



# The Impact of GC Tandem Quadrupole Mass Spectrometry on Food Safety Analysis

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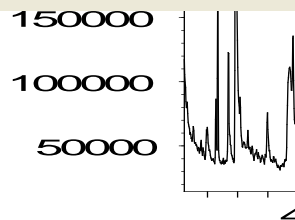
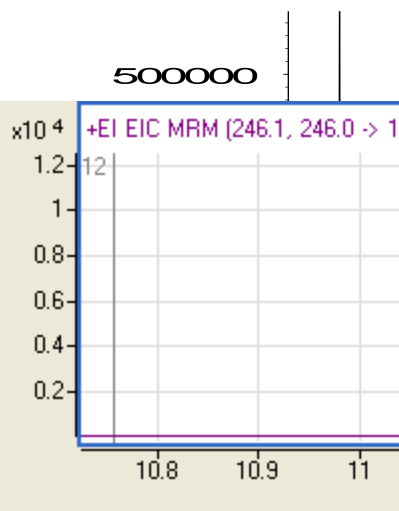
# Outline

- Why GC/MS/MS?
- Analysis of Dioxins, Furans, & PCBs in foods
- Comparison of GC/MS/MS to GC-HRMS
- What's next in food safety analysis?



# Matrix Disappears in GC/MS/MS Leaving Transitions Easy to Find (p,p'-DDE in Spinach)

Abundance

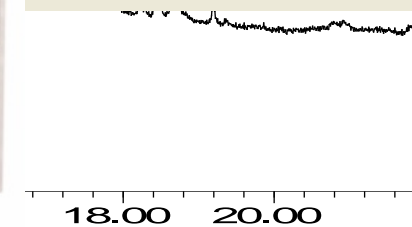
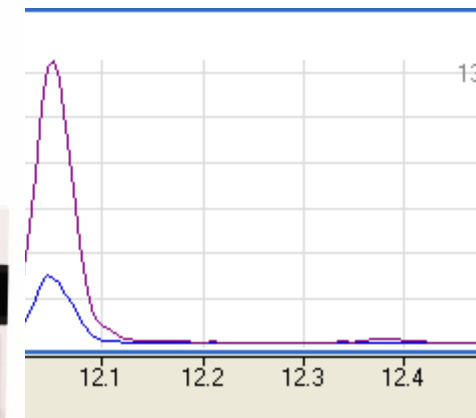


Time-->



ms

p'-DDE



# Dioxin Analysis by GC-MS/MS

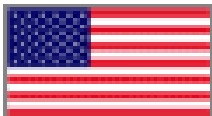
## Collaboration between:



**Prof. Dr. Peter Furst, Dr Thorsten Bernsmann,  
Dominik Baumeister  
CVUA-MEL, Munster, Germany**



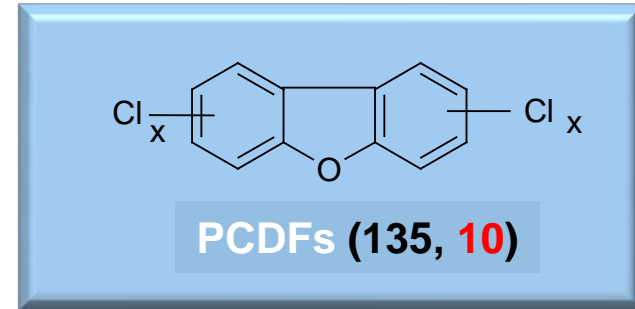
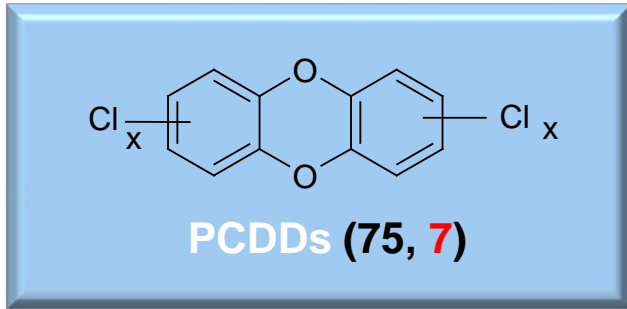
**Chris Sandy, Marc Tischler & Li Sun,  
Agilent Technologies, USA**



# 1. Introduction / Background

## What are Dioxins?

- Dioxins are a group of highly toxic persistent organic pollutants



- Not manufactured deliberately – by-products of waste incineration, chemical and pesticide manufacturing and pulp / paper bleaching
- 80% of Human exposure to Dioxins from food of animal origin
- Dioxins accumulate in the fatty tissues of beef and dairy cattle, pigs, poultry and seafood



