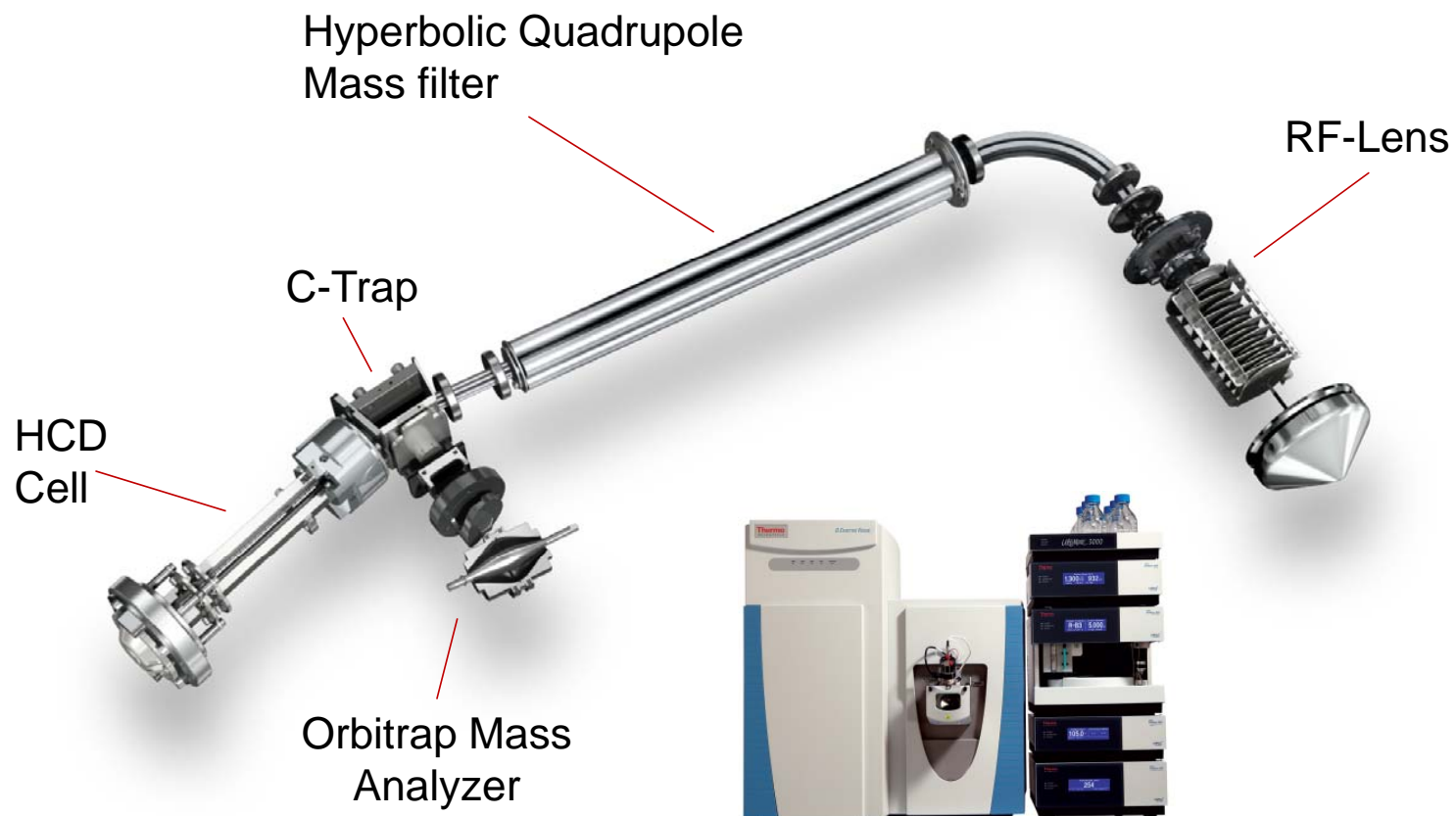


TraceFinder Data Processing

On-site method
by experienced
Special Solutions
Center chemists



Q Exactive Focus – What is New?



