

# Trim Time Not Columns – Multiresidue Pesticides Analysis with an Intuvo GC/TQ

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# Agenda

Pesticide analysis trends

Targeted vs. untargeted analysis

What makes the Intuvo 9000 GC unique

Intuvo/7000D GC/TQ with P&EP MRM database and methods

Sample results

# Forces driving increased pesticide residue analysis

## Population growth

To meet expected demand in 2050, agricultural production needs to increase by 50% vs 2013

## Globalization

Globalization of food supply chain means exporters must accommodate many differing local regulations

## Brand Protection

Negative Press can have lasting effect on Brand success

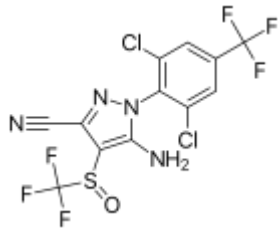
# Why it's important to do suspect/unknowns screening

## EU-banned pesticides found in food in Sweden

Traces of banned pesticides have been found in oranges from Spain, olive oil and grapes from Greece, apples from Belgium and cucumbers from Holland.

Radio Sweden:

<https://sverigesradio.se/sida/artikel.aspx?programid=2054&artikel=6395318>



Fipronil in eggs



## Developing World Still Struggling With Obsolete Pesticides

Adam Allington in Bloomberg BNA ; <https://www.bna.com/developing-world-struggling-n73014471020/>

### Counterfeit & Illegal Pesticides

The global trade in counterfeit and illegal pesticides is growing. With increasing quantities of fake and illegal pesticides produced, marketed and sold by organised criminals around the world, counterfeit and illegal pesticides present real risks to farmer's health, the environment and the economy.

European Crop Protection Association  
<http://www.ecpa.eu/stewardship/counterfeit-illegal-pesticides>

# Targeted v's untargeted Analysis?



## Non-targeted

Data Acquisition

No analyte-specific conditions

Full Scan

Data Analysis

Database searching

Library searching

Molecular formula calculation

Spectral interpretation

e?"

# The nature of target compounds guides technology choice

## Target Screening

- quantifying a set list of pesticides in sample to meet regulation
- Typically domain of GC/SQ or GC/TQ but can be GC/Q-TOF

## Suspect Screening

- Screen sample for a range of pesticides – Quant if standards available
- Can be GC/SQ or GC/Q-TOF

## Non-targeted Screening

- investigate nature of sample through exploratory profiling
- Typically domain of GC/Q-TOF but can be GC/SQ



# Multiple Pesticide Solutions Depending on Need



5977B GC/MSD



Intuvo-7000D GC/TQ

New P&EP Applications Kit  
With Intuvo MRM Database



7250 GC/Q-TOF

Enhanced PCDL for Pesticides  
& Environmental Pollutants

# Target Analysis System

Intuvo-7000D GC/TQ with P&EP MRM database and methods





# Agilent Food and Environmental MRM Databases

- 1161 Total Compounds
  - Up to 10 transitions/compound
  - Over 7,500 Matrix optimized transitions

## Classes of Compounds in the Database

Compound Classification	Total Number
Pesticides	675
Breakdown Products	42
Deuterated Compounds	6
Polybrominated Diphenyl Ether (PBDE)	4
Polybrominated Biphenyl (PBB)	1
Polychlorinated Biphenyl (PCB)	209
Polycyclic Aromatic Hydrocarbon (PAH)	26
Phthalates	17
Additional Semi-volatile Pollutants	94

*\*Note that some compounds overlap classes.*

*\*Note that not every compound class is listed...Only higher priority classes are listed*

# Targeted Screening System

Intuvo-7000D GC/TQ with P&EP MRM database and methods



Backflush methods reduce system downtime

# Targeted Screening System

Intuvo-7000D GC/TQ with P&EP MRM database and methods



Confident compound detection  
using dMRM methods

Backflush methods reduce  
system downtime

# Targeted Screening System

Intuvo-7000D GC/TQ with P&EP MRM database and methods

Intuvo-specific 1100+  
compound MRM database

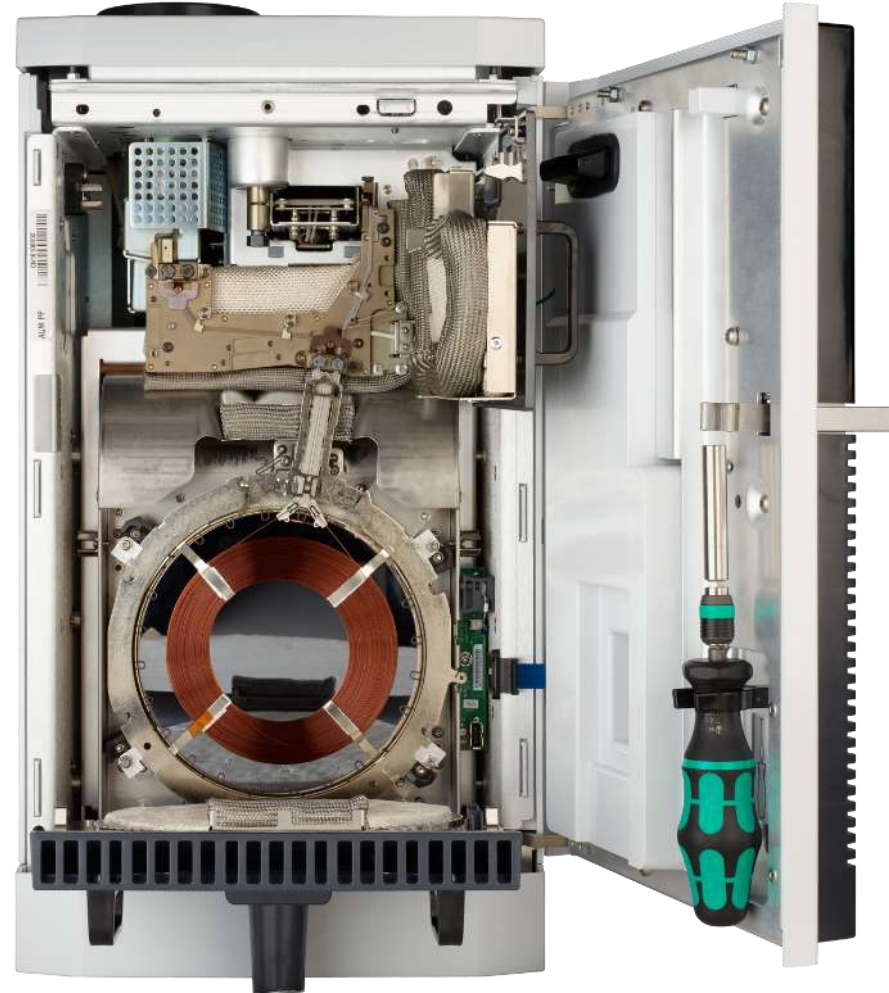
Confident compound detection  
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Backflush methods reduce  
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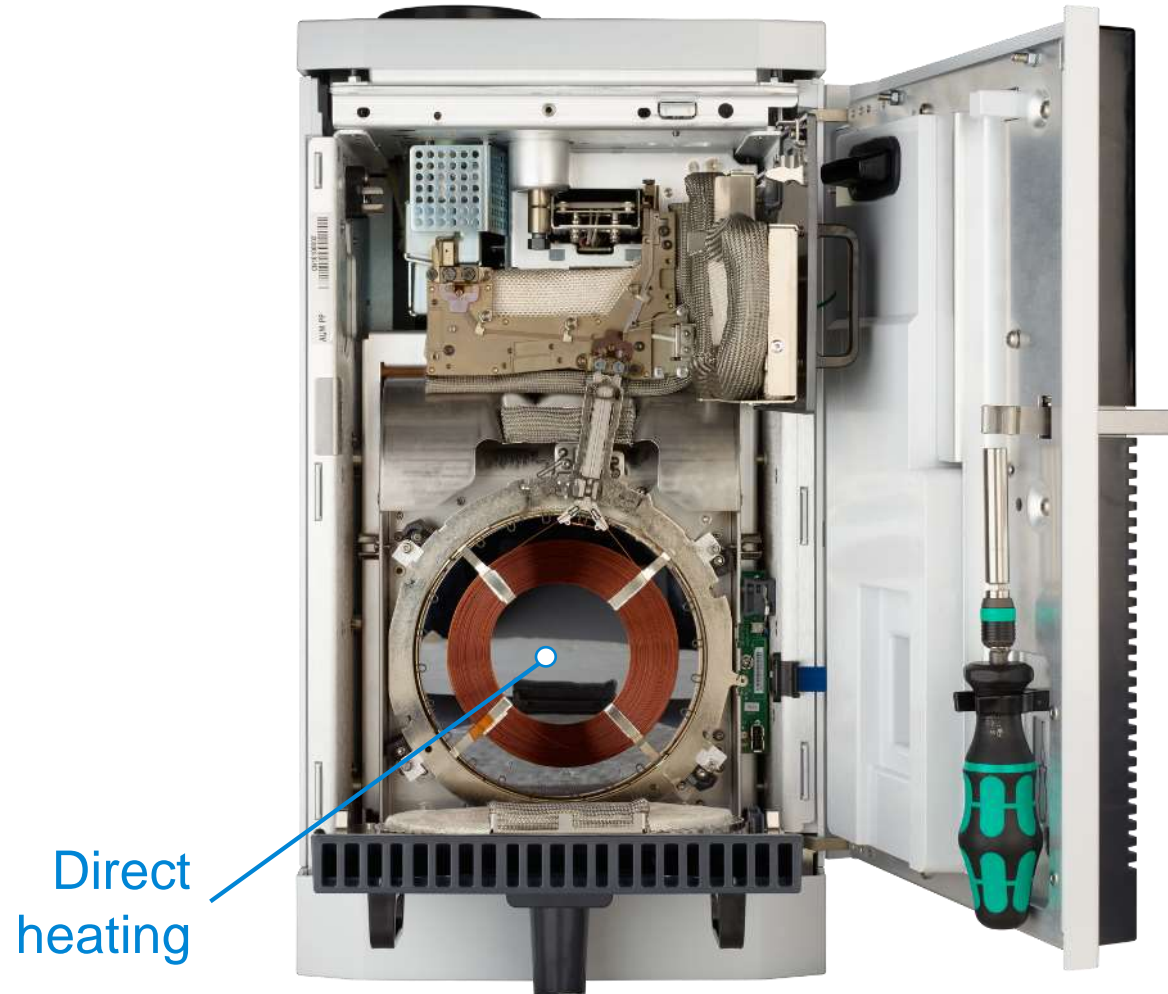
# Targeted Screening System

Intuvo-7000D GC/TQ with P&EP MRM database and methods



# Targeted Screening System

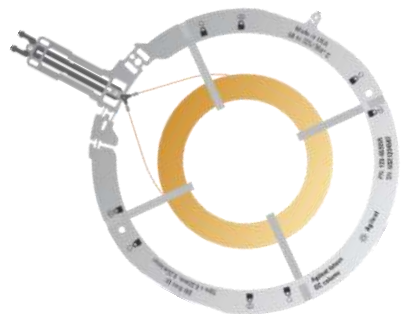
Intuvo-7000D GC/TQ with P&EP MRM database and methods