# Dioxins – Characteristics

- **Highly toxic and linked to serious health effects**
  - **Cancer**
  - **Endocrine disruption**
  - **Reproductive disorders**
  - **Chloracne**
  - **Immune system disorders**



# Several Foodstuff Related 'Dioxin incidents' in the past 20 years



- 1997 USA Contaminated ball clay



- 1998 Brazil citrus peel



- 1999 Belgium Contaminated poultry



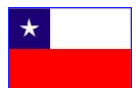
- 2000 Spain Contaminated Choline chlori



- 2004 Netherlands Potato animal feed



- 2005 / 2006 Belgium Contaminated pork meat



- 2008 Chile Contaminated feed for pigs



- 2008 Ireland Contaminated pork and beef



- 2010 Ukraine Contaminated corn

- 2011 Germany Contaminated animal feed, pork, chicken & eggs



# Dioxin Incident, Ireland December 2008

Source : FSAI News

**All pork is recalled after toxin find in pigs**  
Consumers told not to eat pork and bacon after dioxin found in feed and fat samples

**Total recall of pork and bacon after health scare**  
Consumers told not to eat pork and bacon after dioxin found in feed and fat samples

**Routine tests triggered huge recall**

**Public given assurances over dioxin health threat**

**PORK BANNED**  
All pig meat recalled by safety checks in toxic feed scare

**No cause for health concerns, says watchdog**

**Pork products recalled after toxin found in pig carcasses**

**FEARS ENGINE OIL WAS PUT IN PIGS' FEED**

**Pig feed toxins 'were off the scale'**

**Food safety authority's helpline gets 'unprecedented' number of calls**

**EU food authority has few concerns over Irish pork**



# Dioxin Incident, Ireland December 2008

Source : FSAI News



# TEF\* Values – WHO 1998 / WHO 2005

The International Programme  
on Chemical Safety (IPCS)



| Congener                  | TEF Value | TEF Value     |                  | TEF Value | TEF Value      |
|---------------------------|-----------|---------------|------------------|-----------|----------------|
|                           | WHO 1998  | WHO 2005      |                  | WHO 1998  | WHO 2005       |
| Dibenzo-p-dioxins (PCDDs) |           |               | Dioxin-like PCBs |           |                |
| 2378-TCDD                 | 1         | 1             | Non-ortho PCBs   |           |                |
| 12378-PCDD                | 1         | 1             | PCB 77           | 0.0001    | 0.0001         |
| 123478-HxCDD              | 0.1       | 0.1           | PCB 81           | 0.0001    | <b>0.0003</b>  |
| 123678-HxCDD              | 0.1       | 0.1           | PCB 126          | 0.1       | 0.1            |
| 123789-HxCDD              | 0.1       | 0.1           | PCB 169          | 0.01      | <b>0.03</b>    |
| 1234678-HpCDD             | 0.01      | 0.01          |                  |           |                |
| OCDD                      | 0.0001    | <b>0.0003</b> |                  |           |                |
|                           |           |               |                  |           |                |
| Dibenzofurans (PCDFs)     |           |               | Mono-ortho PCBs  |           |                |
| 2378-TCDF                 | 0.1       | 0.1           | PCB 105          | 0.0001    | <b>0.00003</b> |
| 12378-PCDF                | 0.05      | <b>0.03</b>   | PCB 114          | 0.0005    | <b>0.00003</b> |
| 23478-PCDF                | 0.5       | <b>0.3</b>    | PCB 118          | 0.0001    | <b>0.00003</b> |
| 123478-HxCDF              | 0.1       | 0.1           | PCB 123          | 0.0001    | <b>0.00003</b> |
| 123678-HxCDF              | 0.1       | 0.1           | PCB 156          | 0.0005    | <b>0.00003</b> |
| 123789-HxCDF              | 0.1       | 0.1           | PCB 157          | 0.0005    | <b>0.00003</b> |
| 234678-HxCDF              | 0.1       | 0.1           | PCB 167          | 0.00001   | <b>0.00003</b> |
| 1234678-HpCDF             | 0.01      | 0.01          | PCB 189          | 0.0001    | <b>0.00003</b> |
| 1234789-HpCDF             | 0.01      | 0.01          |                  |           |                |
| OCDF                      | 0.0001    | <b>0.0003</b> |                  |           |                |

