



**ThermoFisher**  
SCIENTIFIC

## Two Years On: The Impact of Orbitrap™ GC-MS in Food Analysis

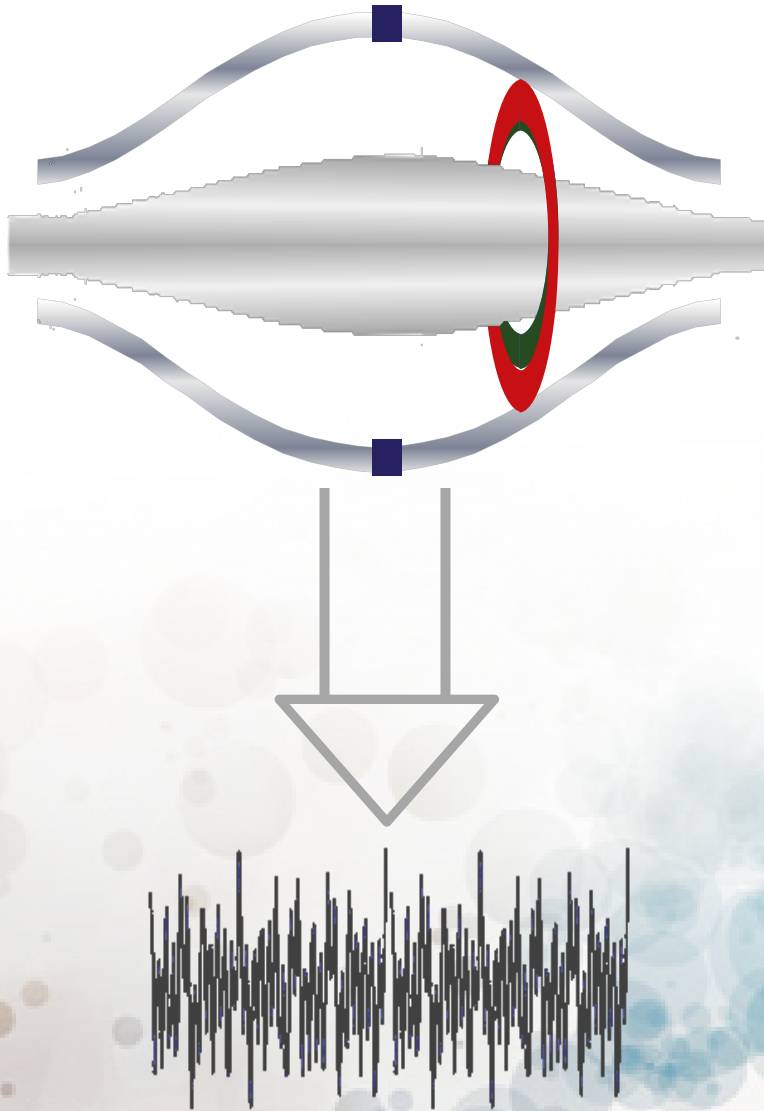
NACRW 2017

*Paul Silcock, Sr. Marketing Manager Orbitrap GC-MS*

PP10570

The world leader in serving science

# Orbitrap Mass Analyzer



$$\omega = \sqrt{\frac{k}{m/z}}$$

- Ions injected into the Orbitrap are trapped in an electrostatic field
- Each ion oscillates axially with a frequency that is proportional to its mass
- An image current of these oscillations is measured using a split outer electrode
- This image is then converted to a mass spectrum using Fourier transform
- The longer a signal (transient) is measured, the higher the resolution

## ***A fully-integrated GC Orbitrap system Opens a new chapter in GC-MS***

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# Orbitrap GC-MS family



**Redefining Routine GC-MS**

RP 60,000 (FWHM @  $m/z$  200)

EI (VeV) / CI; Full-scan; Timed-SIM

**NACRW 2016: Exactive™ GC Orbitrap™ GC-MS System**



**ASMS 2015: Q Exactive™ GC Orbitrap™ GC-MS/MS System**

Unprecedented Depth in Analysis

RP 120,000 (FWHM @  $m/z$  200)

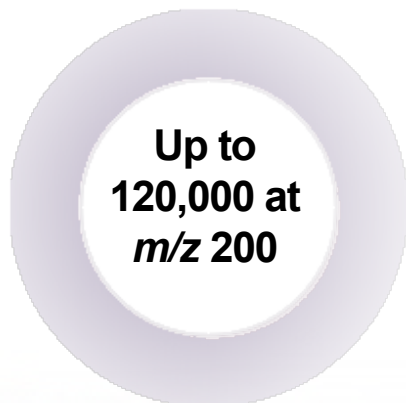
EI (VeV) / CI; Full-scan, Timed-SIM

MS/MS capability

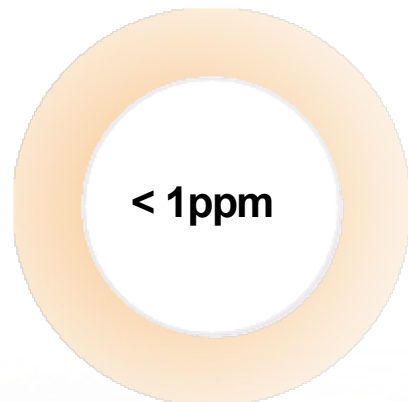


# Orbitrap GC system highlights

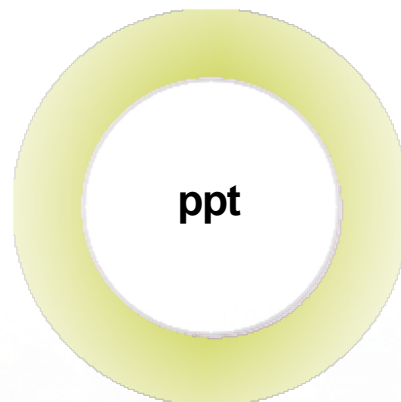
## Resolving Power



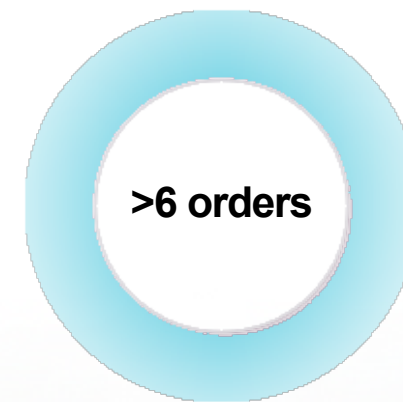
## Mass Accuracy



## Sensitivity



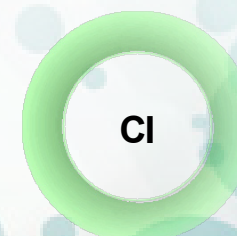
## Dynamic Range



- Standard library searchable spectra



- Molecular ion confirmation (incl. adducts)