3 Ways of Quantitation/Screening 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*

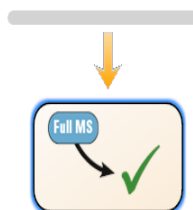
- Post-acquisition - extracted ion chromatograms of parent ions of interest
- Scheduled target (inclusion) list (Rt, m/z)
- Minimum method development (e.g., predefine parent ions, tr)
- Also for screening purposes

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

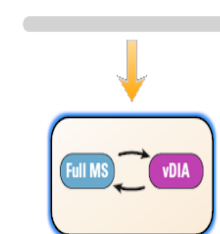
Experiments

- General
- Full MS
- SIM
- PRM
- Full MS - AIF
- Full MS - vDIA



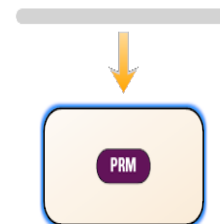
Experiments

- General
- Full MS
- SIM
- PRM
- Full MS - AIF
- Full MS - vDIA

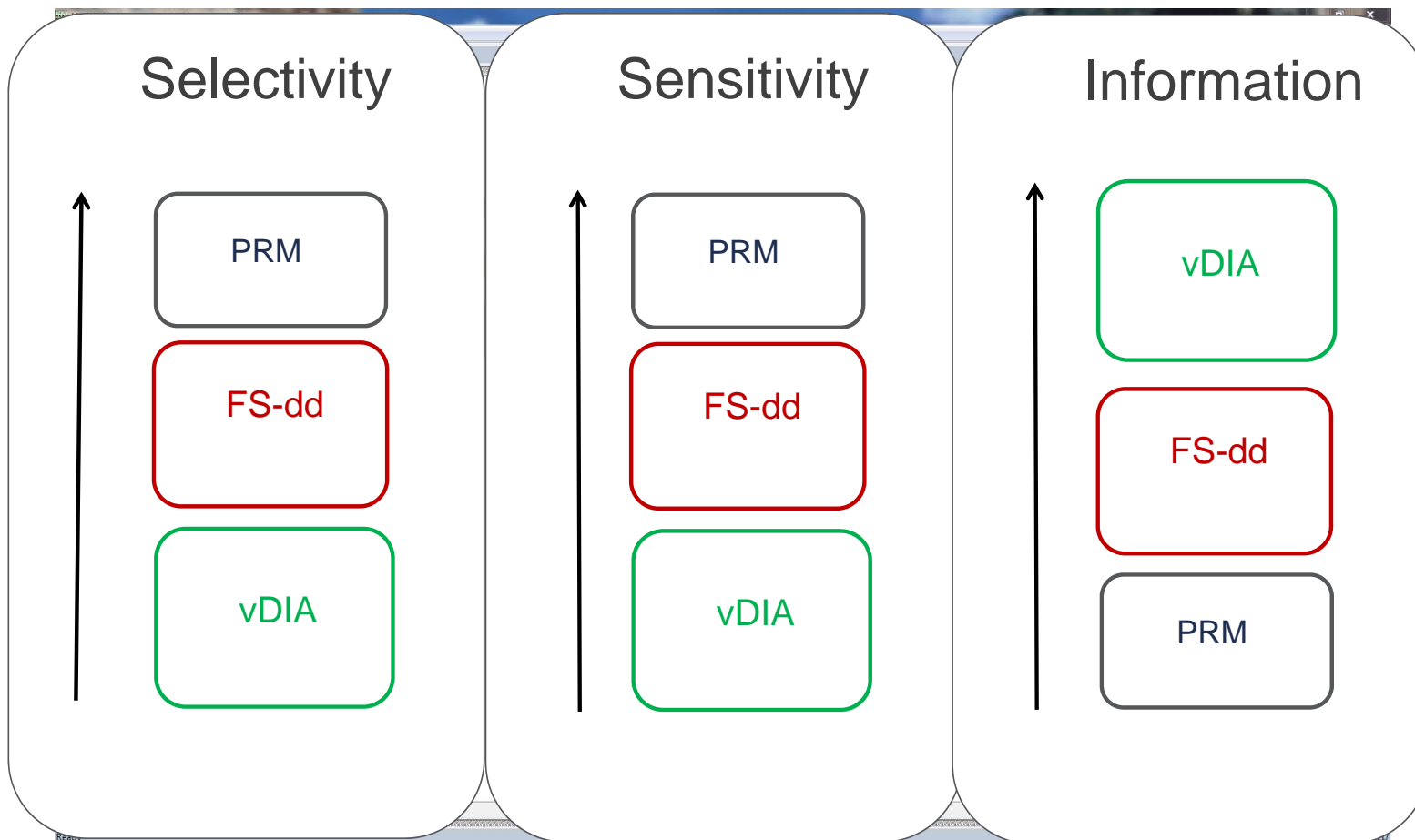


Experiments

- General
- Full MS
- SIM
- PRM
- Full MS - AIF
- Full MS - vDIA



Q Exactive Focus Scan Methods



vDIA method not available in the United States of America

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 μ l**

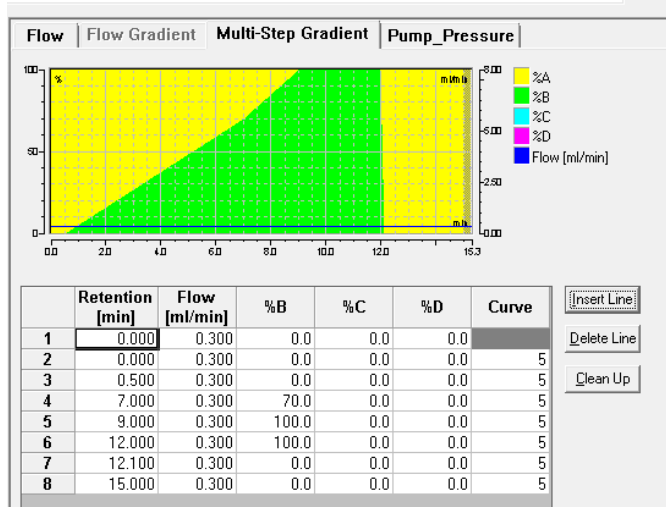
- Column: Accucore aQ column 100 mm x 2.1 mm x 2.6 μ m

- Column temperature: 25°C

- Flow rate: 300 μ l/min

- Run time: 15 min

- Gradient:



Thermo Scientific™ UltiMate™ XRS LC

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 <input type="checkbox"/> 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 <input type="checkbox"/> Hot link		

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 Exclusion	—

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 range	50 to 150 m/z
vDIA isolation range	140 to 240 m/z
vDIA isolation range	230 to 330 m/z
vDIA isolation range	320 to 420 m/z
vDIA isolation range	410 to 510 m/z
vDIA isolation range	500 to 600 m/z
vDIA isolation range	590 to 690 m/z
vDIA isolation range	680 to 780 m/z
CE / stepped CE	30, 50, 70
Fixed first mass	—
AGC target	5e5
Spectrum data type	Centroid

Targeted 330 Compounds – vDIA Screening Method

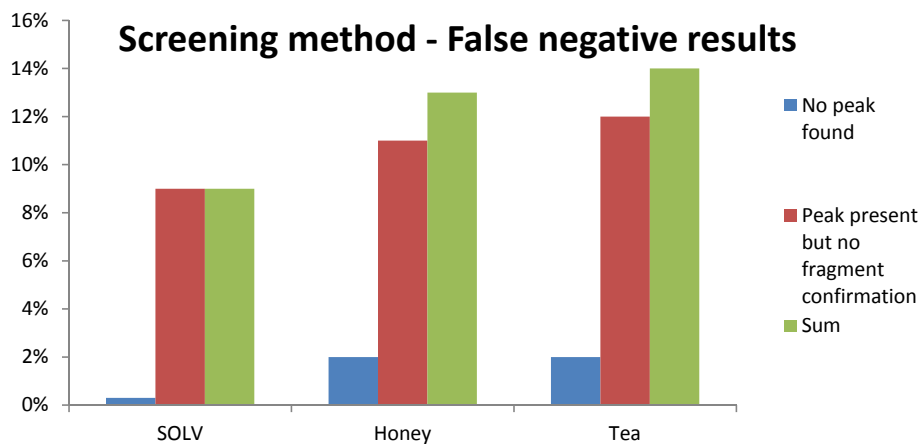