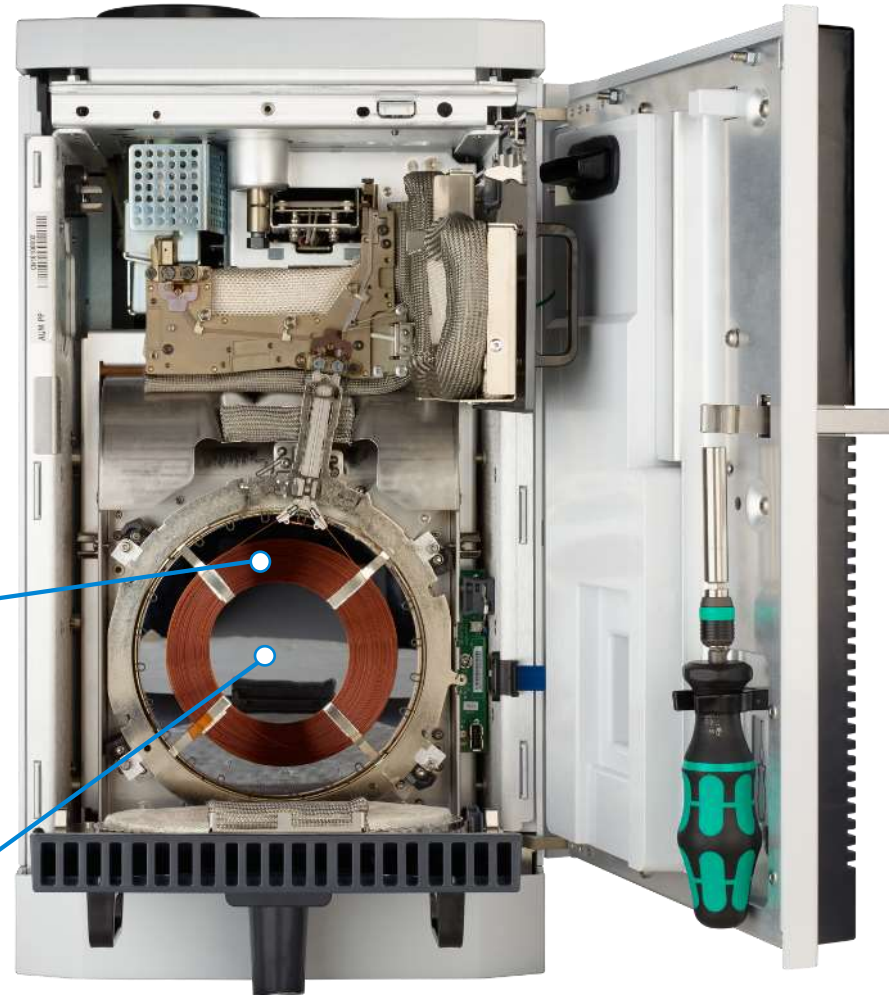
# Targeted Screening System

Intuvo-7000D GC/TQ with P&EP MRM database and methods



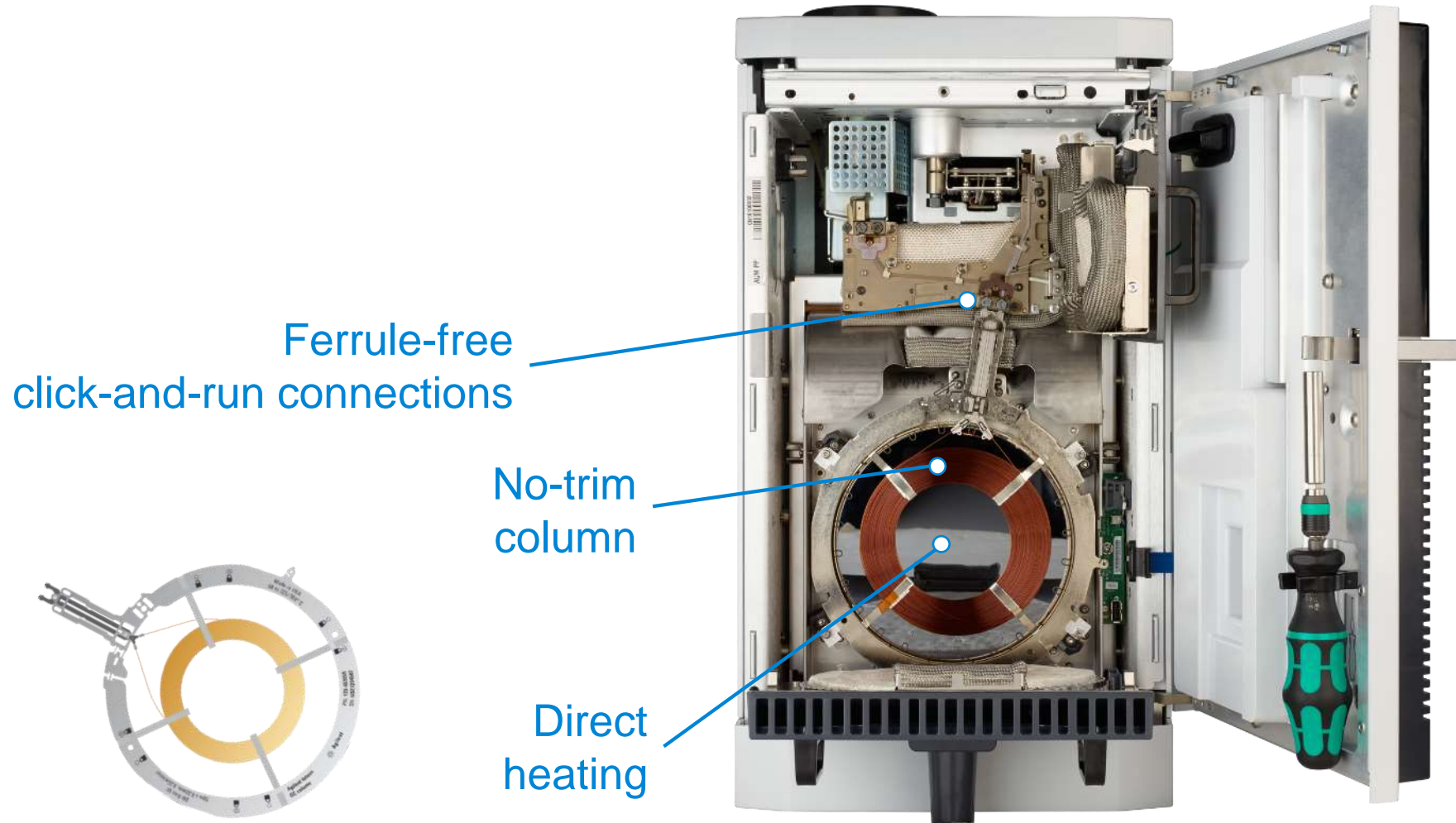
No-trim  
column

Direct  
heating



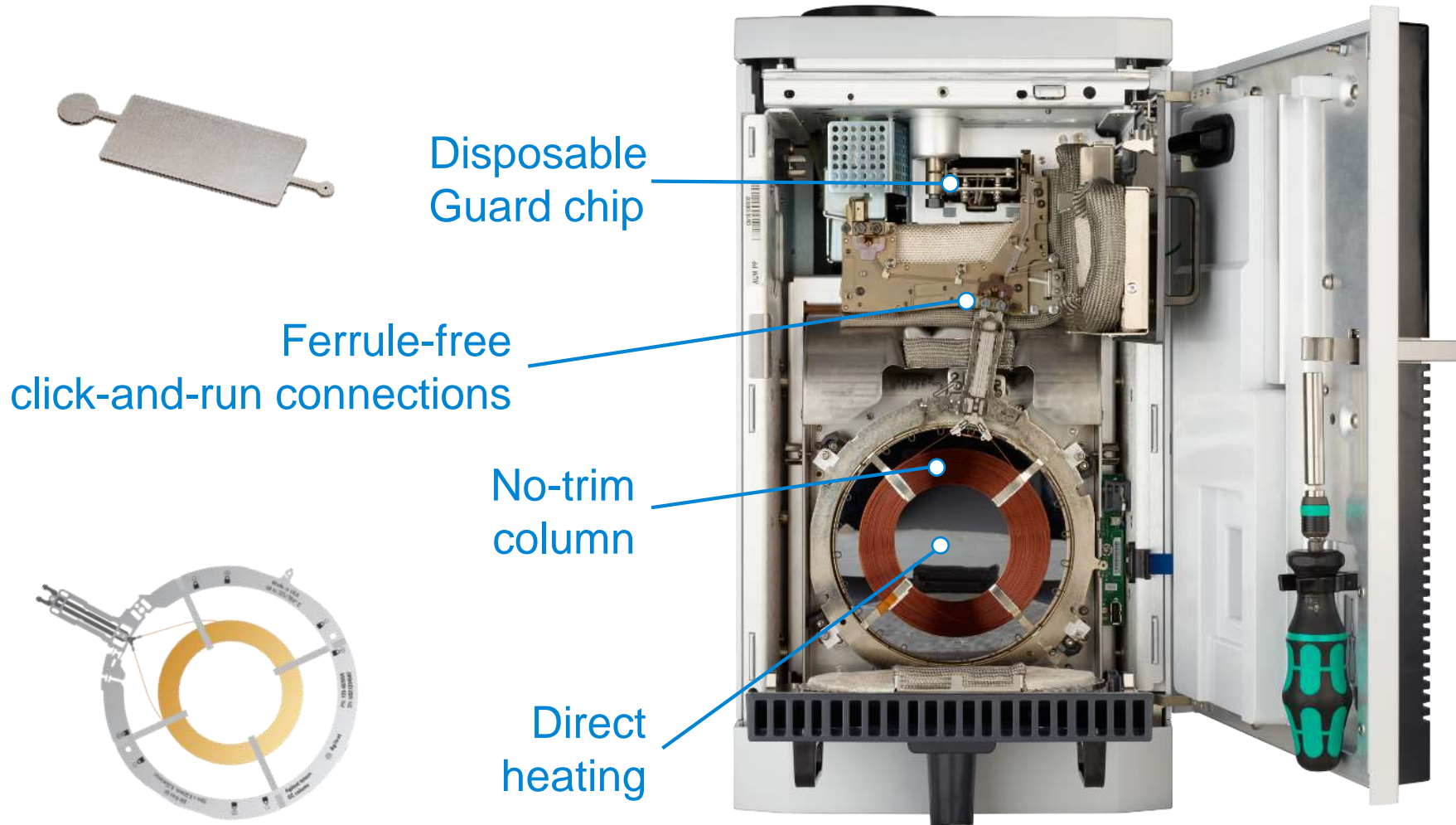
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Intuvo-7000D GC/TQ with P&EP MRM database and methods