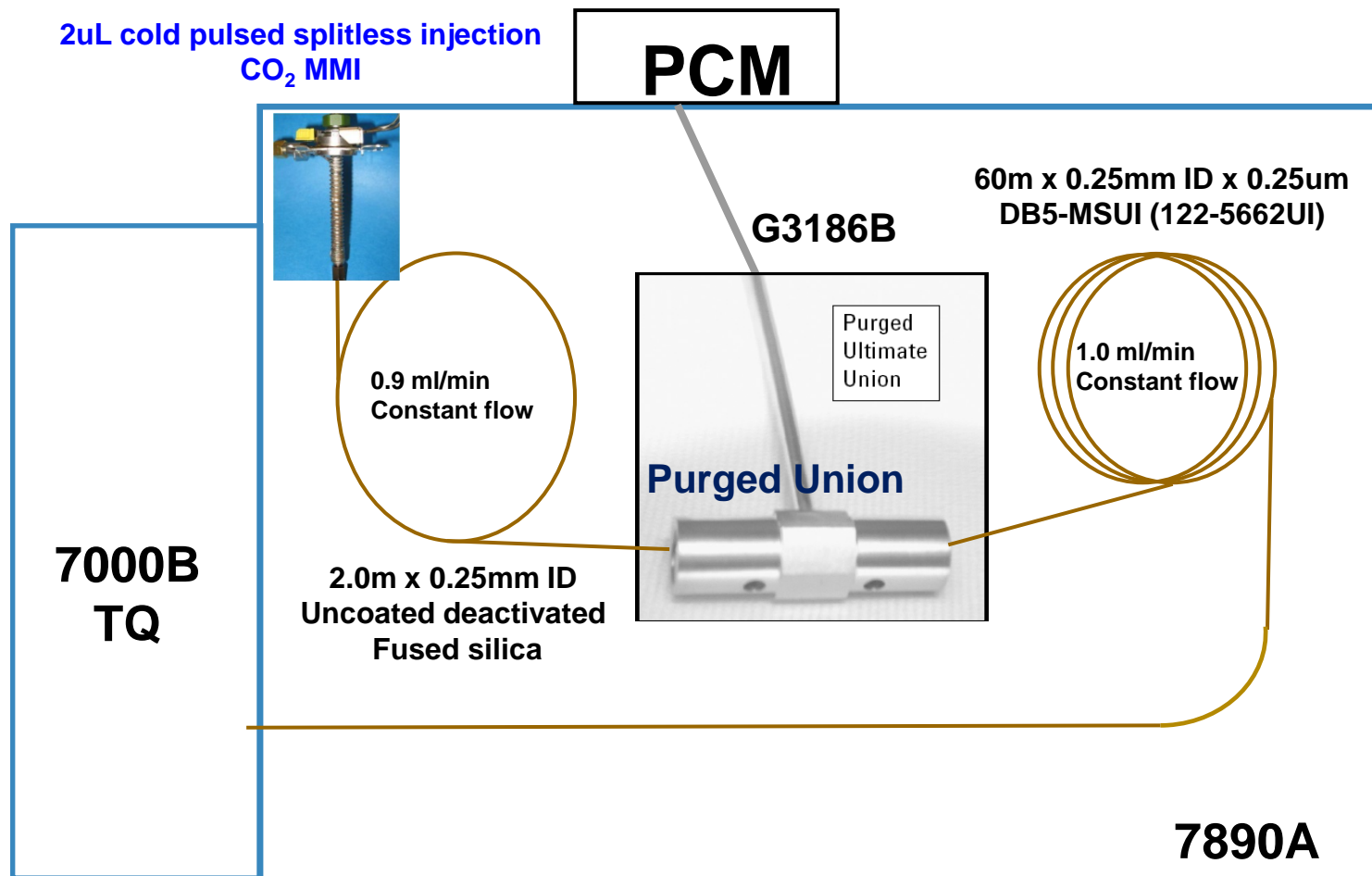
# Dioxins / Furans Total TEQ\* for Hen's Egg extract