Acephate	Bromacil	Cumyluron	Dinotefuran	Fenthion-sulfone	Heptenophos	Methabenzthiazuron	Penconazole	Pyridaben	Thiacloprid
Acetamiprid	Bromuconazole	Cyanazine	Dioxacarb H	Fenthion-sulfoxide	Hexaconazole	Methamidophos	Pencycuron	Pyridate e	Thiamethoxam
Acibenzolar-S-methyl	Bupirimate	Cyazofamid	Disulfoton	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	Fonicamid T	Imazalil	Methiocarb-sulfone	Phoxim	Quinoxifen	Thiodicarb
Aldicarb	Butocarboxim	Cymoxanil	Epoxiconazole	Florasulam	Imazaquin	Metholcarb	Picoxystrobin	Quizalofop T	Thiofanox
Aldicarb sulfone	Butoxy-carboxim	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	Isophos	Metosulam	Pretilachlor	Sethoxydim	Triazophos
Anilofos	Carbosulfan	Desmedipham	Ethirimol	Fluopicolide	Isopropcarb	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
Azamefthios	Chlorantraniliprole	Dichlorvos	Etozaxole	Flurochloridone	Isoxadifen-ethyl	Mevinphos	Prometon	Spiroxamine	Trifloxystrobin
Azinphos-ethyl	Chlorbromuron	Diclobutrazol	Etrifos	Fluroxypr	Isoxaflutole	Mexacarbate	Prometryn	Sulfotep	Triflumizole
Azinphos-methyl	Chlorfenvinphos	Dicrotophos	Famoxadone	Flusilazole	Isoxathion	Monocrotophos	Propamacarb	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	Vamidotion
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	Terbutylazine	DNOC (neg)
Benzoylprop-ethyl	Clomazone	Dimethoate	Fenoxycarb	Furathiocarb	Mesotrione	Omthoate	Pymetrozine	Terbutryn	Fluazinam (neg) H
Bifenazate	Clopyralid	Dimethomorph	Fenpiclonil	Griseofulvin	Metalaxyl	Oxadixyl	Pyraclostrobin	Tetraclorvinphos H	Flubendiamide (neg)
Bitertanol	Clothianidin	Dimetilan	Fenpyroximate	Halofenozide	Metamitron	Oxamyl	Pyrazophos	Tetraconazole	MCPA (neg)
Boscalid	Coumaphos	Dimoxystrobin	Fensulfthion	Haloxypop	Metazachlor	Oxyfluorfen	Pyrethrin I	Tetramethrin	Tepraloxymid (neg)
Brodifacoum	Crotoxyphos	Diniconazole	Fenthion	Haloxypop-methyl	Metconazole	Paclbutrazol	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