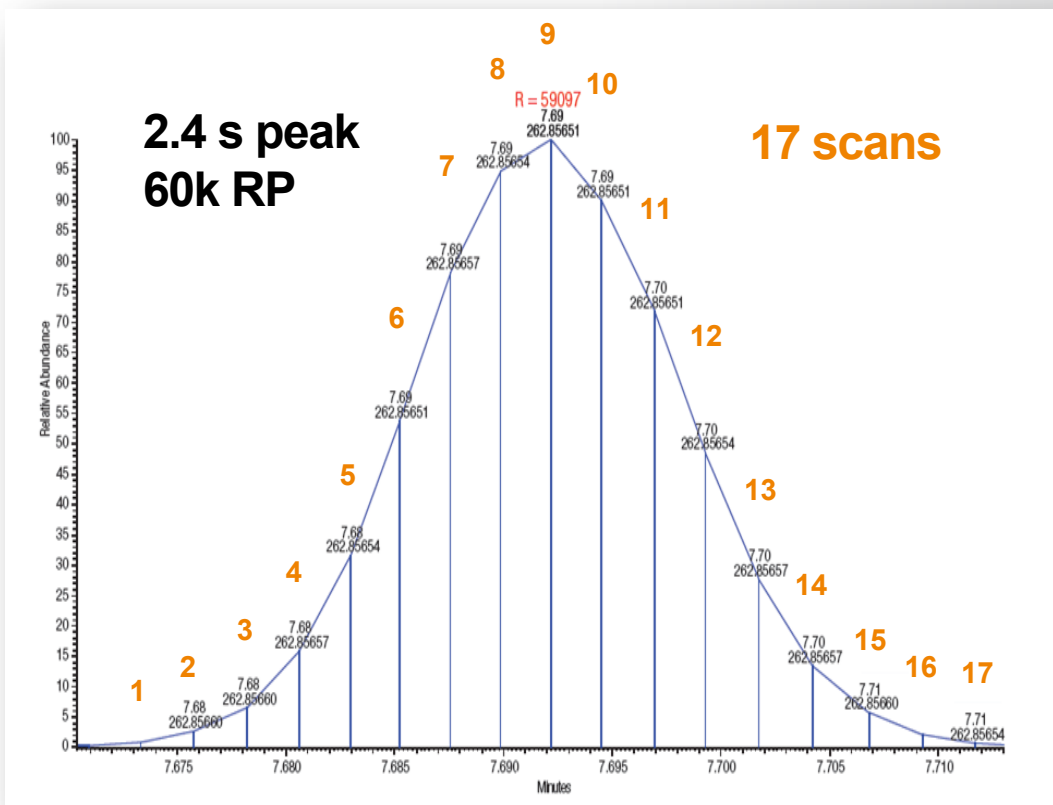


Harder

Ionization Range

Softer

## “Orbitrap is too slow for GC”

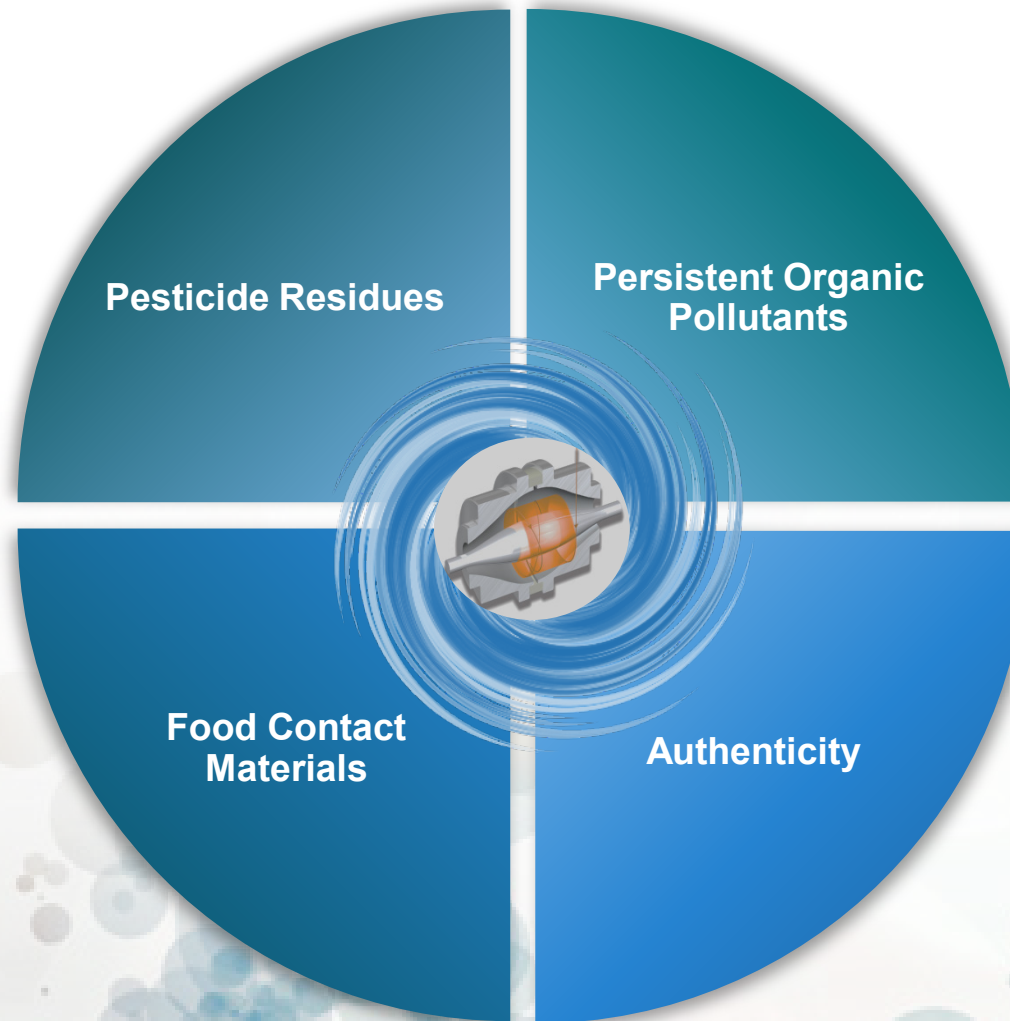


Dieldrin 100pppb in baby food 60,000 RP (m/z 200)

## “Orbitrap spectra are not library searchable”

Compound	NIST SI GC QToF	NIST SI Orbitrap
124-trichlorobenzene	890	834
Nitrobenzene	776	871
HCB	930	811
Acenaphtene	924	901
Aniline	730	715
2-Chlorophenol	745	842
1,3- Dichlorobenzene	930	900
Hexachlorethane	930	924
Hexachlorbutadiene	936	940
<b>Average</b>	<b>866</b>	<b>860</b>

# The impact of Orbitrap GC-MS in food analysis

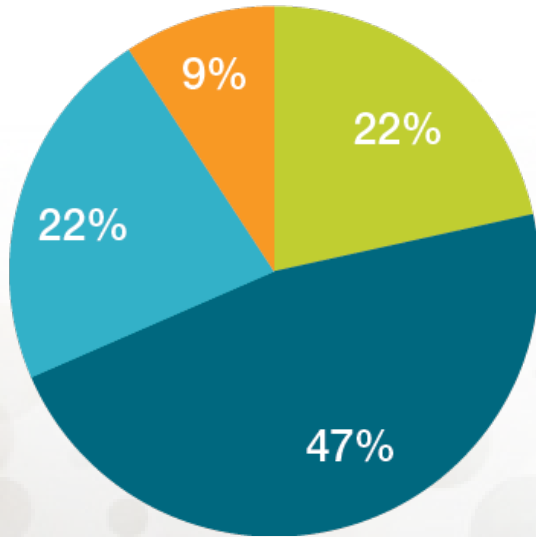


# Instrument Detection Limits (Orbitrap vs. Triple Quad)

150 compounds in mixed vegetable matrix (QuEChERS)