|         | Analyte       | Analytical result | TEF Value                   | TEQ               |          |
|---------|---------------|-------------------|-----------------------------|-------------------|----------|
|         |               | pg/g Fat          |                             | pg/g Fat          |          |
| Dioxins | 2378-TCDD     | 0.1166            | 1                           | 0.1166            |          |
|         | 12378-PCDD    | 0.1151            | 1                           | 0.1151            |          |
|         | 123478-HxCDD  | 0.0800            | 0.1                         | 0.0080            |          |
|         | 123678-HxCDD  | 0.4060            | 0.1                         | 0.0406            |          |
|         | 123789-HxCDD  | 0.1609            | 0.1                         | 0.0161            |          |
|         | 1234678-HpCDD | 2.3862            | 0.01                        | 0.0239            |          |
|         | OCDD          | 3.7235            | 0.0001                      | 0.0004            |          |
|         |               |                   |                             | Dioxins Total TEQ | pg/g fat |
| Furans  | 2378-TCDF     | 15.4824           | 0.1                         | 1.5482            |          |
|         | 12378-PCDF    | 3.3510            | 0.05                        | 0.1676            |          |
|         | 23478-PCDF    | 3.1453            | 0.5                         | 1.5727            |          |
|         | 123478-HxCDF  | 0.5844            | 0.1                         | 0.0584            |          |
|         | 123678-HxCDF  | 0.3724            | 0.1                         | 0.0372            |          |
|         | 234678-HxCDF  | 0.2297            | 0.1                         | 0.0230            |          |
|         | 123789-HxCDF  | 0.0688            | 0.1                         | 0.0069            |          |
|         | 1234678-HpCDF | 0.6626            | 0.01                        | 0.0066            |          |
|         | 1234789-HpCDF | 0.1051            | 0.01                        | 0.0011            |          |
|         | OCDF          | 0.7111            | 0.0001                      | 0.0001            |          |
|         |               |                   | Furans Total TEQ            | pg/g fat          | 3.422    |
|         |               |                   | Total (Dioxins + Furans)TEQ | pg/g fat          | 3.742    |
|         |               |                   | Max permitted level TEQ     | pg/g fat          | 3        |

\*TEQ = Toxic Equivalent Concentration

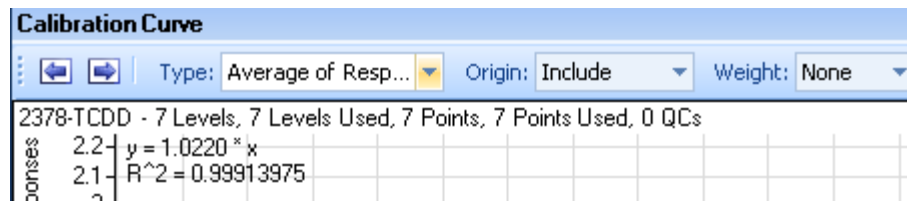
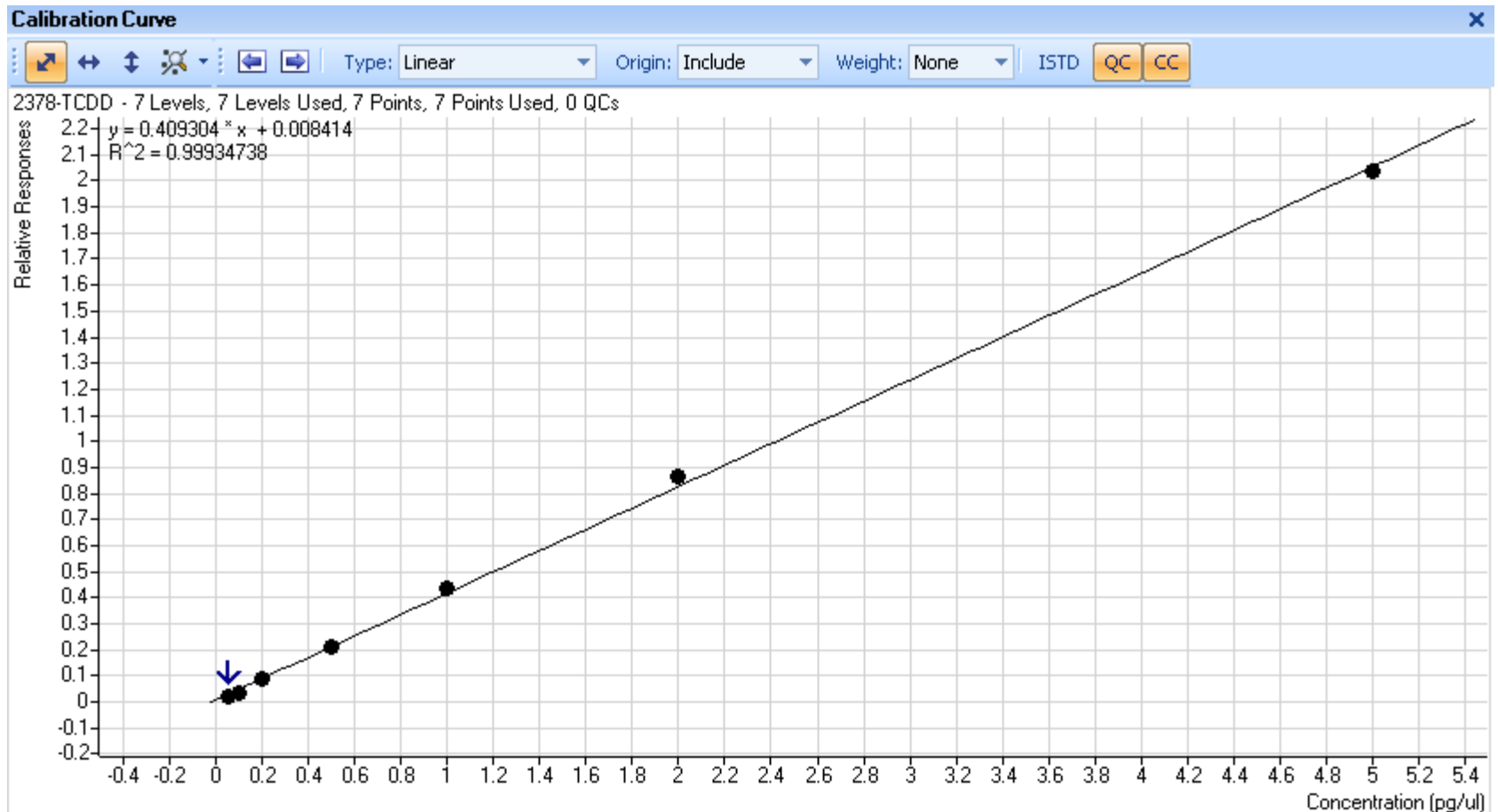
Total TEQ = Sum of analytical results for 17 Dx/DBFs, expressed as pg-TEQ/g Fat