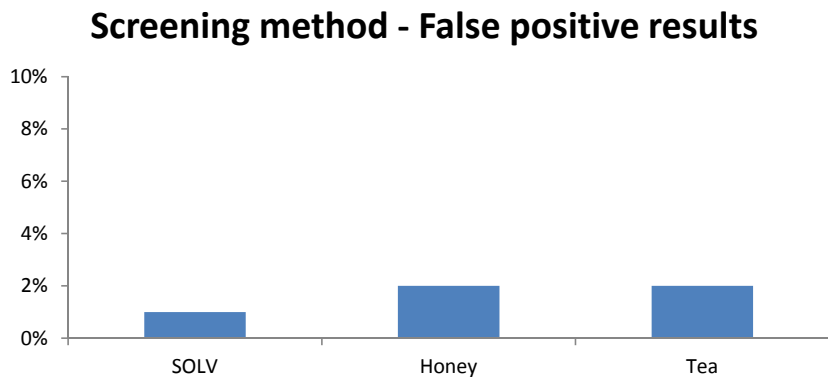
Validation Parameters

- 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

Screening Method Efficiency – % of 330 Target Pesticides



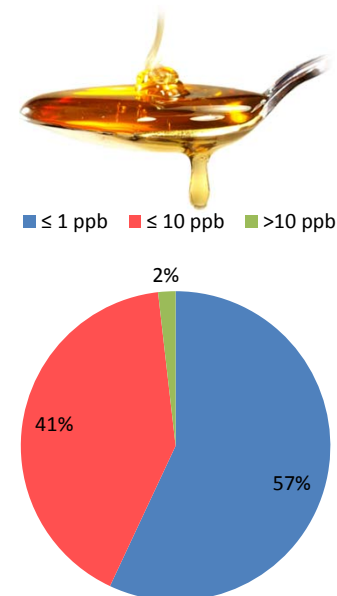
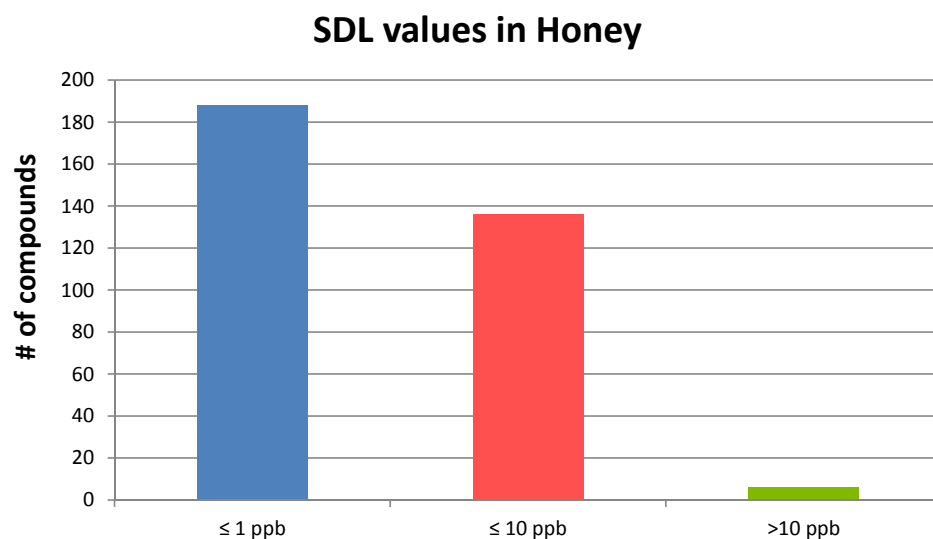
Peak confirmation criteria:
 t_R , HRAM with 5 ppm accuracy and fragment ion presence