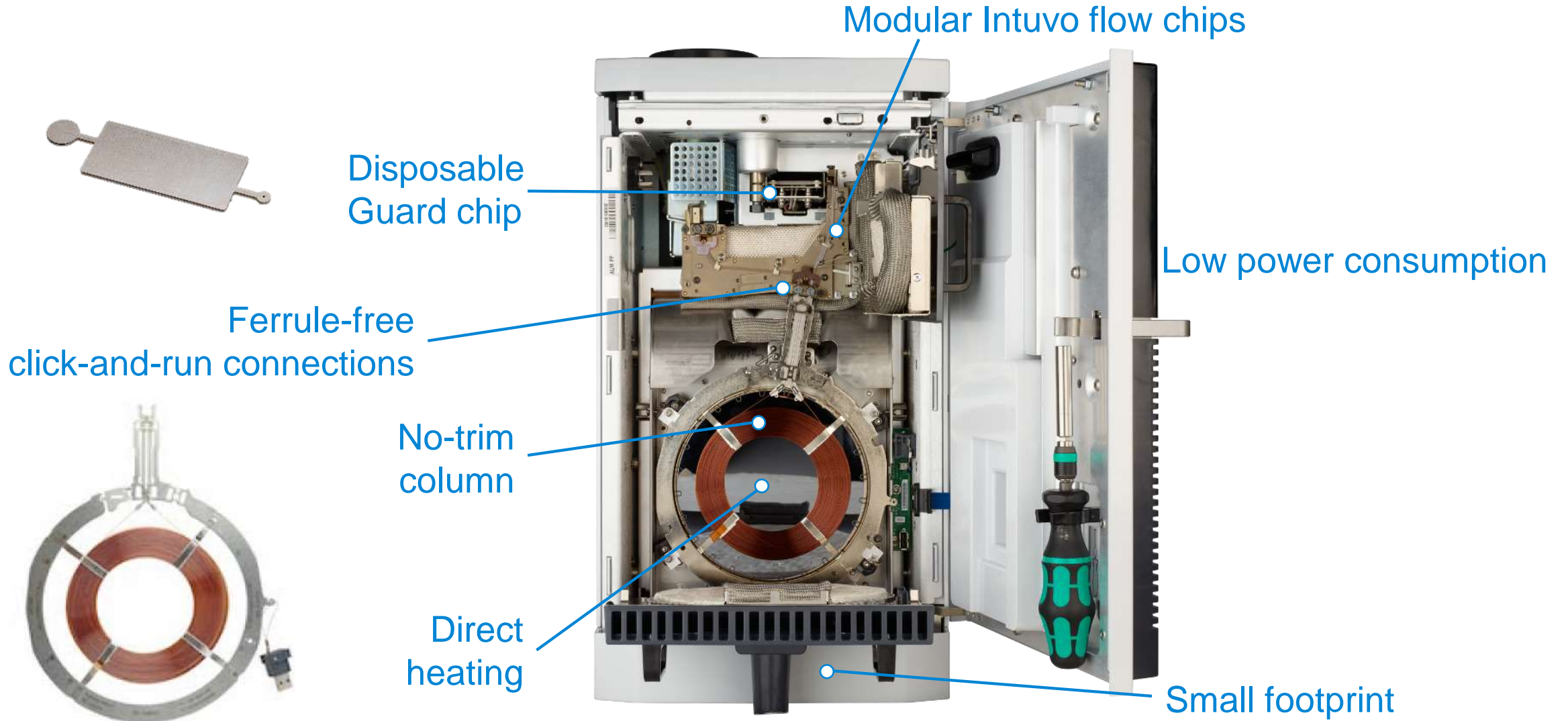
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Intuvo-7000D GC/TQ with P&EP MRM database and methods



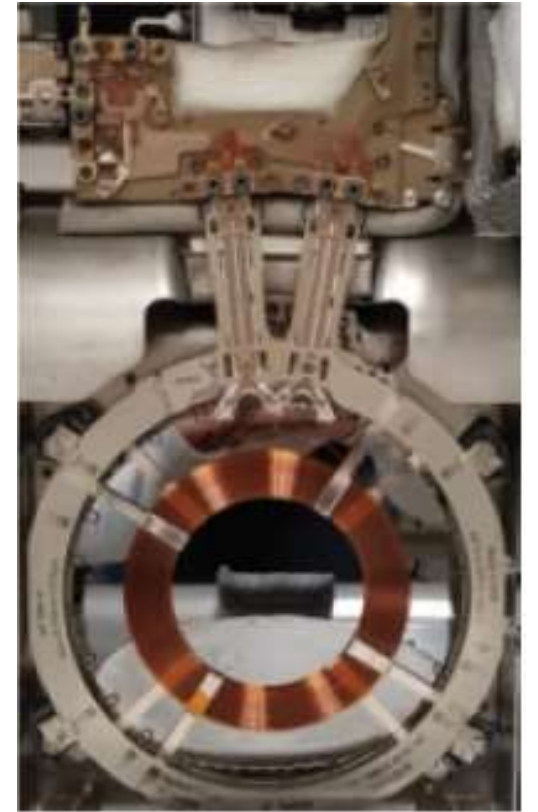
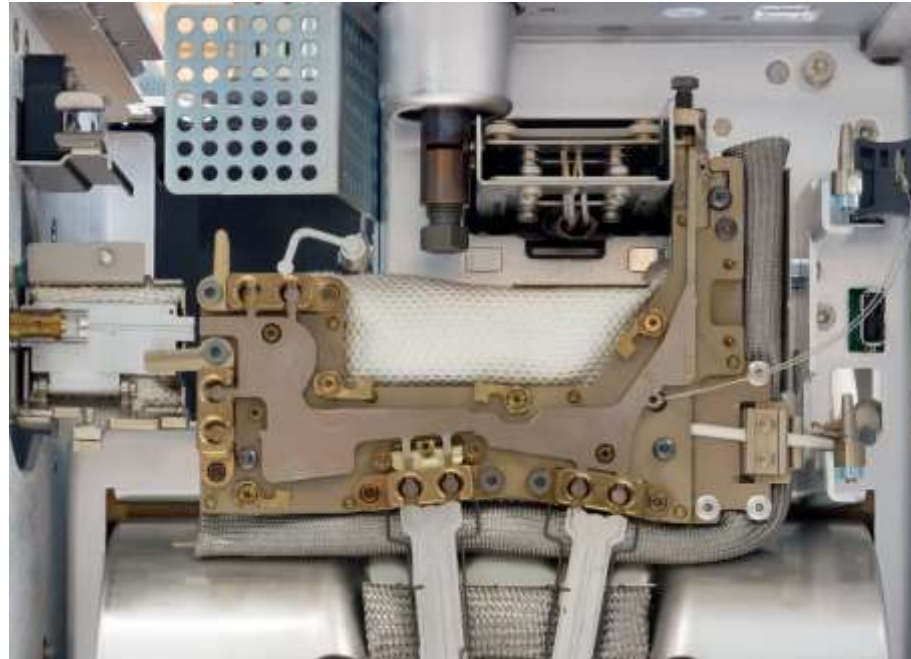
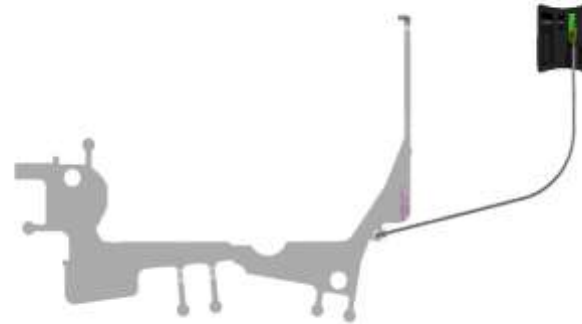
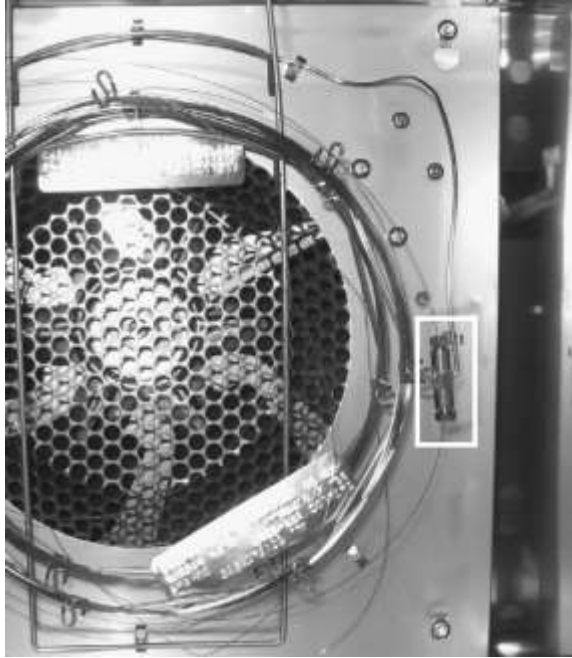
# Targeted Screening System