# 7890-7000B GC-MS/MS Configuration for Dioxins with Pre-column Back flush



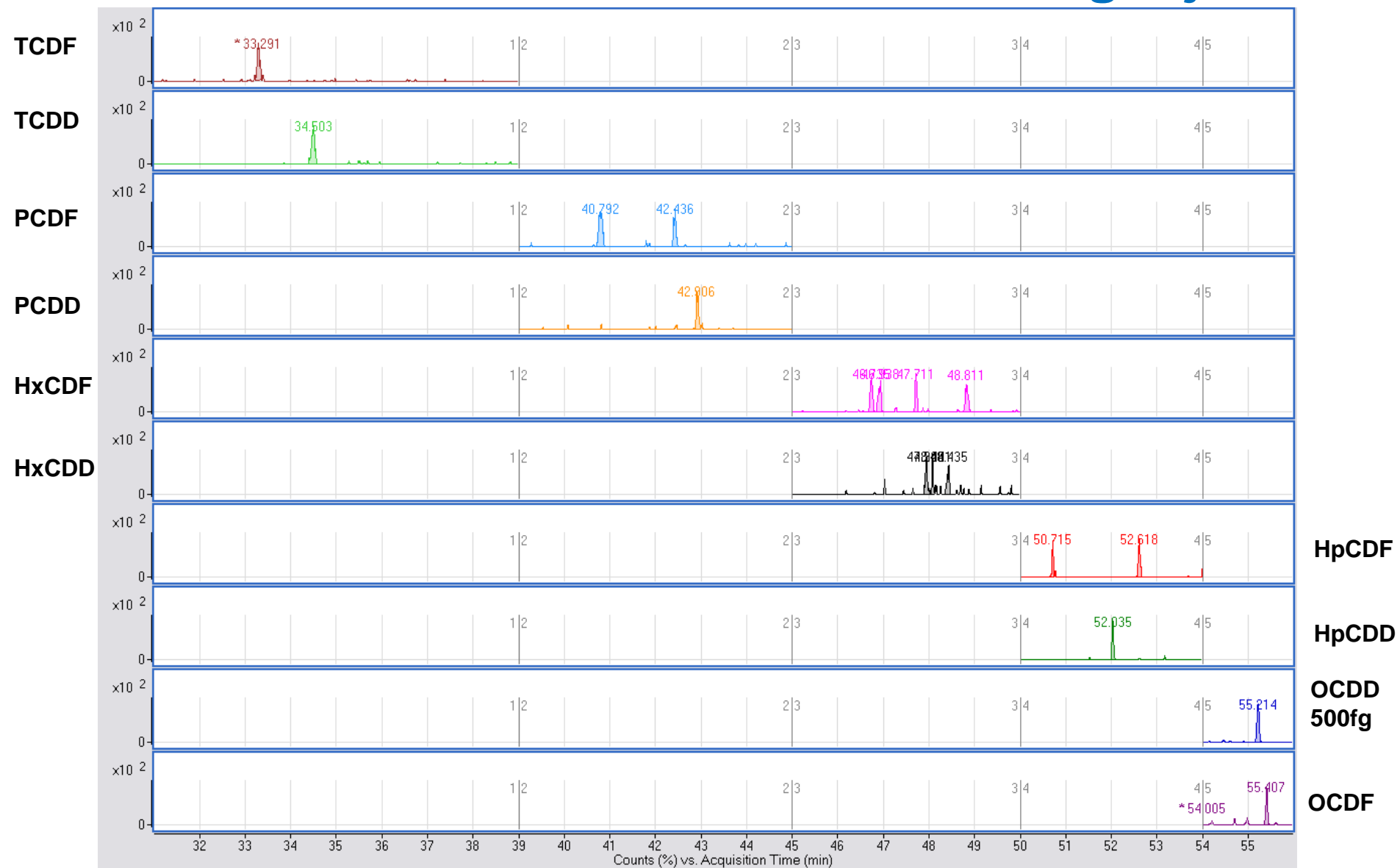
Inlet temp program : 100 (0.05) – 600 deg C/min – 300 deg C  
Oven temp program : 130 (2) – 10 – 220 (16) – 5 – 235 (7) – 5 – 350 (0) deg C