DG SANCO defines:
False negative < 5 %
No criteria for false positives

Results vDIA – Sensitivity Overview Honey

- Screening Detection Limits (SDL) in honey matrix

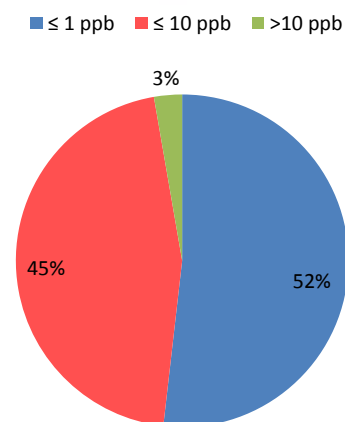
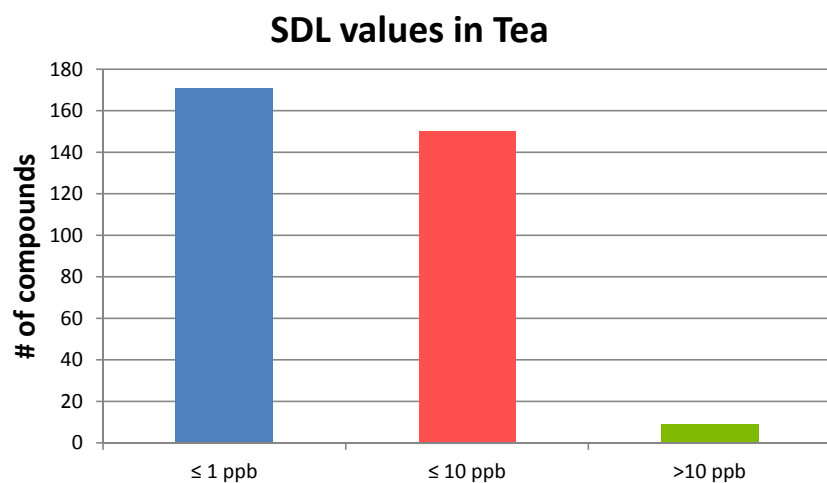


SUM = 330 compounds; 324 compounds SDL ≤ 10 µg/kg

SDL determination according to SANCO12571/2013

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

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.