## GC Orbitrap

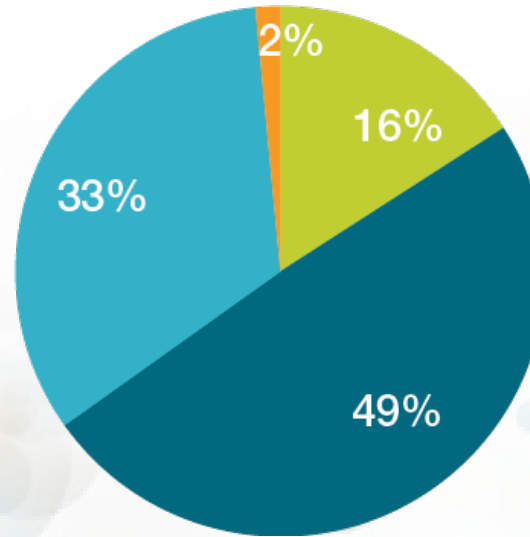
IDL ppb



Full-scan

## GC-MS/MS

IDL ppb



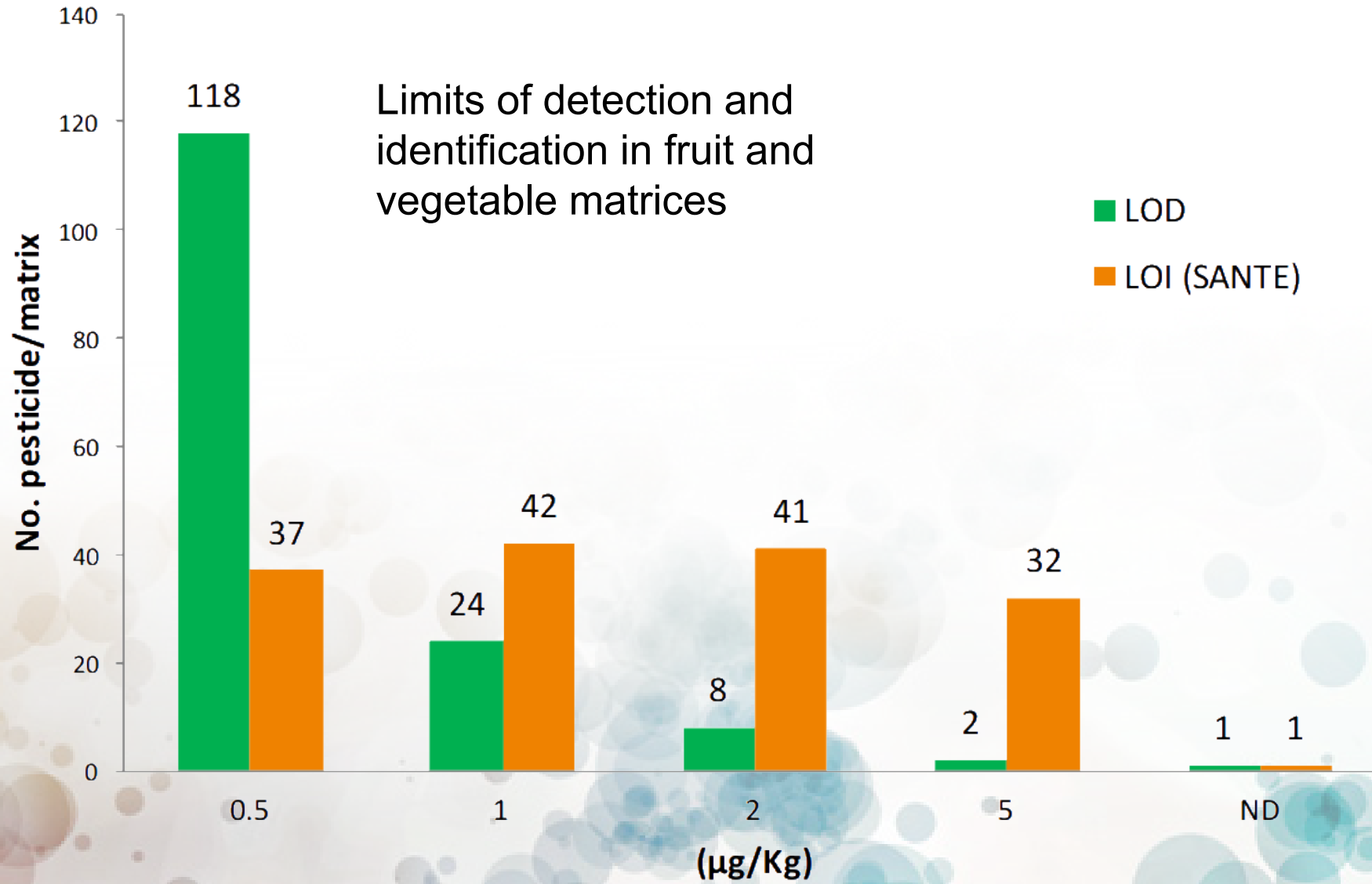
SRM

Pesticide Residues

**Triple quadrupole level sensitivity possible with a non-target acquisition**

\*Acquired on the Q Exactive GC system – the Exactive GC system provides equivalent performance





Pesticide Residues

“The overall outcome of the evaluation is that GC-EI-full scan Orbitrap HRMS is **considered highly suited for pesticide residue analysis**. With that, it provides an **alternative to GC-triple quadrupole MS**, with the advantage that the measurement is **more straightforward**, and that **besides quantitative determination an additional screening can be performed** for other analytes.”

H.G.J. Mol, M. Tienstra, P. Zomer, Evaluation of gas chromatography -electron ionization - full scan high resolution Orbitrap mass spectrometry for pesticide residue analysis, *Analytica Chimica Acta* (2016)



Pesticide Residues

“These **good results** present the **advantages derived from full scan analysis** applicable to other compounds not present in the selected and retrospective evaluation together with an **easier scope management** compared with GC-TQ-MS/MS.”

Ucles, S., A., Lozano, A., M.J. Martínez Bueno, Fernández-Alba A.R. SHIFTING THE PARADIGM IN GAS CHROMATOGRAPHY MASS SPECTROMETRY PESTICIDE ANALYSIS USING HIGH RESOLUTION ACCURATE MASS SPECTROMETRY, Journal of Chromatography A (2017)