Intuvo-7000D GC/TQ with P&EP MRM database and methods



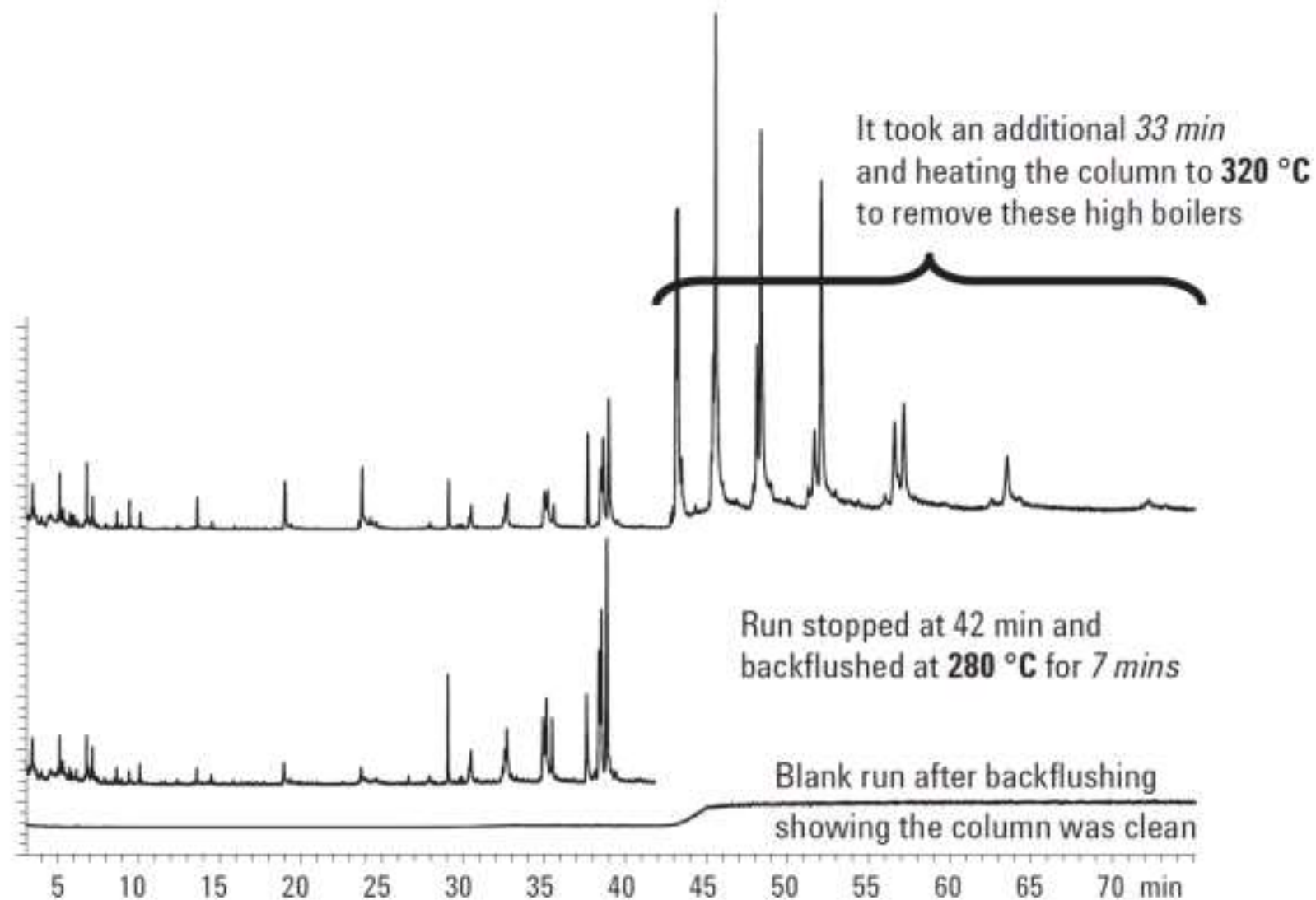


# Intuvo – Backflush made easier



# Benefits of Backflush GC Methods

## Mid-Column Backflush





# A Choice of Methods

- 20 minute method
  - Target screening of less than 300 compounds
- 40 minute method
  - For the most comprehensive coverage
- Both with mid-column backflush

# Intuvo-7000D GC/TQ Acquisition Methods

## Agilent 9000 Intuvo GC

Parameter	Value
Inert flow path configuration	Mid-column backflush
Syringe	10 µL (p/n G4513-80220); PTFE-tip plunger
Sandwich injection	Reversed 3-Layer Switch (L3,L1,L2) L1 (standard or sample) 0.5 µL L2 (ISTD) 0.5 µL L3 (matrix) 0.5 µL
Carrier gas	He
Inlet	MMI
Injection mode	Pulsed Splitless
Purge flow to split vent	30 mL/min at 1 minutes
Septum purge flow	3 mL/min
Gas saver	20 mL/min after 2 minutes
Intuvo Guard Chip	Track Oven
Columns	Agilent Intuvo HP5-MS UI (19091S-431UI-INT)
Column constant flow	1.2 mL/min (column 1) & 1.4 mL/min (column 2)
Oven temperature program	60 °C (hold 1 min) then 40 °C/min to 170 °C, then 10 °C/min to 310 °C (hold 3 min)

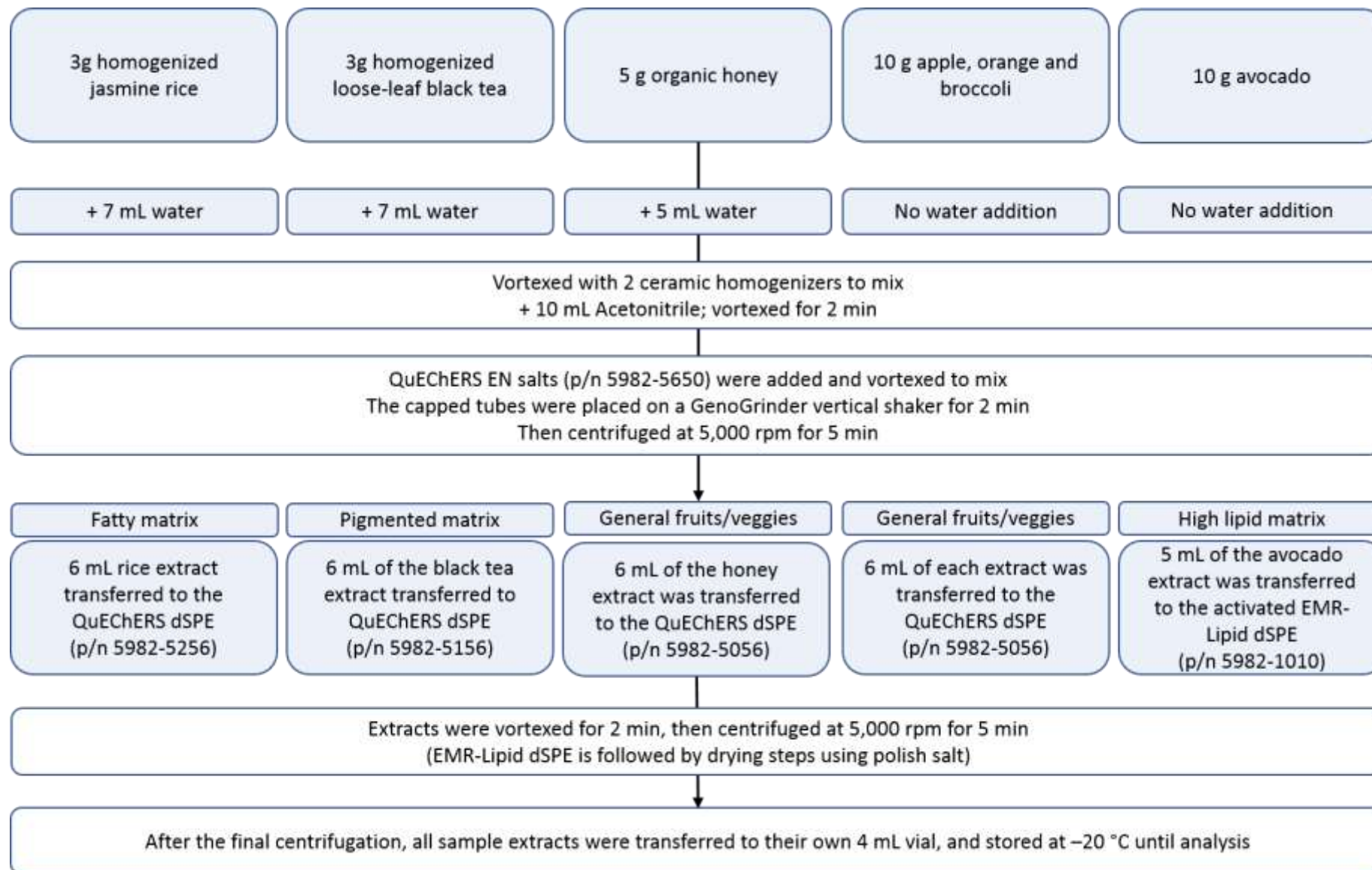
## Midcolumn Backflush

Timing	5 min duration during post-run
Oven temperature	310 °C
Aux EPC pressure	~30 psi
Inlet pressure	~2 psi

## Agilent 7000C Triple Quadrupole GC/MS/MS

Parameter	Value
Tune file	atunes.eiex.tune
Transfer line	280 °C
Source temperature	280 °C
Quad temperatures	150 °C
Collision Cell Gas Flows	1.5 mL/min N2 & 2.25 mL/min He
Scan Type	dMRM
Electron Energy	70 eV
EM gain	10
MS1 & MS2 resolution	Wide
Quant/Qual transitions	P&EP Intuvo MRM Database
Right & Left RT Deltas	0.2 min
Dwell times	Optimized by dMRM
Min Dwell Time (ms)	10
Cycles Per Second	3.07

# Optimized Sample Prep



# Confident Results

## Accuracy and Precision

### Observations

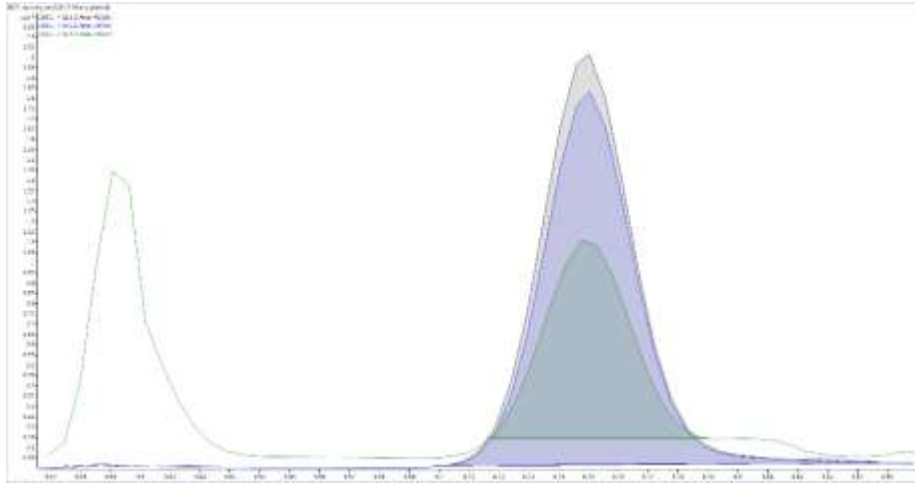
12 replicates @ ~ 25 ppb

Variability:

- Honey & Rice std dev < 1.06
- Tea std dev < 6.00

Tea experienced higher %RSDs

Recovery errors  $\leq$  30%



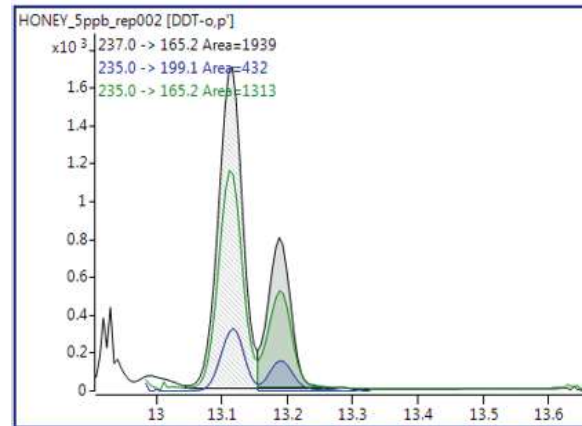
2-Phenylphenol at ~25ppb in Rice

CMPD	Honey Recovery		Rice Recovery		Tea Recovery	
	%RSD	% Error	%RSD	% Error	%RSD	% Error
EPTC	8.70	7.12	10.16	9.09	12.70	10.42
2-Phenylphenol	5.26	4.78	7.78	6.19	11.16	9.37
Propachlor	6.98	6.15	11.70	9.51	29.58	25.96
Simazine	6.77	4.82	11.78	9.81	27.06	22.48
Atrazine	7.57	6.71	15.50	12.95	25.07	21.50
Chlorpyrifos-methyl	4.40	3.12	12.68	10.59	27.24	23.84
Alachlor	3.23	2.58	16.12	13.03	25.23	18.13
Heptachlor	9.01	8.04	9.92	7.93	28.56	27.74
Metalaxyl	3.54	3.00	16.64	14.04	25.28	17.52
Metolachlor	5.13	4.10	13.55	11.73	17.40	15.05
Aldrin	6.19	4.64	8.70	6.99	17.71	13.25
Heptachlor exo-epoxide	3.34	2.54	11.85	9.37	23.99	19.83
Chlordane-trans	8.43	7.41	16.78	14.12	22.62	17.07
Myclobutanil	11.53	9.12	11.10	9.13	27.21	24.91
Endosulfan II (beta isomer)	15.31	13.96	8.88	6.86	29.24	24.10
DDT-o,p'	17.66	16.84	8.14	5.70	29.81	27.46
Nuarimol	8.61	7.03	6.28	4.75	18.61	17.93
Tetradifon	14.06	9.86	8.53	7.09	21.75	17.54
Permethrin, (1R)-cis-	24.26	23.75	6.36	5.48	21.49	21.49
Permethrin, (1R)-trans-	17.02	15.43	9.45	9.05	29.32	26.17