# Cal Curve : 2378-TCDD 100fg – 10pg Injected

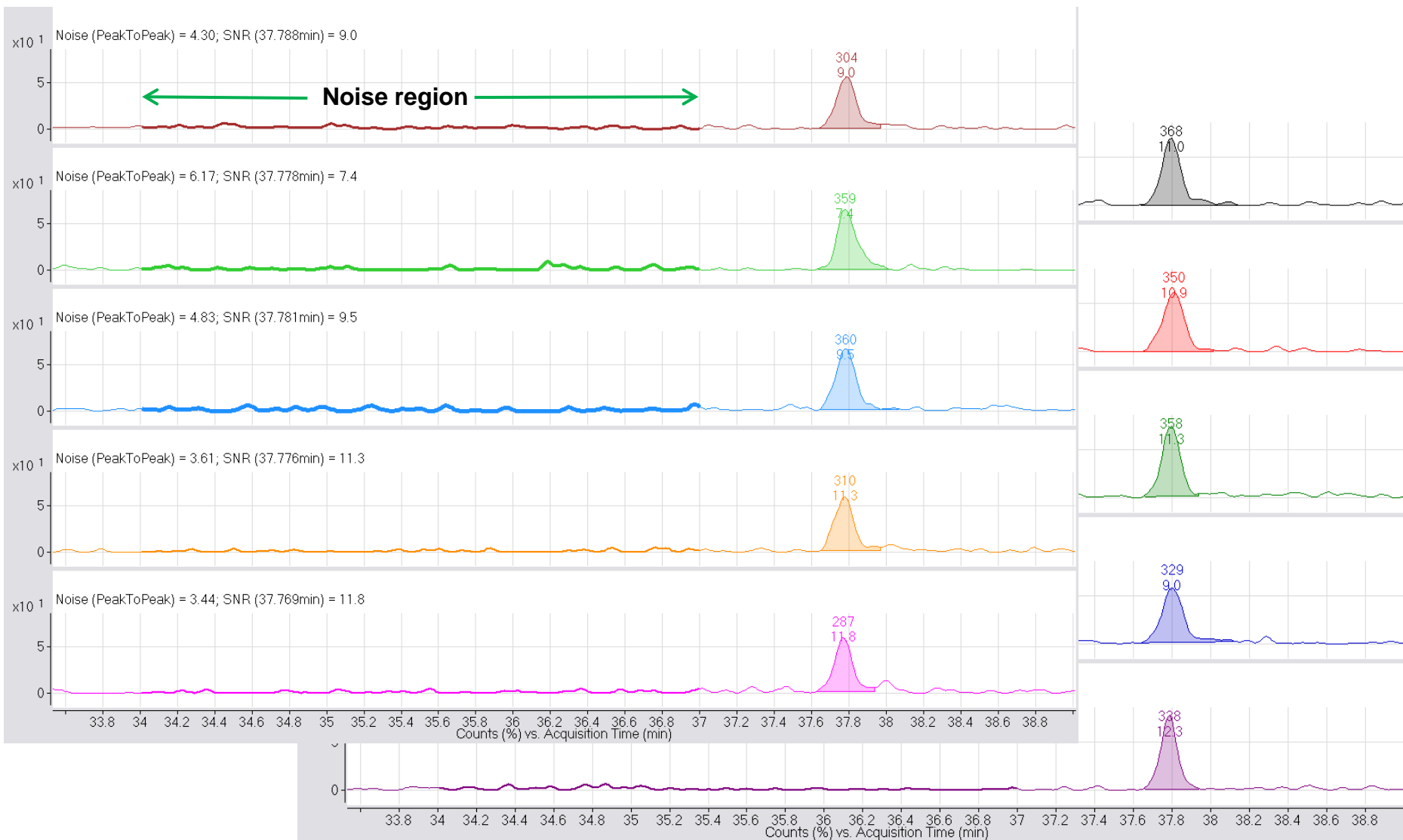


Source : CVUA-MEL

# Native PCDDs / PCDFs - Standard 100fg Injected



# 10 Replicate injections of 