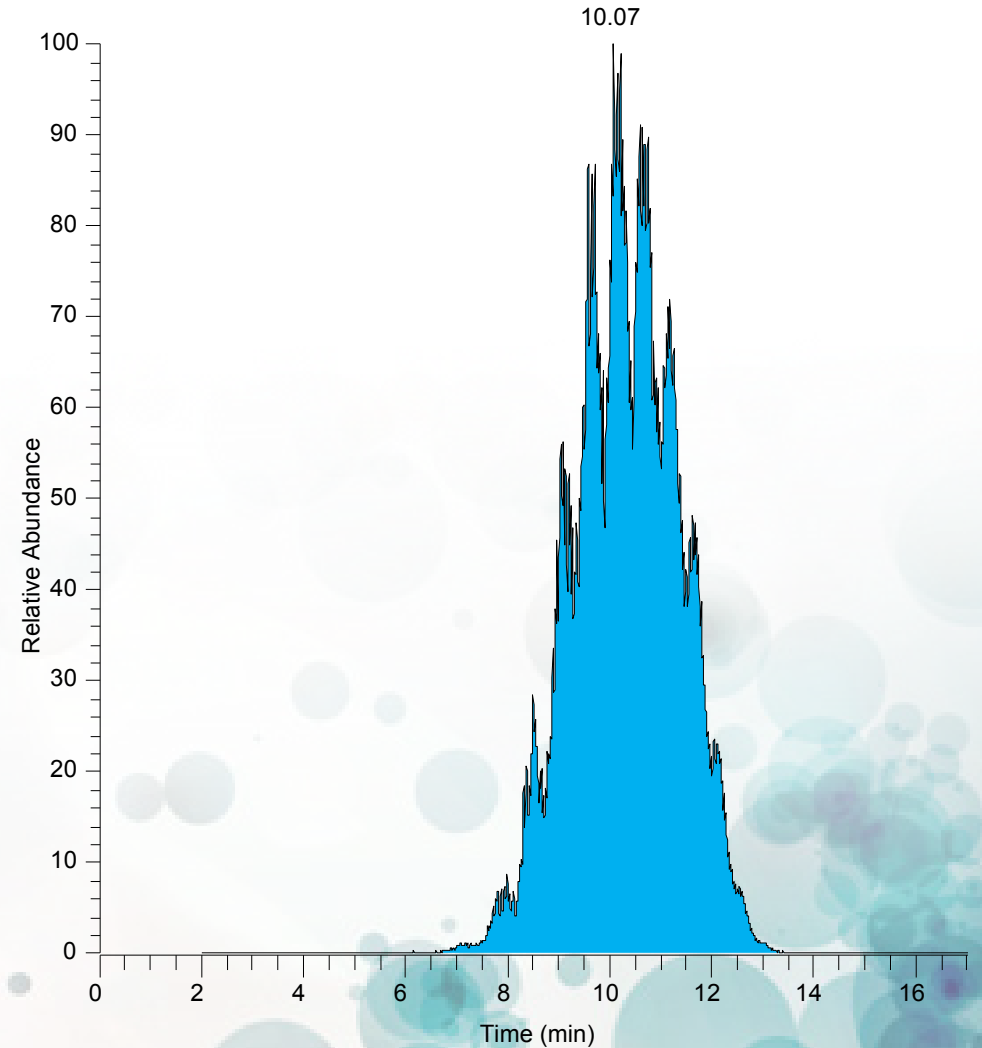


Pesticide Residues

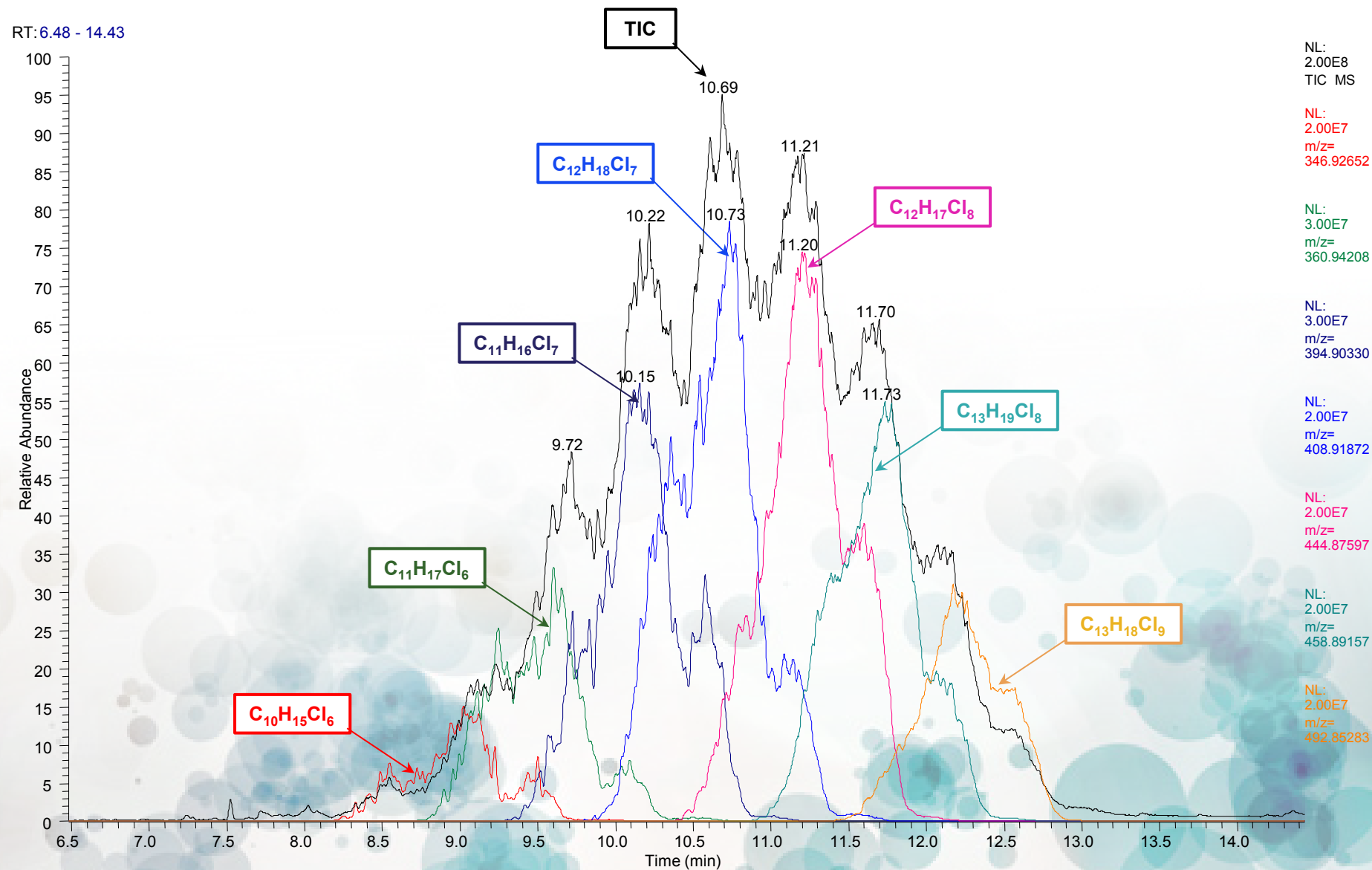
# Chlorinated paraffins

- Currently there is no consensus for the use of a validated analytical procedure for routine monitoring of CPs in food and feed.
- SCCPs and MCCPs have thousands of homologues and isomers that cannot be separated chromatographically.
- This, together with low concentrations makes their detection and quantification difficult.