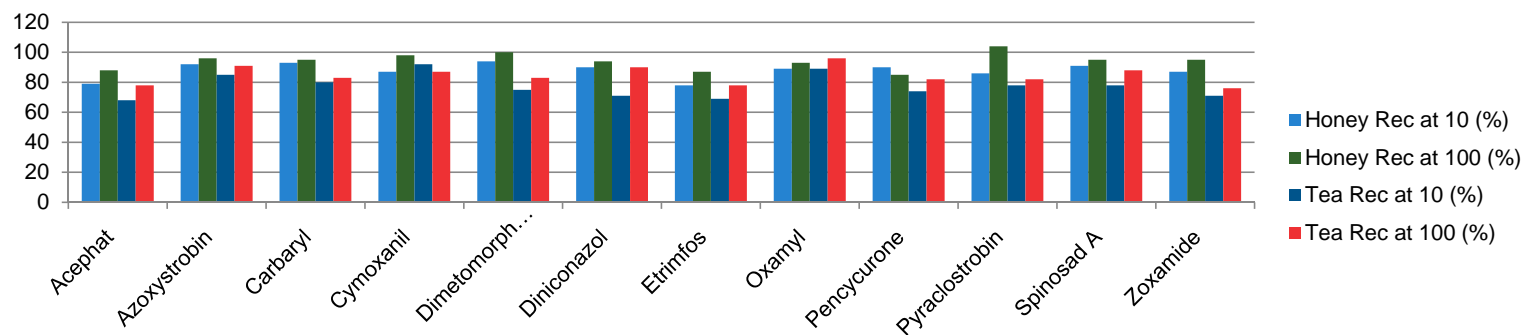
n.d. - not defined

Method Sensitivity For 12 Representative Compounds – vDIA

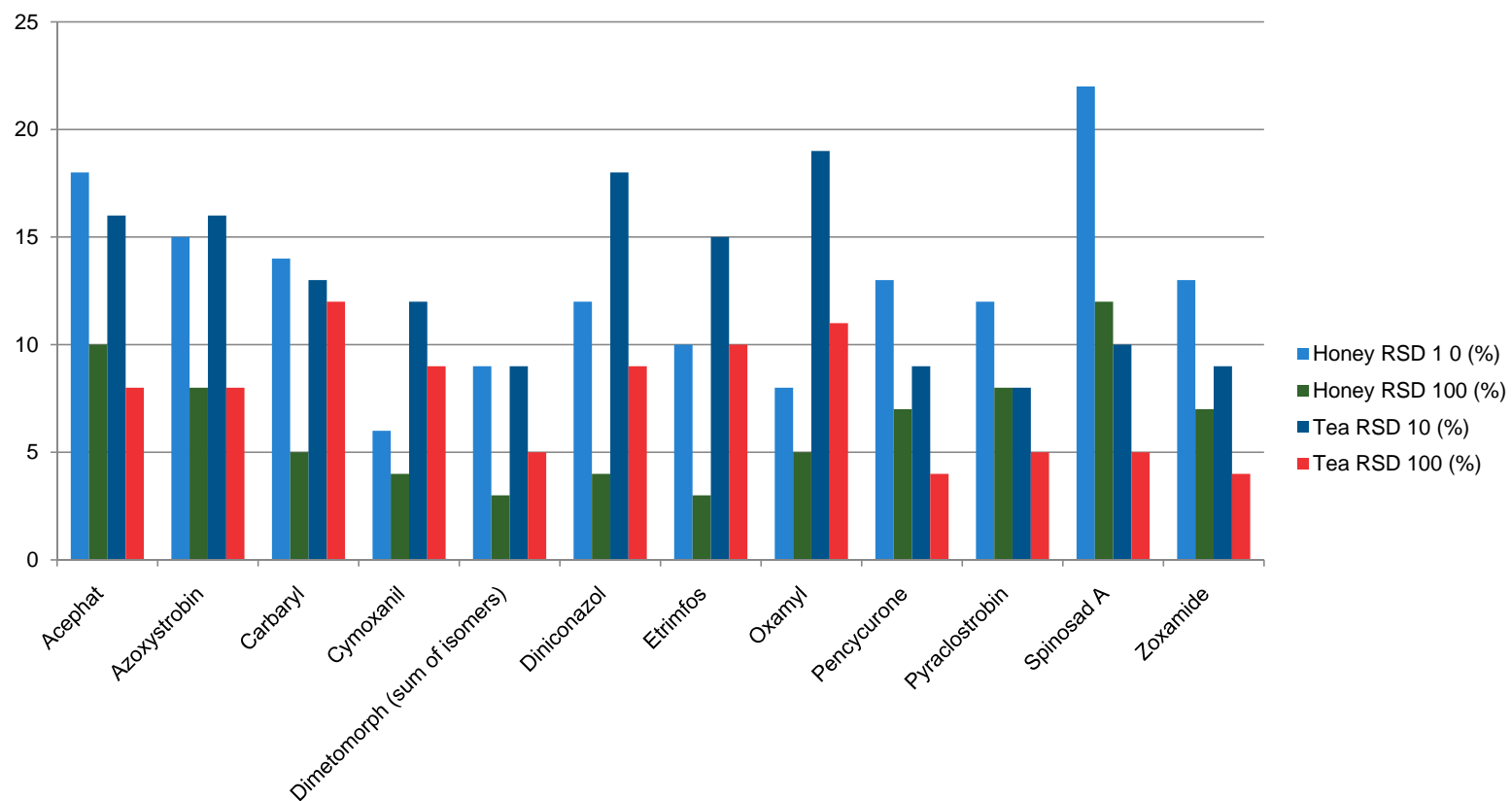
Analyte	Solvent ($\mu\text{g}/\text{kg}$)	Honey ($\mu\text{g}/\text{kg}$)	Tea ($\mu\text{g}/\text{kg}$)	MRL's ($\mu\text{g}/\text{kg}$)	
	LOQ	LOQ	LOQ	Honey	Tea
Acephate	2.5	10	10	20	50
Azoxystrobin	0.25	0.75	1.25	50	100
Carbaryl	0.25	2.5	3	50	50
Cymoxanil	0.25	1.25	5	50	50
Dimetomorph (sum of isomers)	12.5	12.5	25	50	50
Diniconazol	2	2.5	10	50	50
Etrifos	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