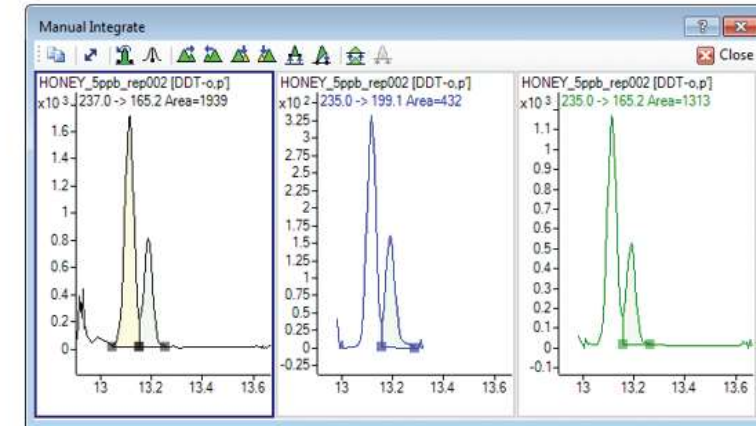
# Meeting EU MRL Requirements

## Quantitation of pesticide residues at the low ppb level - Honey

Compound	Results for honey		
	EU MRLs (ppb)	MDL (ppb)	iLOQ (ppb)
Aldrin	10	0.39	1.43
Atrazine	50	0.21	0.77
Alachlor	10	0.89	3.28
2-Phenylphenol	50	0.16	0.60
Chlordane	10	0.64	0.30
Chlorpyrifos-methyl	n/a	0.34	1.24
DDT	50	2.94	2.53
Heptachlor	10	0.45	1.65
Metalaxyl	50	0.43	1.59
Metolachlor	50	1.31	4.80
Myclobutanil	50	0.35	1.27
EPTC	20	0.04	0.15
Propyzamide	50	1.37	5.03
Propachlor	20	0.02	0.09
Simazine	10	0.29	1.06
Permethrin	n/a	0.21	2.92
Triadimefon	50	0.42	1.54



Overlay of MRM transitions for DDT-o,p' at 5ppb in Honey



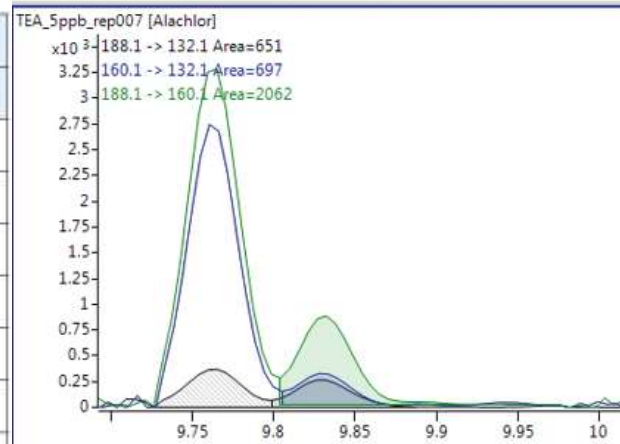
Separated extracted ions of MRM transitions for DDT-o,p' at 5ppb in Honey



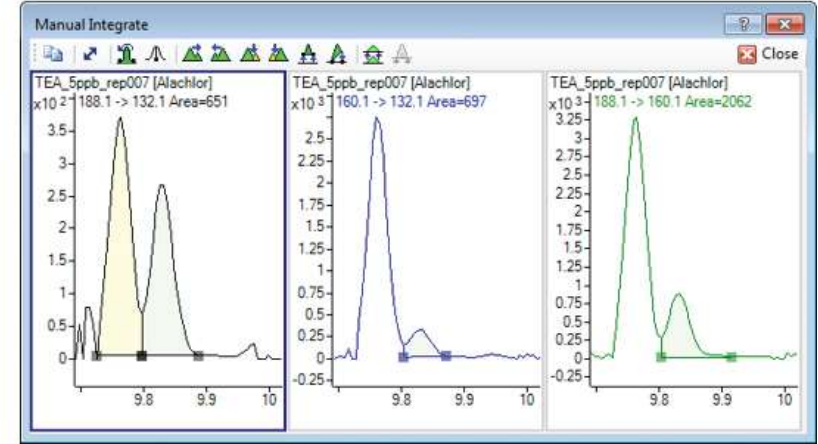
# Meeting EU MRL Requirements

## Quantitation of pesticide residues at the low ppb level - Tea

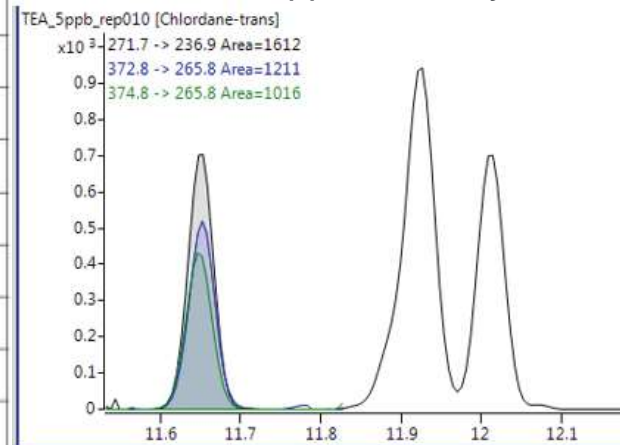
Compound	Results for tea		
	EU MRLs (ppb)	MDL (ppb)	iLOQ (ppb)
Aldrin	20	6.15	16.42
Atrazine	100	0.09	0.30
Alachlor	50	3.39	12.46
2-Phenylphenol	100	5.63	19.96
Chlordane	20	12.03	9.77
Chlorpyrifos-methyl	100	0.17	0.45
DDT	200	151.34	150.81
Heptachlor	20	0.16	0.34
Metalaxyl	50	1.93	7.10
Metolachlor	50	0.04	0.12
Myclobutanil	50	5.85	21.53
EPTC	50	1.17	3.74
Propyzamide	50	0.40	1.20
Propachlor	100	0.36	1.20
Simazine	50	0.10	0.30
Permethrin	100	4.49	13.24
Triadimefon	50	3.80	13.97



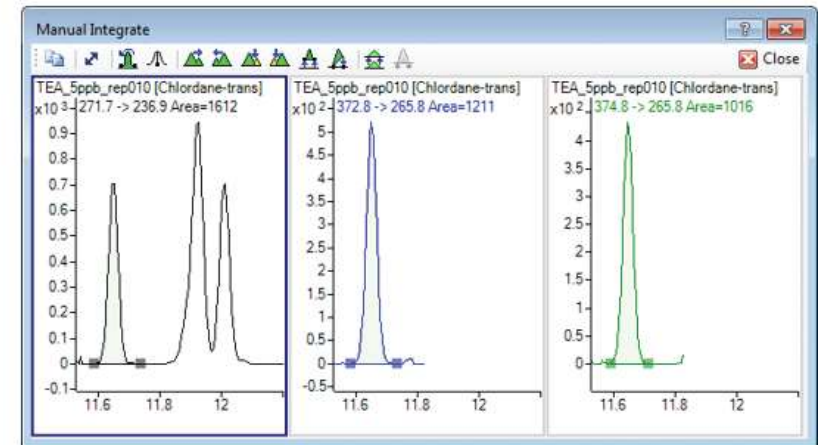
Overlay of MRM transitions for alachlor at 5ppb in Honey