Persistent  
Organic  
Pollutants



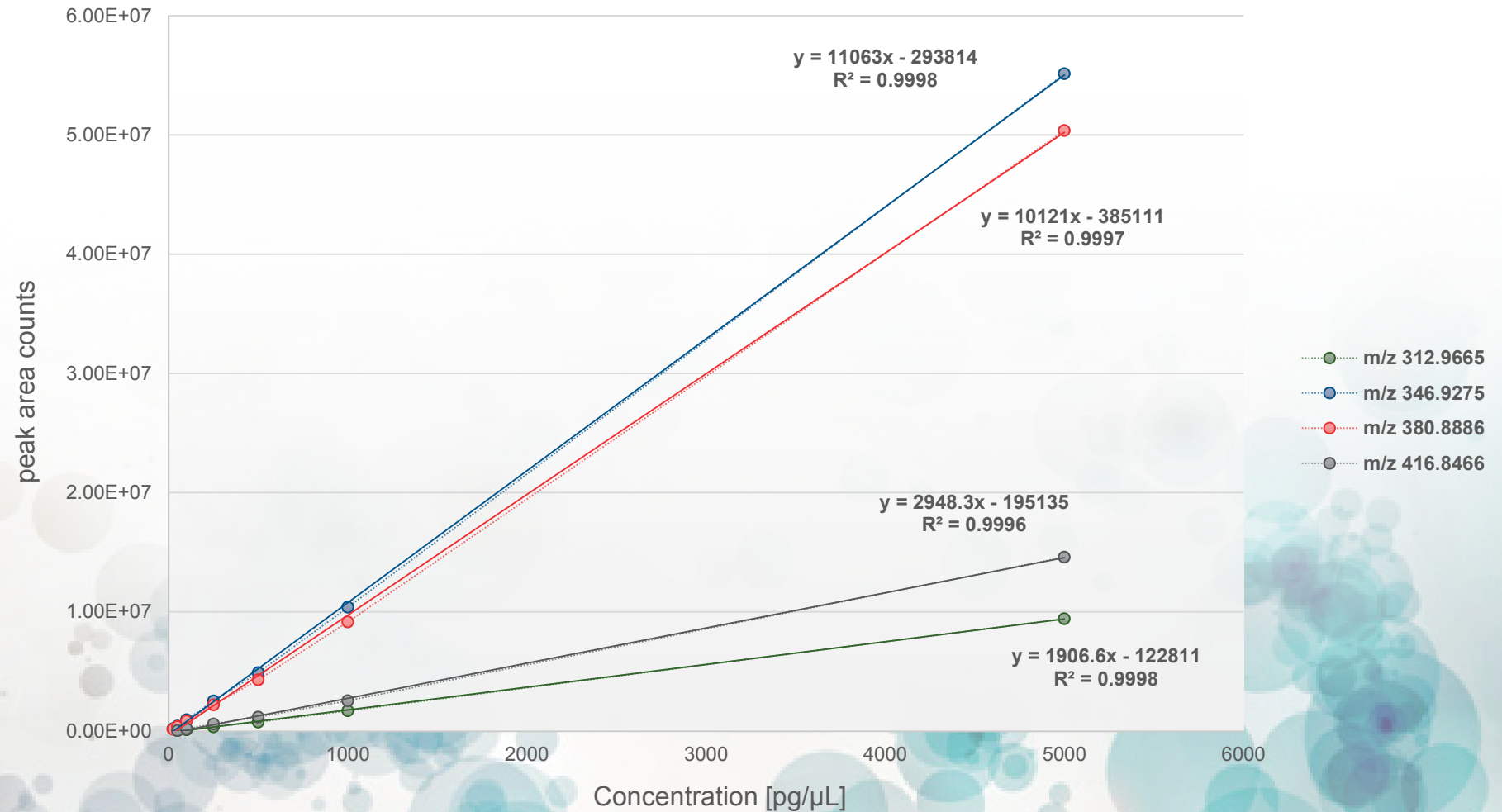
# High resolution accurate mass selectivity 63% C<sub>10</sub>-C<sub>13</sub> technical mix, NCI, 60k resolution



Persistent  
Organic  
Pollutants

# Negative chemical ionization: Linearity for SCCP 63% C10

Excellent compound linearity (25-5,000 ppb) was obtained for these C10 chlorinated homologues present in the SCCP 63% technical mixture.



Persistent  
Organic  
Pollutants



“Using high resolution, accurate mass Orbitrap-MS **enables much deeper insights** into the pattern and content of CPs **without having to fear mass interferences** from other CPs or halogenated compounds such as PCBs. Preliminary results suggest that determination of both CPs and PCBs in the same sample in one run is possible, representing **a potential for shorter sample preparation and quicker analyses** of these types of POPs in food.”

HIGH RESOLUTION ACCURATE MASS SCREENING FOR CHLORINATED PARAFFINS IN FOOD SAMPLES USING GC-ORBITRAP MASS SPECTROMETRY (Kerstin Krätschmer et al. Dioxin 2017)

# Polybrominated diphenyl ethers

**C S B** Consorci Sanitari  
de Barcelona



Agència  
de Salut Pública

- European guidelines stipulate extremely low concentrations
- Analytical methods with a limit of quantification of 0,01 ng/g wet weight or lower
- BDE 209 (decabromo) limit is 10 ppt in the sample

5.3.2014

EN

Official Journal of the European Union

L 65/39

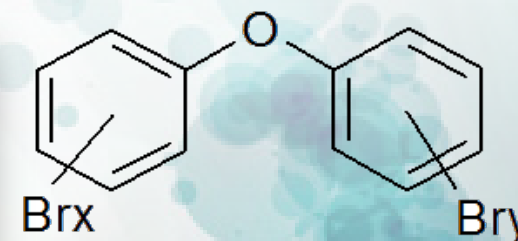
## COMMISSION RECOMMENDATION

of 3 March 2014

on the monitoring of traces of brominated flame retardants in food

(Text with EEA relevance)

(2014/118/EU)