Method Recovery, Repeatability, Linearity – vDIA

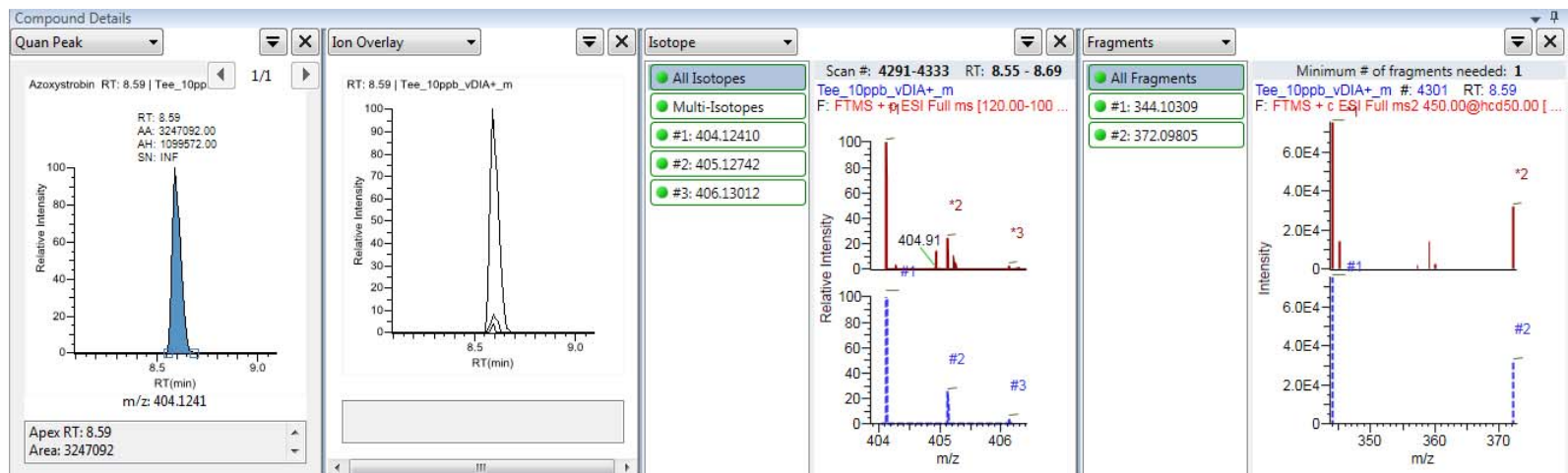
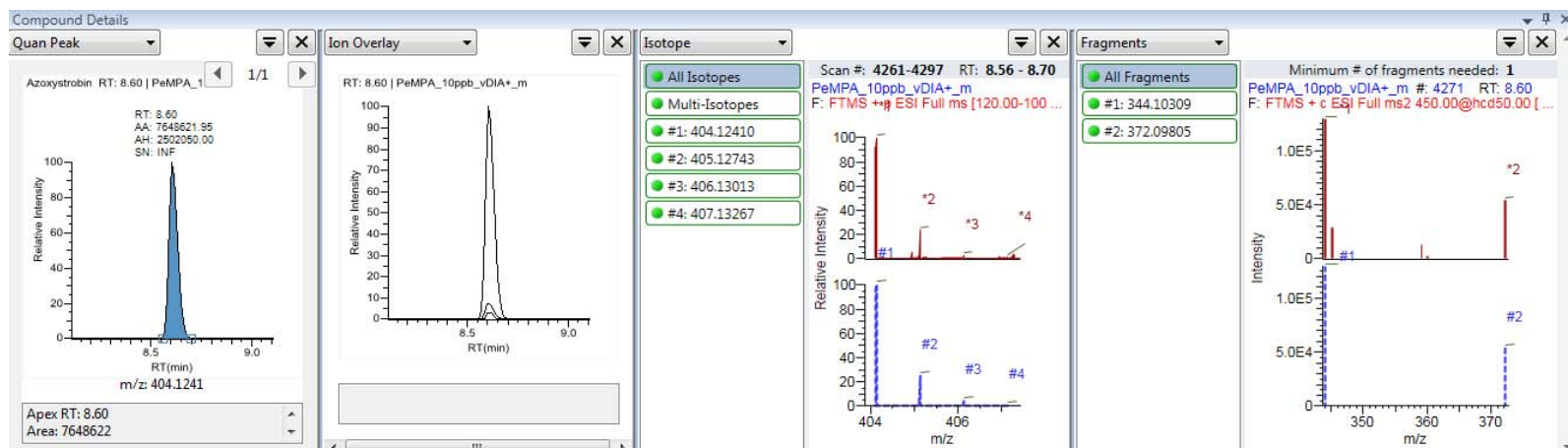
Analyte	Sp. Level 1 (µg/kg)	Sp. Level 2 (µg/kg)	Honey				Tea				Linearity in solvent
			RSD 1 (%)	RSD 2 (%)	Rec 1 (%)	Rec 2 (%)	RSD 1 (%)	RSD 2 (%)	Rec 1 (%)	Rec 2 (%)	
Acephat	10	100	18	10	79	88	16	8	68	78	0.9902
Azoxystrobin	10	100	15	8	92	96	16	8	85	91	0.9879
Carbaryl	10	100	14	5	93	95	13	12	80	83	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
Etrinfos	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 – Repeatability – For 12 Representatives