100fg 2378-TCDD



Mean Peak-Peak S/N = 10 :1

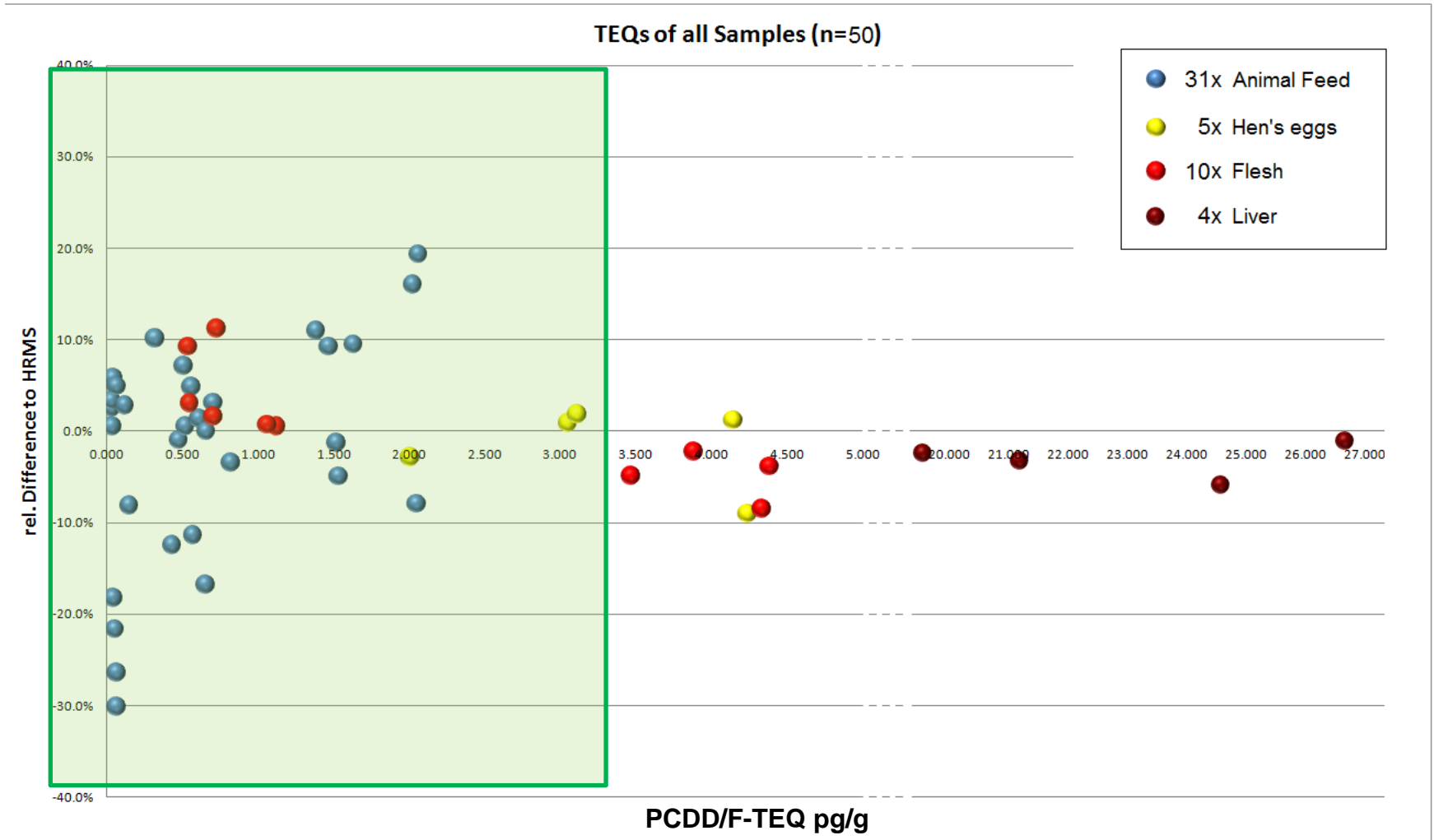
Peak Area %RSD = 8.3

# Comparative performance of the 7000 GC-MS/MS System vs GC-HRMS for Dioxins In