$x=1-5, y=0-5$

Persistent  
Organic  
Pollutants

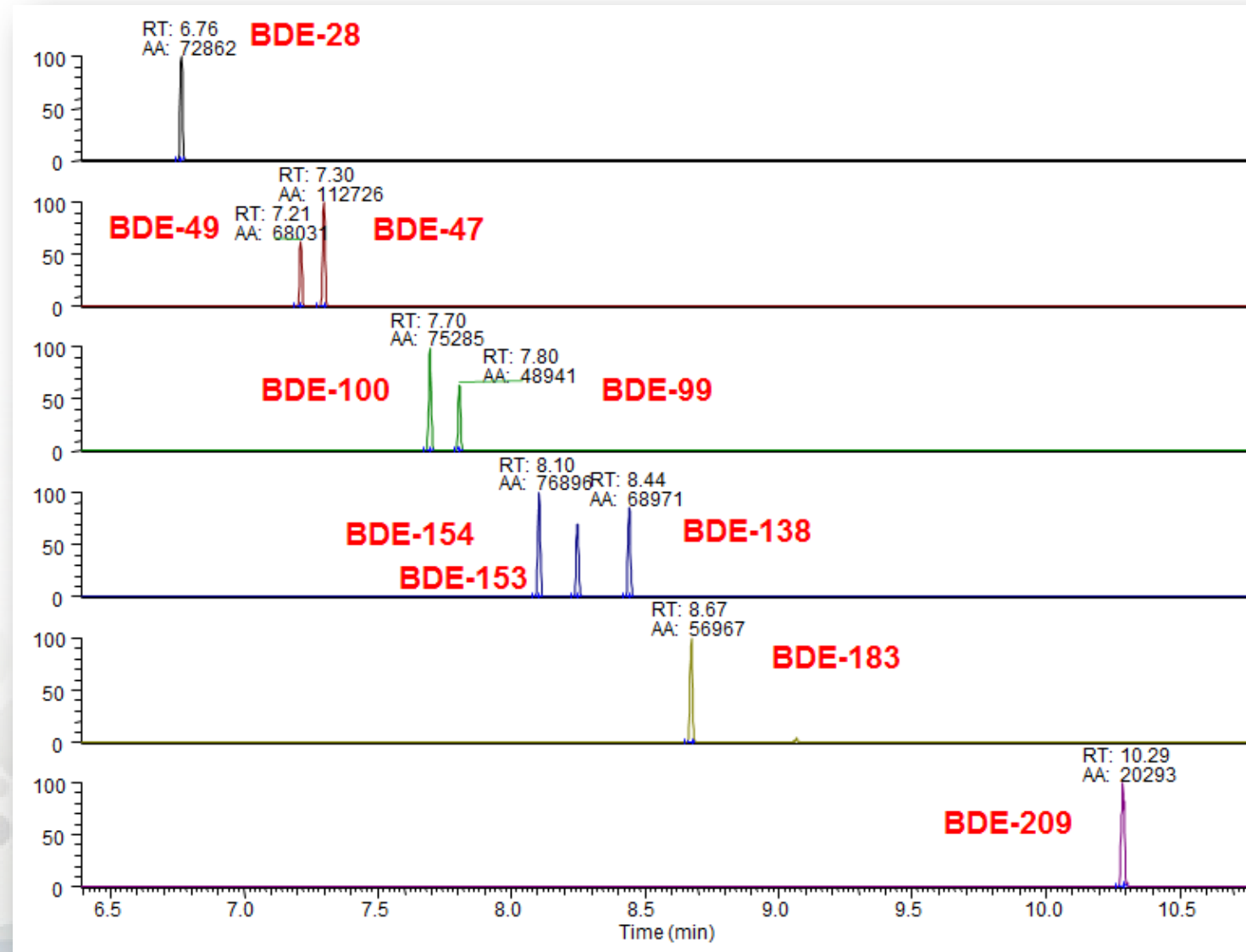


# Tuna sample spiked 0.01 ng/g PBDEs

**C S B** Consorci Sanitari de Barcelona



Agència de Salut Pública



Persistent Organic Pollutants

**C S B** Consorci Sanitari  
de Barcelona



Agència  
de Salut Pública

“GC-Orbitrap is a useful tool for control labs,  
**outstanding sensitivity...high selectivity** when  
analyzing complex matrices...**high robustness**  
...helps to fulfill new regulations with  
extremely low limits (e.g. PCBs, PBDEs).”



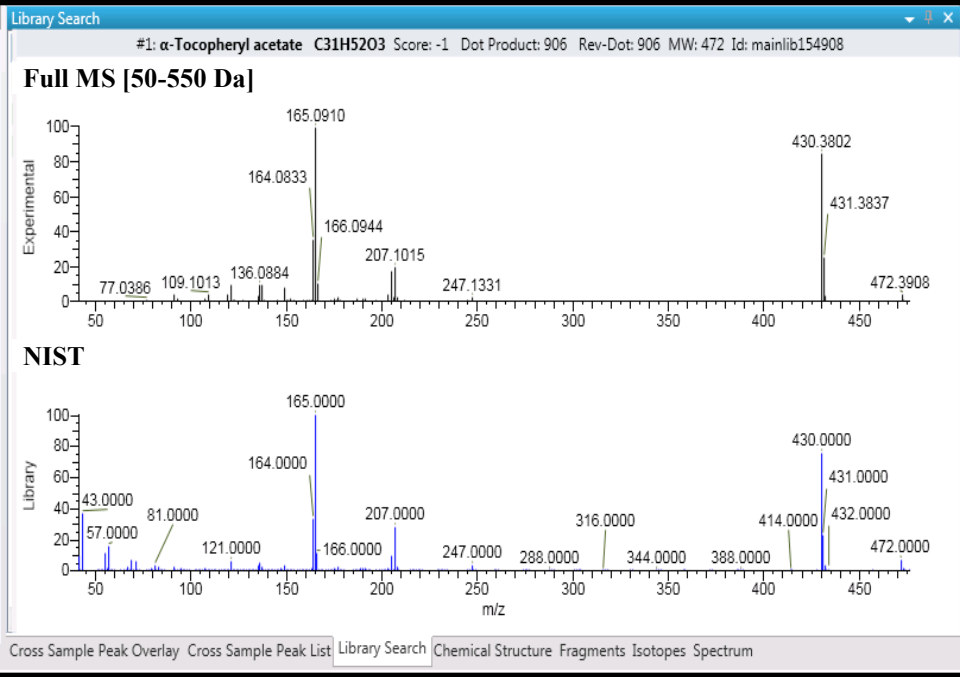
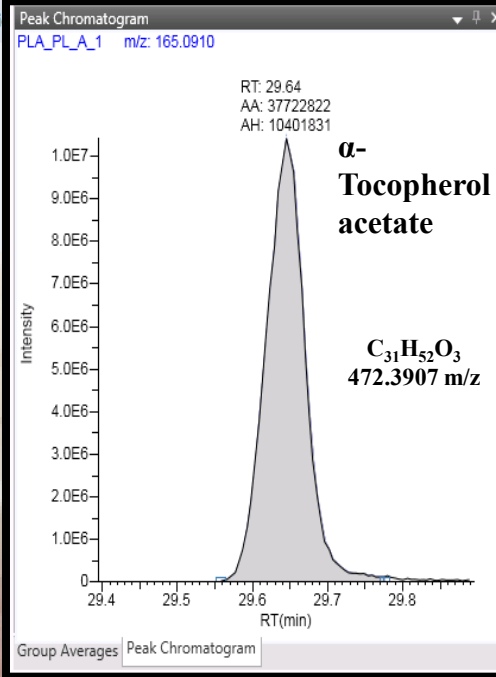
Persistent  
Organic  
Pollutants

Practical Experiences of Implementing POPs Methods using  
Orbitrap™ GC-MS. Nuria Cortés-Francisco, BFR 2017

# Food contact materials

## Food Contact Materials

	Retention Time	M/Z	Mass	Control_A_1 MS Area	Control_A_2 MS Area	Control_B_1 MS Area	Control_B_2 MS Area	PLA_A_1 MS Area	PLA_A_2 MS Area	PLA_B_1 MS Area	PLA_B_2 MS Area	PLA_PL_A_1 MS Area	PLA_PL_A_2 MS Area	PLA_PL_B_1 MS Area	PLA_PL_B_2 MS Area	Solvent_1 MS Area	Solvent_2 MS Area
89	21.31	71.0856	71.0856	2,906,189	3,181,645	4,973,355	4,376,546	6,522,861	5,096,158	4,548,565	7,137,853	7,200,242	3,972,469	4,531,869	3,869,464	606,119	514,351
90	21.67	71.0855	71.0855	21,633,096	24,353,864	9,332,591	8,416,549	7,326,185	8,545,067	7,670,251	7,607,553	8,933,675	7,946,563	3,007,003	2,974,601	1,668,692	603,850
91	21.90	149.0232	149.0232	850,309,194	960,182,684	4,914,320,782	4,461,895,103	128,133,678	143,271,661	1,936,903,895	886,832,343	435,124,627	408,752,566	515,268,113	520,984,280	466,252	500,020
92	22.96	71.0855	71.0855	21,150,295	24,194,477	4,371,689	4,268,147	6,612,378	7,111,942	5,499,518	5,442,136	8,505,315	8,101,392	2,056,985	2,314,785	1,593,835	533,879
93	24.21	71.0855	71.0855	22,899,636	25,669,032	12,414,868	13,434,321	11,731,892	13,033,318	13,406,816	12,142,680	12,774,764	12,267,400	7,189,117	8,220,336	1,475,356	1,061,623
94	25.45	71.0855	71.0855	13,052,045	15,748,047	4,228,435	4,618,454	7,094,313	7,470,742	6,678,613	6,561,106	8,343,610	8,147,282	3,092,596	2,946,050	1,320,256	761,956
95	26.65	71.0855	71.0855	11,114,346	11,662,670	5,808,105	6,091,809	7,403,231	7,576,025	7,007,032	7,080,239	8,530,663	8,134,808	3,461,096	3,296,232	490,321	572,124
96	27.82	71.0855	71.0855	5,037,916	9,642,655	6,901,563	2,892,324	5,146,173	4,076,177	4,431,101	3,934,276	4,678,423	4,872,961	2,130,416	1,792,576	833,340	904,271
97	29.21	71.0855	71.0855	6,603,453	2,209,004	2,255,612	1,919,226	2,540,297	2,651,372	2,320,035	2,259,485	2,312,559	5,176,497	1,890,298	2,215,720	709,901	810,219
98	29.64	165.0910	165.0910	12,548,640	16,629,091	6,327,452	6,173,967	9,186,869	11,273,683	12,972,526	17,214,053	37,722,822	37,156,586	12,535,053	12,783,470	257,481	213,234