Separated extracted ions of MRM transitions for alachlor at 5ppb in Honey



Overlay of MRM transitions for chlordane at 5ppb in Honey

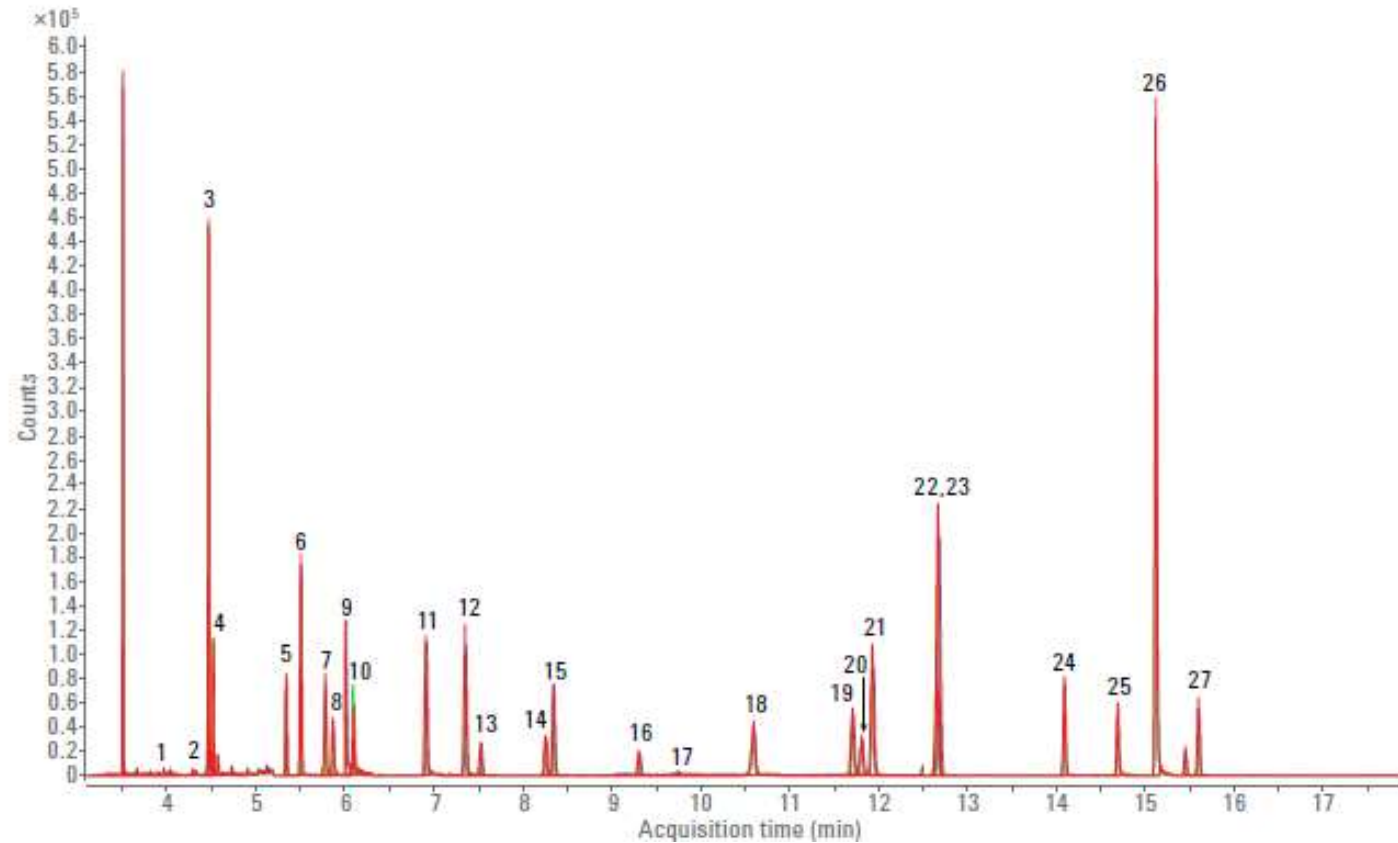


Separated extracted ions of MRM transitions for chlordane at 5ppb in Honey



# Repeatability and robustness

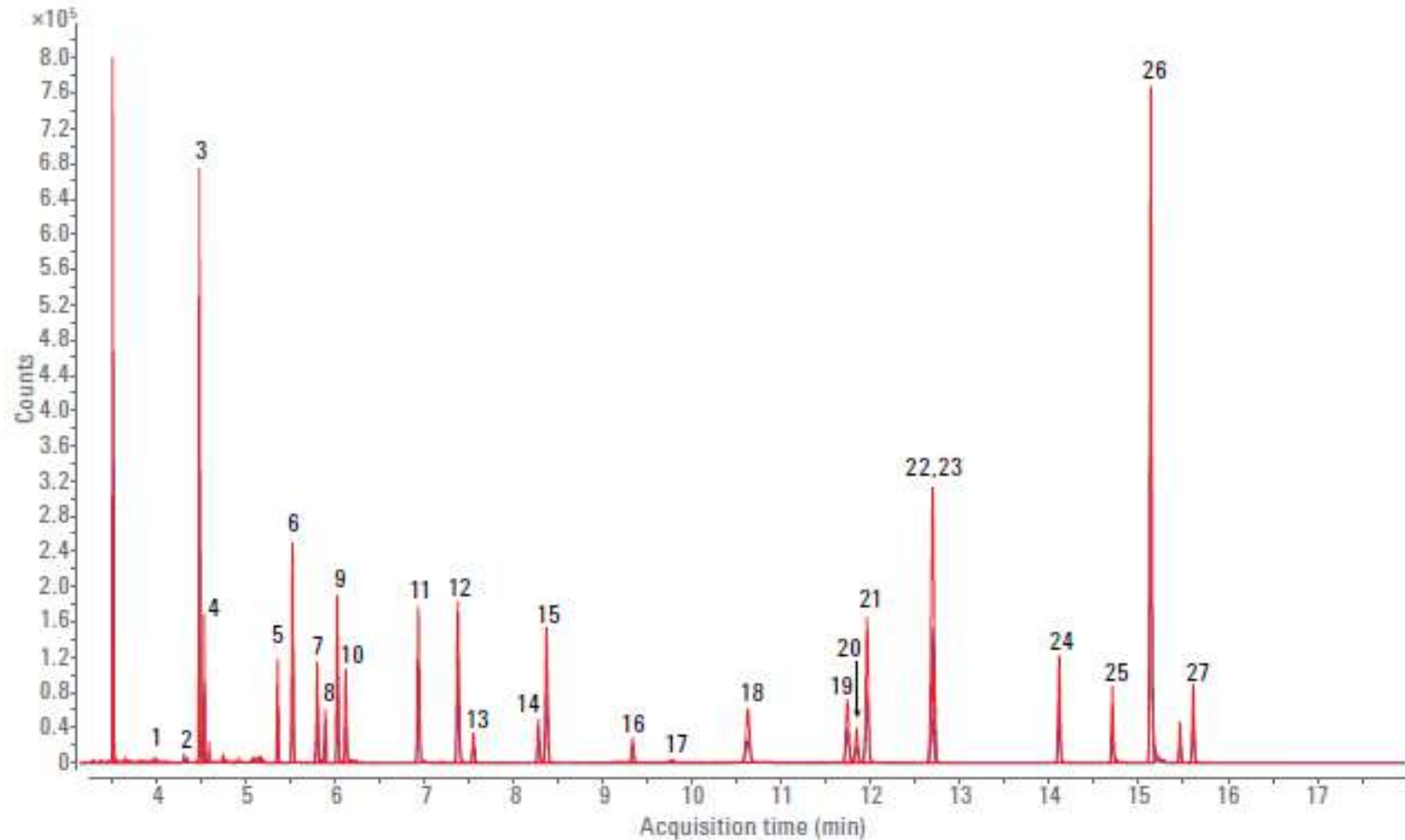
## Honey



- Blue – Initial 50ng/mL calibration check
- Red - following 60 honey extract injections.
- Green - following liner and guard chip replacement.

# Repeatability and robustness

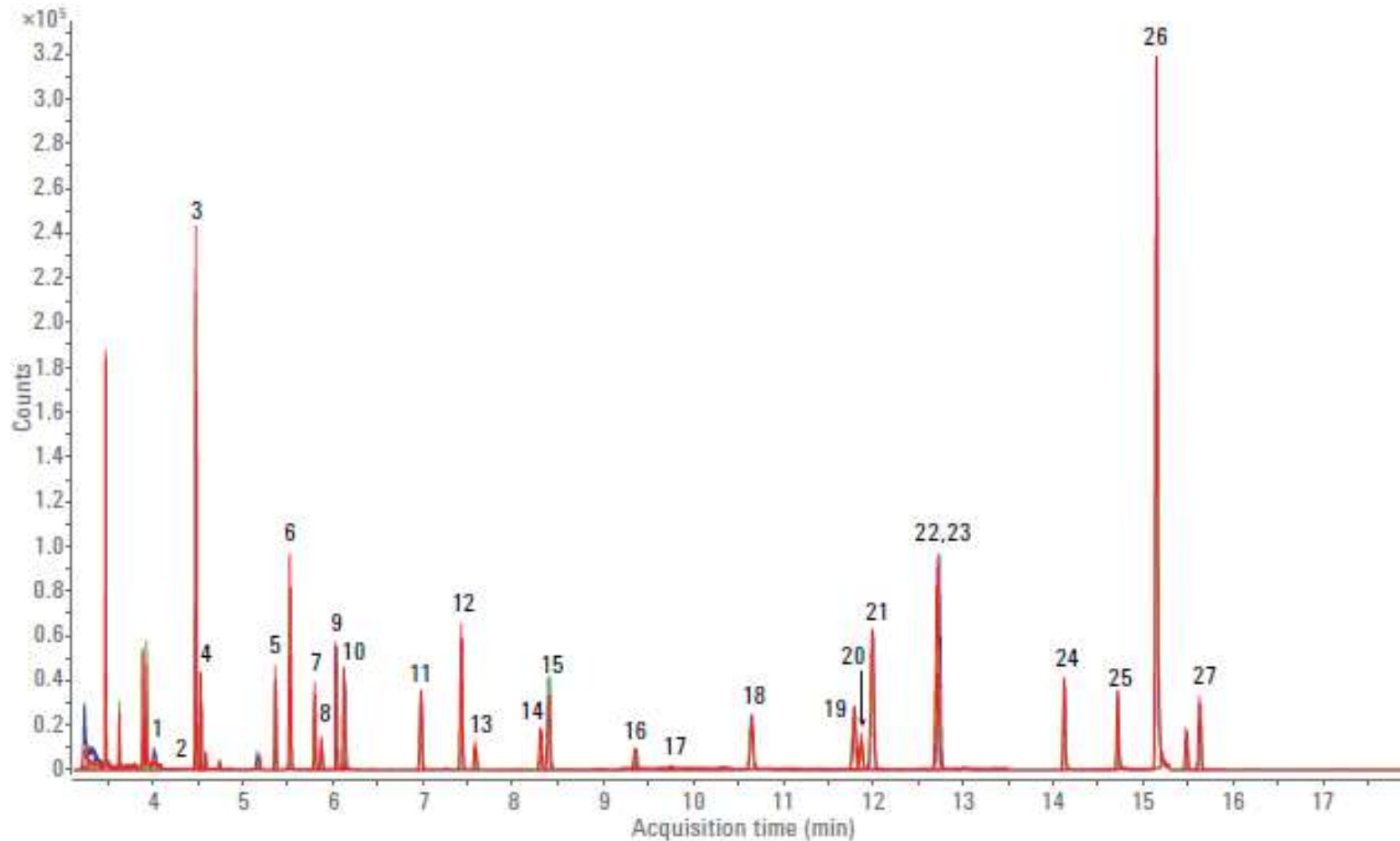
## Rice



- Blue – Initial 50ng/mL calibration check
- Red - following 60 rice extract injections.

# Repeatability and robustness

## Black Tea



- Blue – Initial 50ng/mL calibration check
- Red - following 60 black tea extract injections.
- Green - following liner and guard chip replacement.