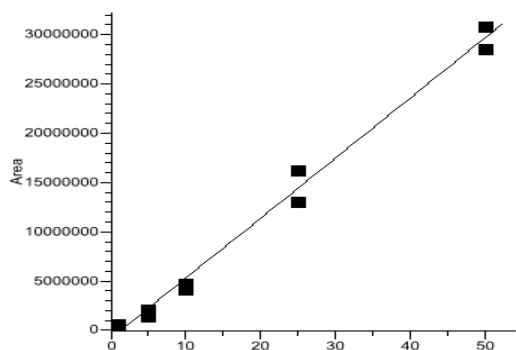


Azoxystrobin in Solvent and Tea at 10 ppb [$\mu\text{g}/\text{kg}$]

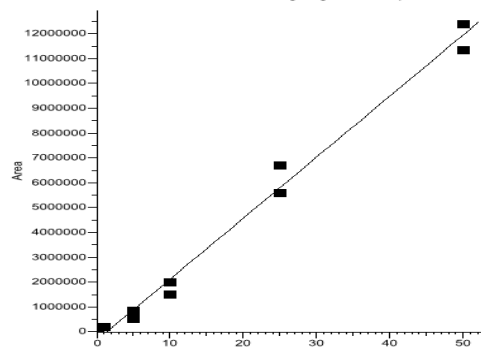


Calibration Curves in Honey Matrix

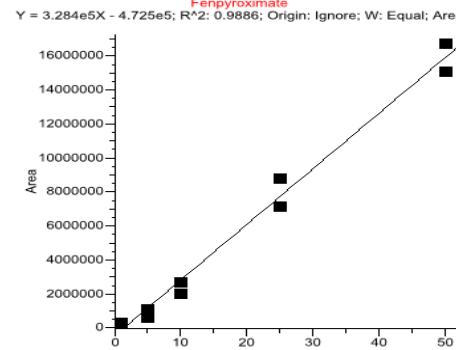
Azoxystrobin
Y = 6.127e5X - 8.579e5; R²: 0.9879; Origin: Ignore; W: Equal; Area



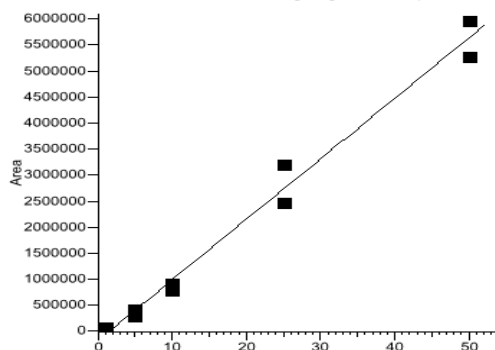
Benzoximate
Y = 2.459e5X - 3.338e5; R²: 0.9892; Origin: Ignore; W: Equal; Area



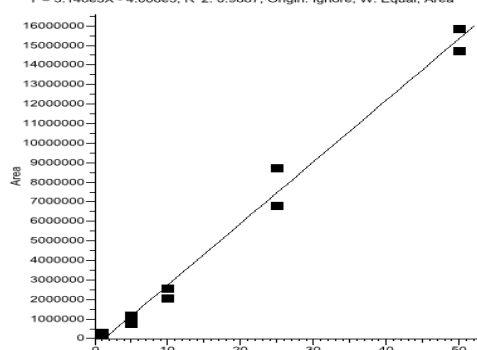
Fenpyroximate
Y = 3.284e5X - 4.725e5; R²: 0.9886; Origin: Ignore; W: Equal; Area



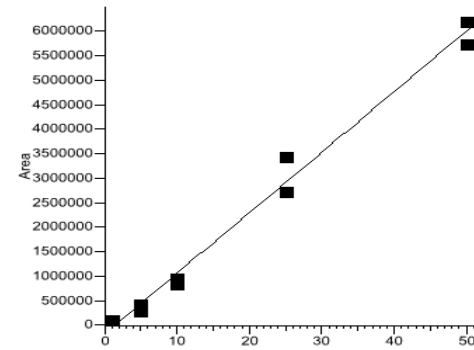
Formothion
Y = 1.16e5X - 1.689e5; R²: 0.9855; Origin: Ignore; W: Equal; Area



Neburon
Y = 3.148e5X - 4.006e5; R²: 0.9887; Origin: Ignore; W: Equal; Area



Tebuconazole
Y = 1.236e5X - 1.733e5; R²: 0.9892; Origin: Ignore; W: Equal; Area



Summary

- Complete workflow solution for multi-pesticide analysis has been evaluated
- Performance parameters of a complete routine method were tested and demonstrated that the vast majority of routinely measured LC amenable compounds can be analysed with high degree of confidence
- <10ppb (ug/kg) screening detection limit was achieved for >95 % of targeted compounds in all matrices (tea and honey)
- Excellent values under repeatability conditions
- TraceFinder software package allows streamlined method optimization, data acquisition and fast processing and reporting



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