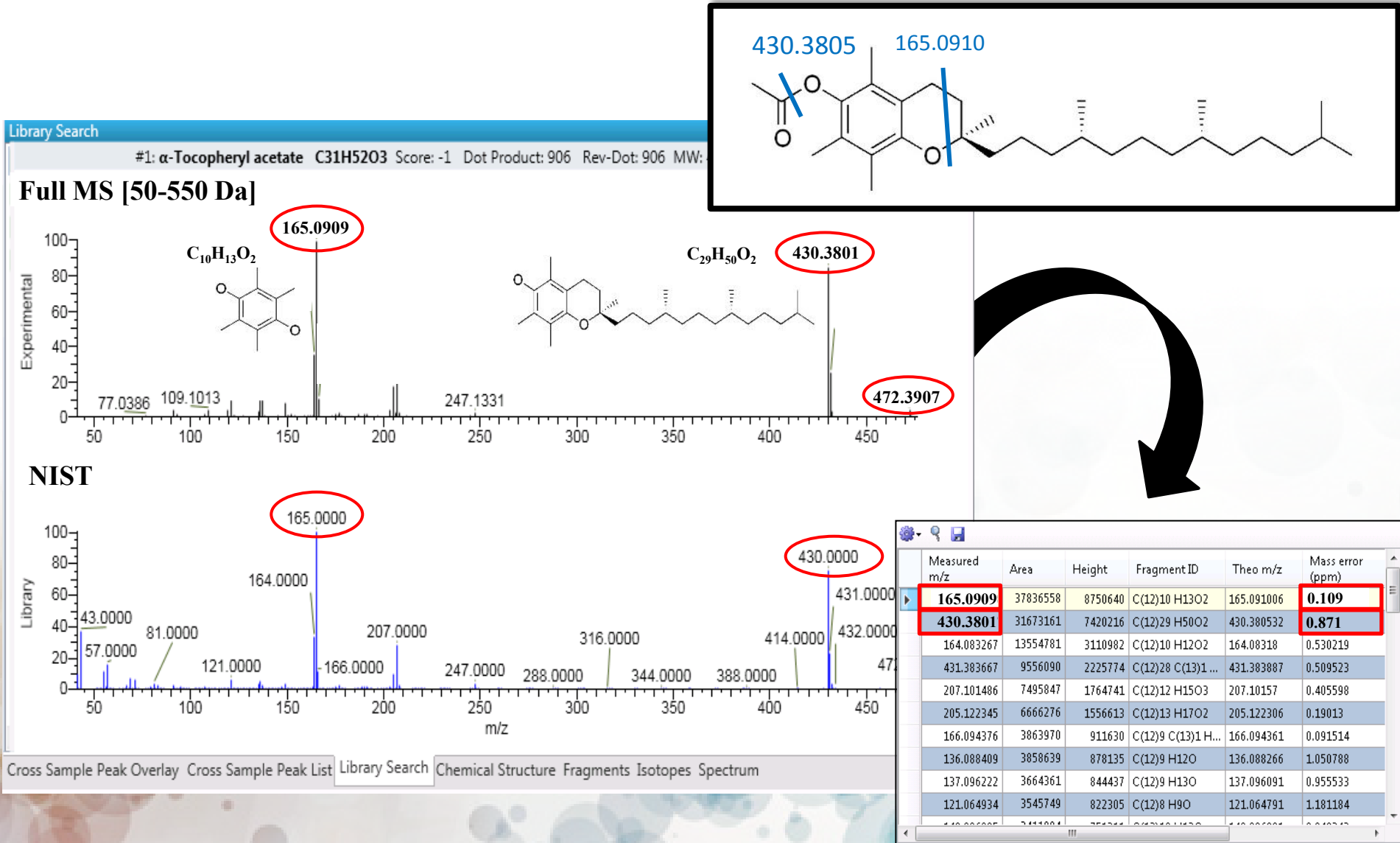
ID Source Detail	Match Result Name	Formula	Isot
mainlib	<b>alpha-Tocopheryl acetate</b>	<b>C31H52O3</b>	
mainlib	alpha-Tocopherol-beta-D-manr	C35H60O7	
mainlib	(±)-alpha-Tocopherol acetat	C31H52O3	
mainlib	Vitamin E	C29H50O2	

HRF values > 95



# Food contact materials

Food Contact Materials



PRECURSOR ION						FRAGMENT IONS			
Rt	Accurate mass value (m/z)	Formula Proposed	SI*	Score *	HRF *	Accurate mass value (m/z)	Formula proposed	Mass Deviation* (ppm/mDa)	Identified compounds
9.8	300.1567	C <sub>15</sub> H <sub>24</sub> O <sub>6</sub>	827	96.6	98.0	113.0597	C <sub>6</sub> H <sub>9</sub> O <sub>2</sub>	1.4 / 0.2	<b>tripropylene glycol diacrylate</b>
						55.0178	C <sub>3</sub> H <sub>3</sub> O	1.6 / 0.1	
11.0	294.3281	C <sub>21</sub> H <sub>42</sub>	820	96.4	99.0	69.0699	C <sub>5</sub> H <sub>9</sub>	0.5 / 0.03	<b>10-Heneicosene</b>
						83.0855	C <sub>6</sub> H <sub>11</sub>	0.3 / 0.02	
29.6	472.3911	C <sub>31</sub> H <sub>52</sub> O <sub>3</sub>	898	97.5	99.8	430.3801	C <sub>29</sub> H <sub>50</sub> O <sub>2</sub>	0.9 / 0.4	<b>alpha-Tocopherol acetate</b>
						165.0909	C <sub>10</sub> H <sub>13</sub> O <sub>2</sub>	0.8 / 0.1	



“HRAMS has shown to be **a useful analytical approach** for the elucidation of NIAS based on the accurate mass measurement in full scan and fragmentation modes using the Q-Orbitrap-MS analyser.

the combination of accurate mass matching and explaining the ions observed in the spectrum provides **a fast and confident route to the identification of unknown compounds.**”