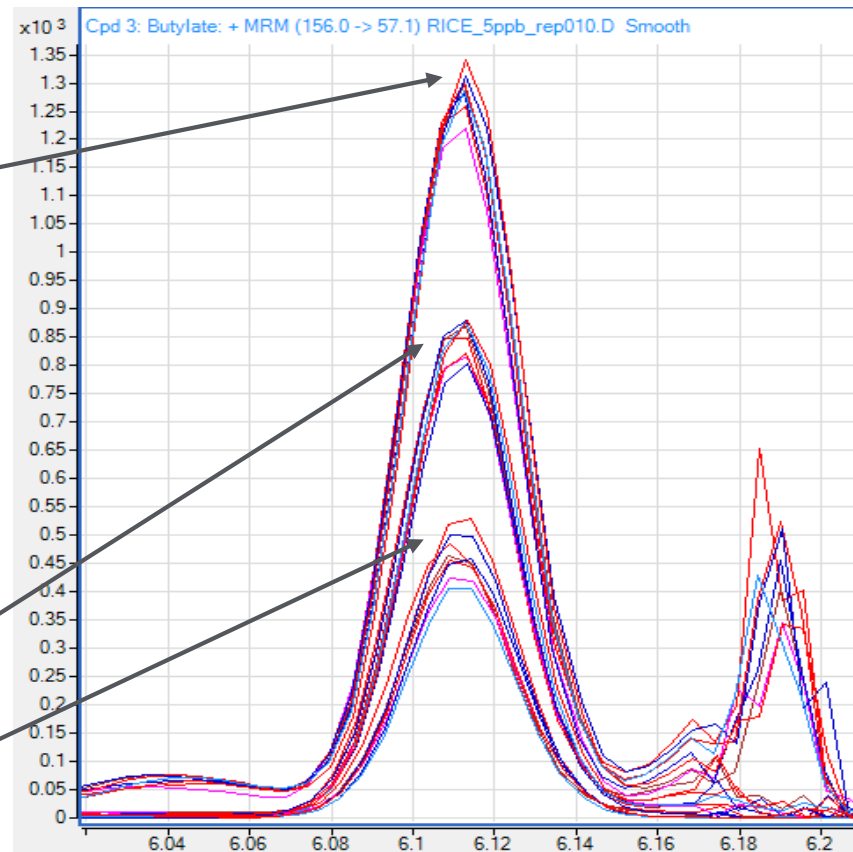
# Repeatability and robustness

Butylate in Jasmine Rice – 5.19ppb

MRM 156.0 -> 57.1

MRM 146.1 -> 90.0

MRM 146.1 -> 57.1



8 Replicates

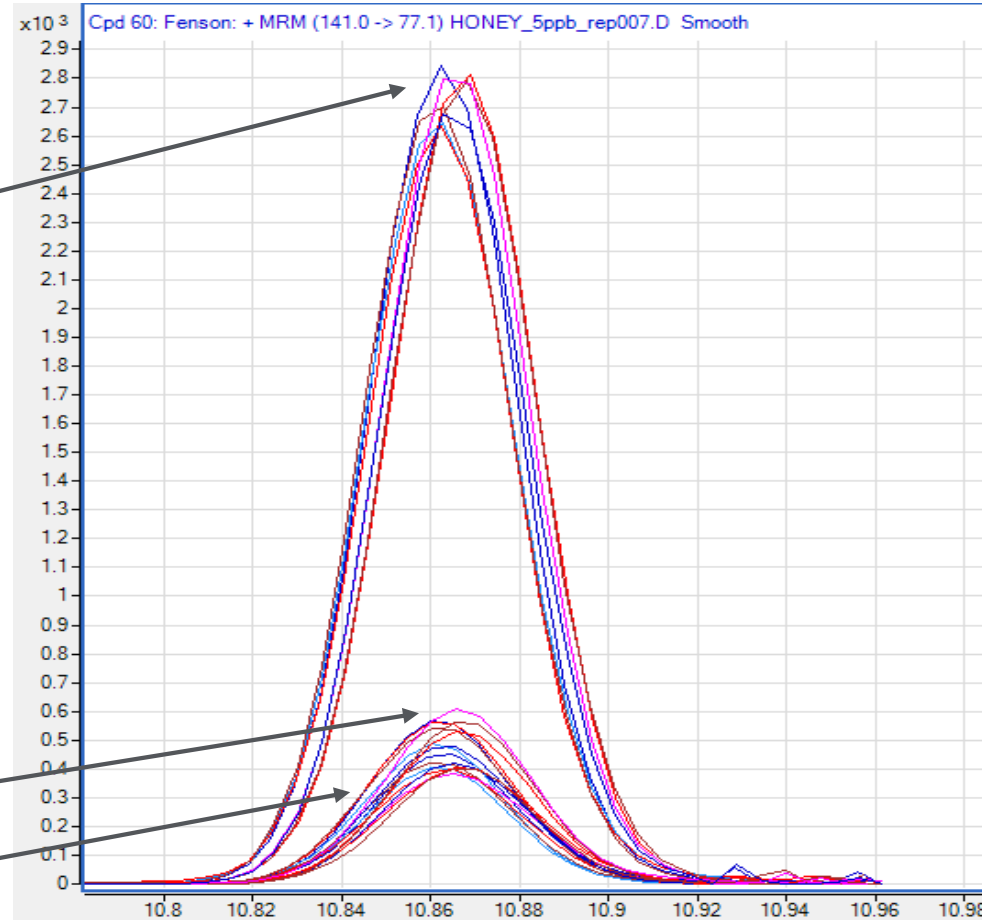
# Repeatability and robustness

Fenson in Organic Honey – 5.08ppb

MRM 141.0 -> 77.1

MRM 267.9 -> 77.1

MRM 267.9 -> 141.1



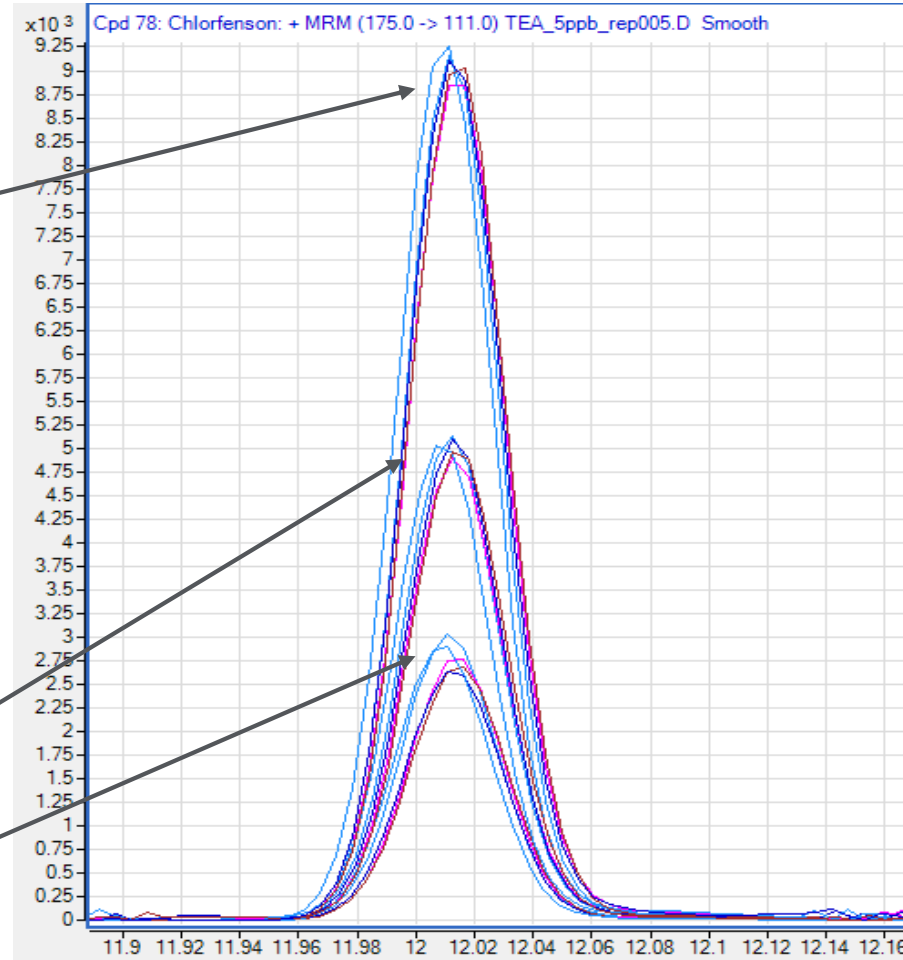
8 Replicates

# Repeatability and robustness

Chlorfenson in Organic Honey – 5.08ppb

MRM 175.0 ->  
111.0

MRM 111.0 -> 75.0  
MRM 177.0 -> 113.0

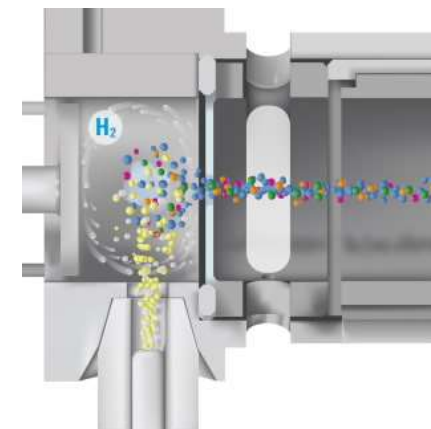


8 Replicates



# Jetclean

- Jetclean self-cleaning ion source can reduce maintenance time significantly
  - Minimizes the need to vent and manually clean the system
- Very low usage of H<sub>2</sub>
- Multiple modes of operation
- Ability to schedule at any time
  - Concurrent
  - Mid sequence
  - End of sequence
  - 2.30 am on Monday before we come to work for the week



# Suspect Screening

## Agilent 7250 GC/Q-TOF



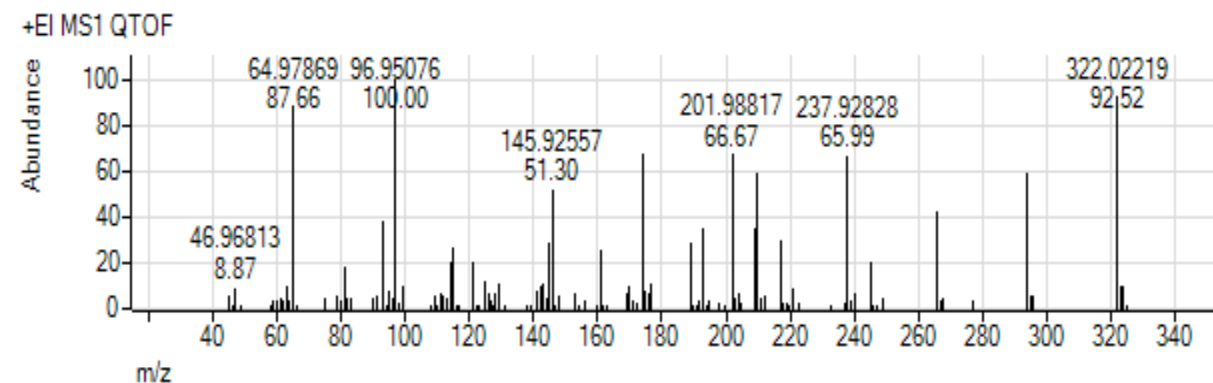
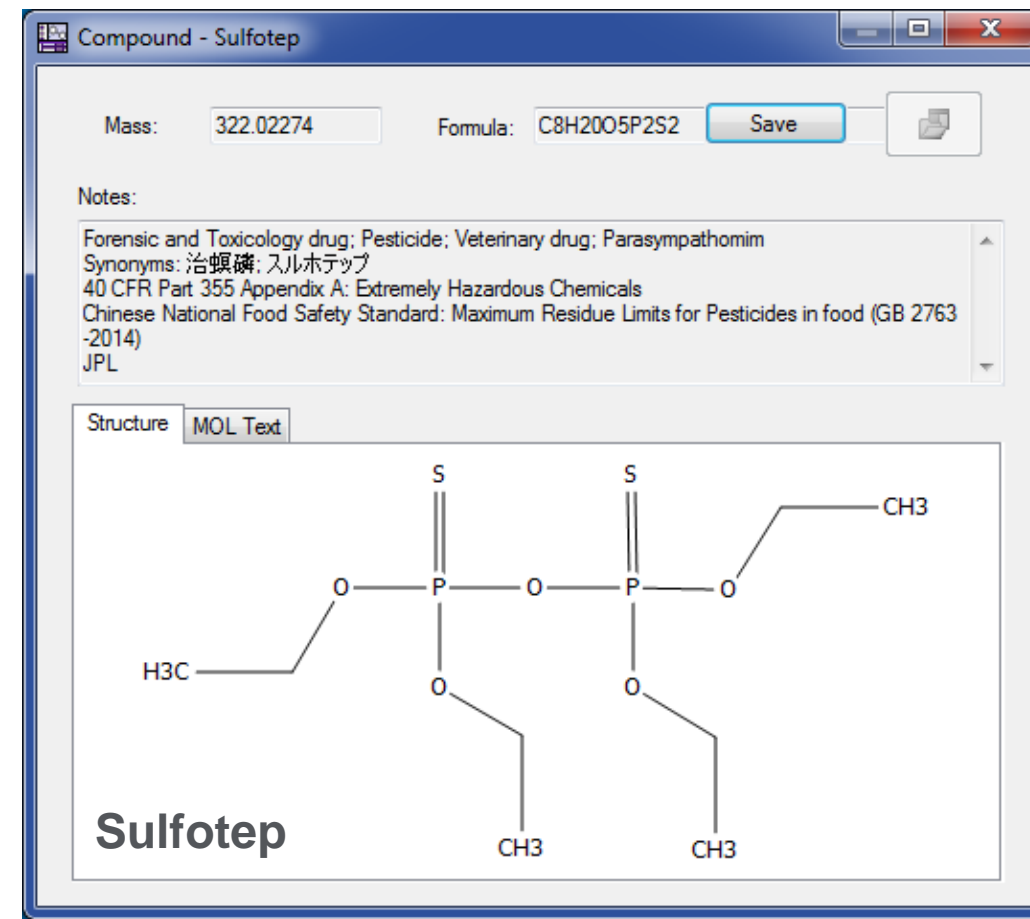
# Expanded Pesticides PCDL GC/Q-TOF