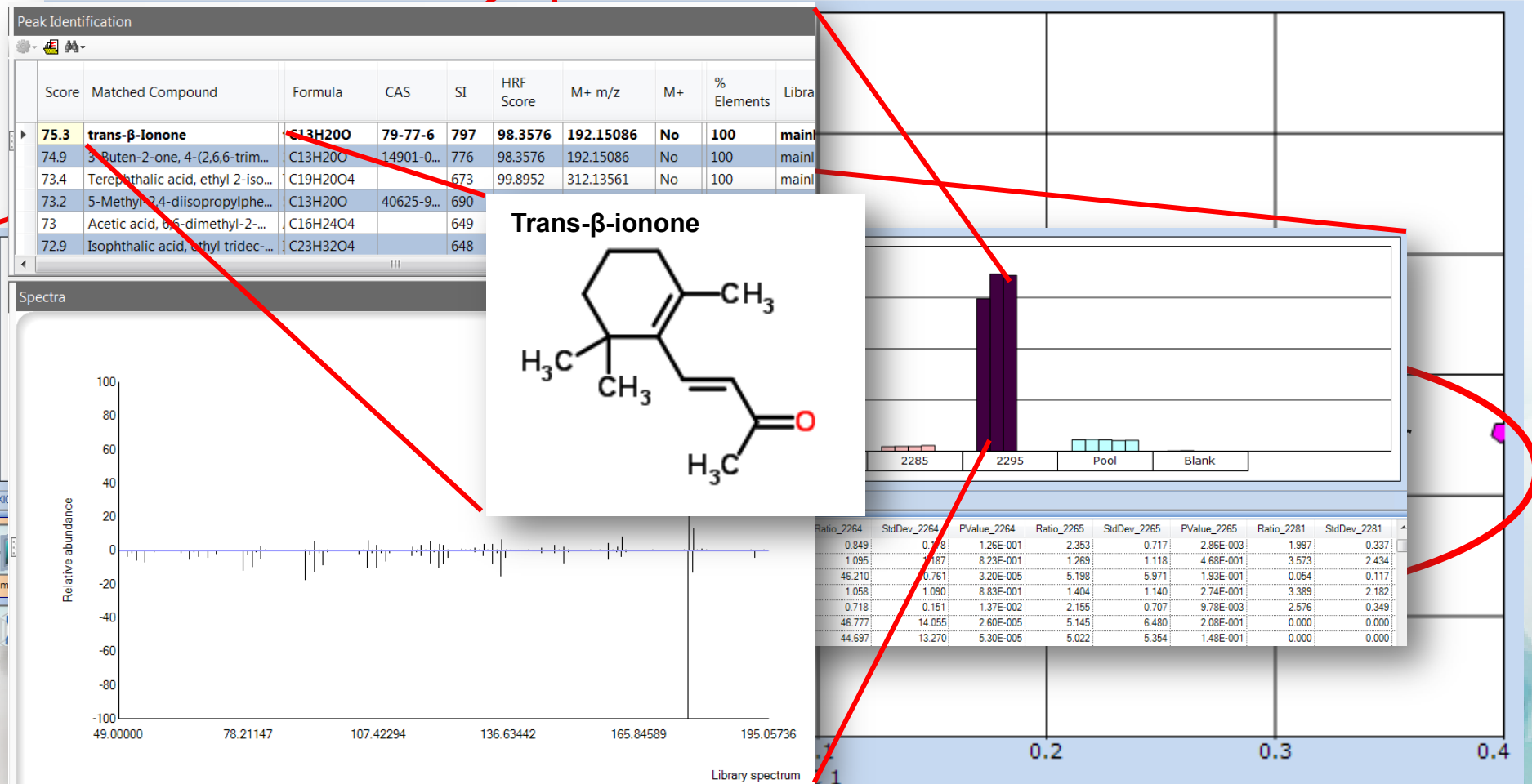
Identification of non-intentionally added substances in food packaging nano films by gas and liquid chromatography coupled to Orbitrap mass spectrometry  
M.J. Martínez-Bueno, M.D. Hernando, S. Uclés, L. Rajski, S. Cimminoc, A.R. Fernández-Alba: Talanta 172 (2017) 68–77



# Whiskey authenticity

## Authenticity

PCA : Bourbon and 3 wood aged clearly different from other whiskeys.  
Single distillery whiskeys also show clear differences.



“GC coupled with Orbitrap MS is **a major step forward**...Q Exactive GC provides a **comprehensive chemical profile** of a sample, detecting both major and minor components with a **high degree of confidence** (spectral quality and linearity)...Sophisticated, yet **simple to use, software tools** provides fast isolation of peaks of interest and **intelligent compound identification** with sub 1 ppm mass accuracy.”

Professor Jana Hajslova, Jana Pulkrabova, Michal Stupák  
– RAFA 2016



**UNIVERSITY OF CHEMISTRY AND TECHNOLOGY, PRAGUE**  
Faculty of Food and Biochemical Technology  
Department of Food Analysis and Nutrition

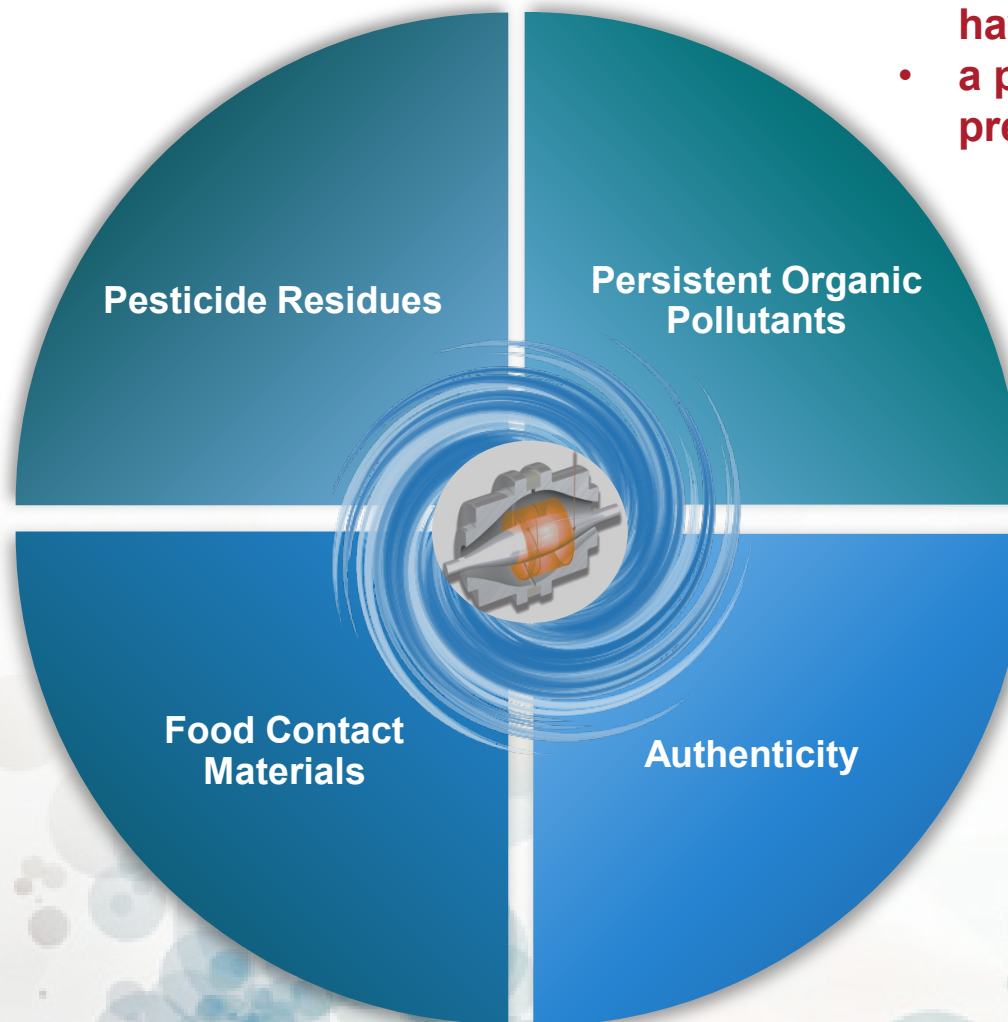




# The impact of Orbitrap GC-MS in food analysis

- **Considered highly suited for pesticide residue analysis**
- **Alternative to GC-triple quadrupole MS systems**
- **More straightforward,**
- **Easier scope management**

- **a fast and confident route to the identification of unknown compounds**



- **enables much deeper insights without having to fear mass interferences**
- **a potential for shorter sample preparation and quicker analyses**

- **outstanding sensitivity**
- **high selectivity**
- **high robustness**

- **a major step forward**
- **comprehensive chemical profile**
- **high degree of confidence**
- **simple to use, software tools**
- **intelligent compound identification**