## Personal Compound Database and Library

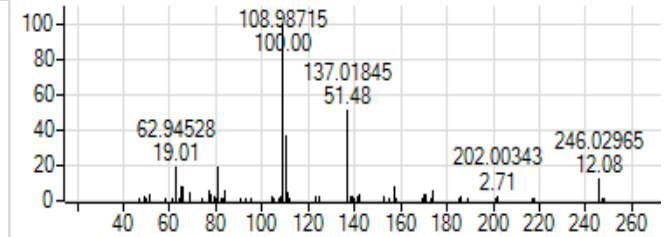
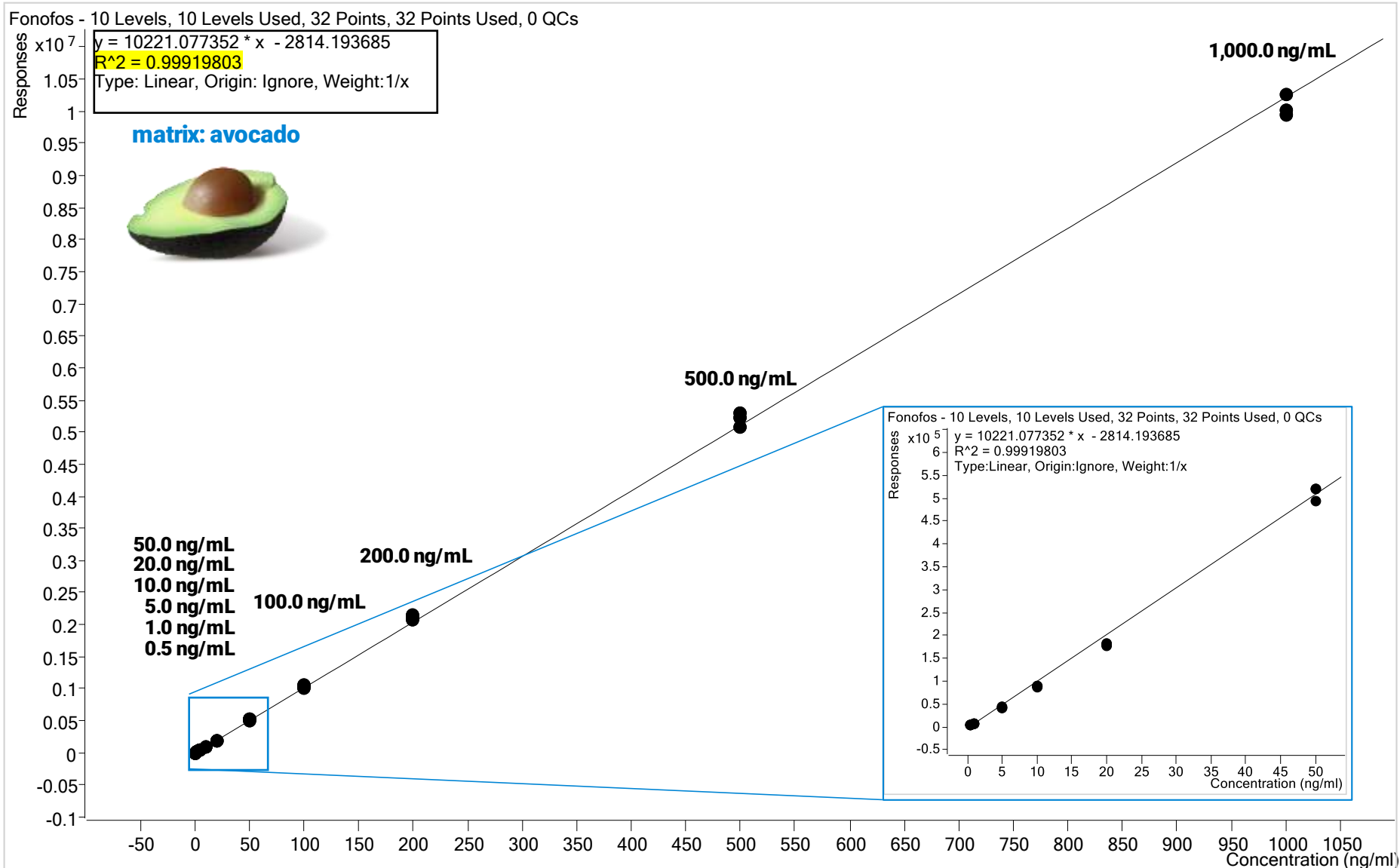
- ~1000 compounds
- Pesticides and Environmental Pollutants
- Retention time information
- Extensive metadata
- High resolution, curated accurate mass spectra

## Also included with Pesticides PCDL

- **Pesticides Workflow Guide** – Comprehensive guide to implement a dual qualitative and quantitative screening approach
- **Two GC Methods** – A pair of optimized GC Methods developed in conjunction with leading experts



# Quantitative Linear Dynamic Range



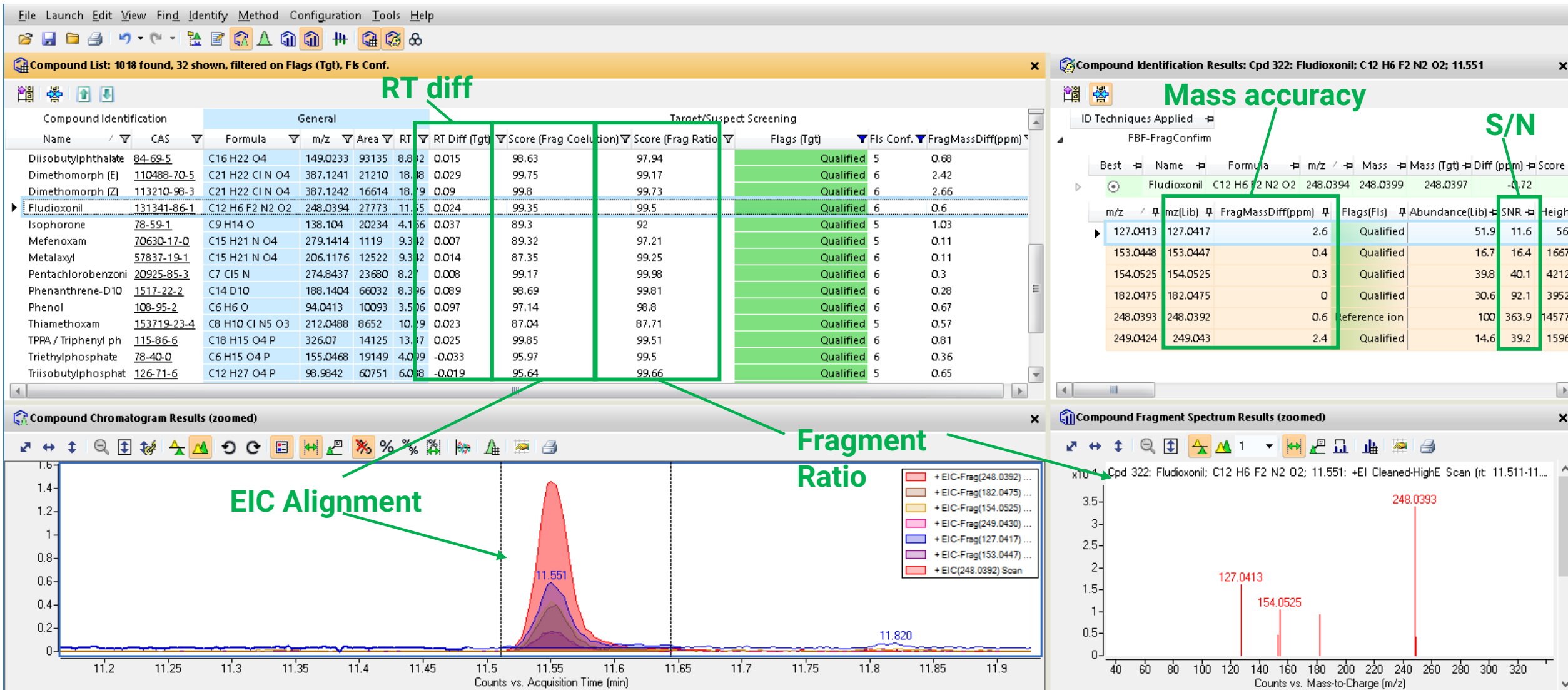
**Compound: Fonofos**  
**High Resolution Library**

**3.5+ Orders of Magnitude  
 Linear Dynamic Range in  
 complex matrix**

**Excellent Linearity**

**Consistent Response  
 Factors**

# Identifying compounds





# Increased Productivity Options



5977B GC/MSD



Intuvo-7000D GC/TQ

New P&EP Applications Kit  
With Intuvo MRM Database



7250 GC/Q-TOF

Enhanced PCDL for Pesticides  
& Environmental Pollutants

**Thank you!**