Foodstuffs



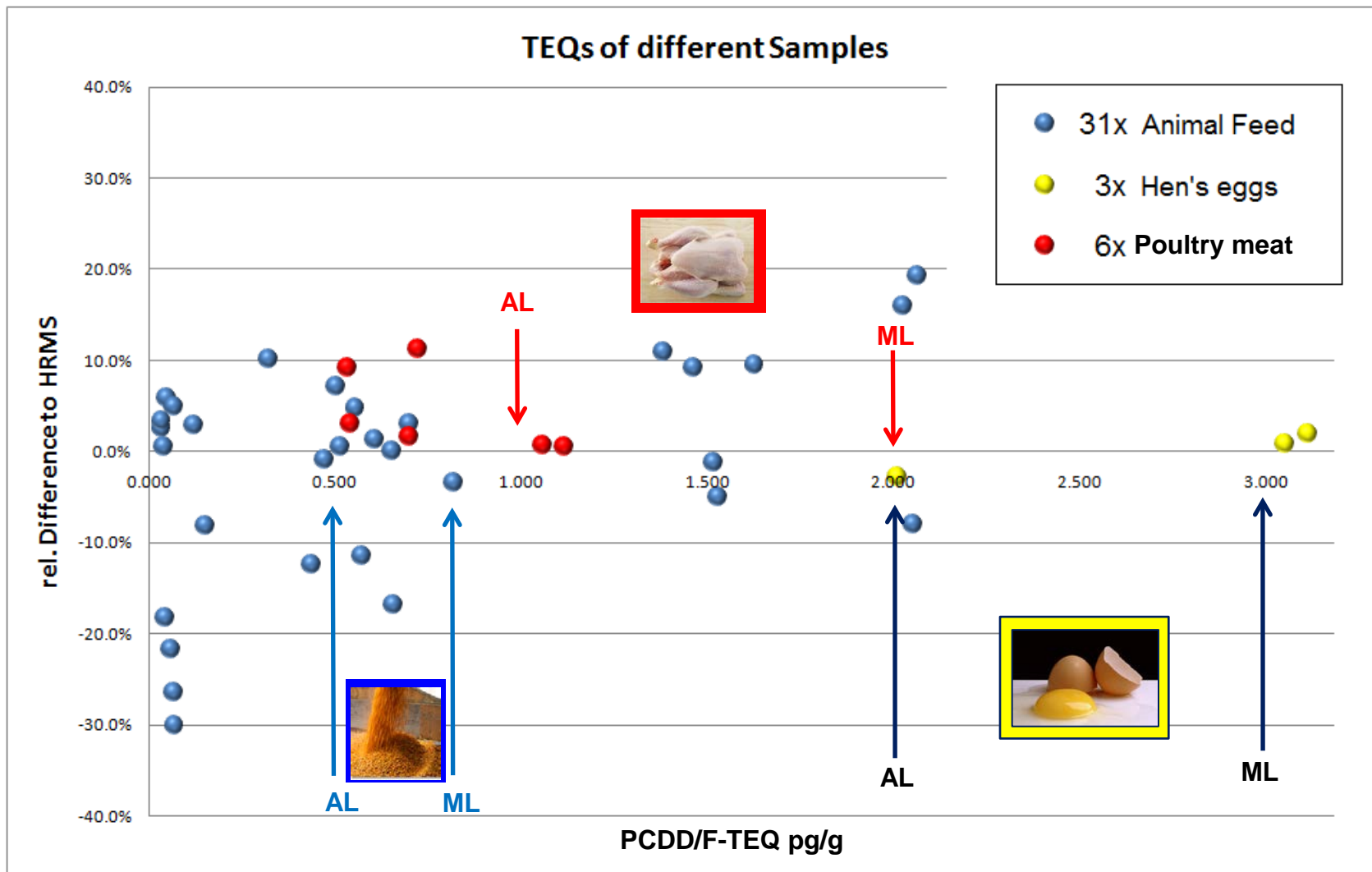


# Difference between GC-HRMS results and GC-MS/MS results TEQ (upper bound)



# Difference between GC-HRMS results and GC-MS/MS results

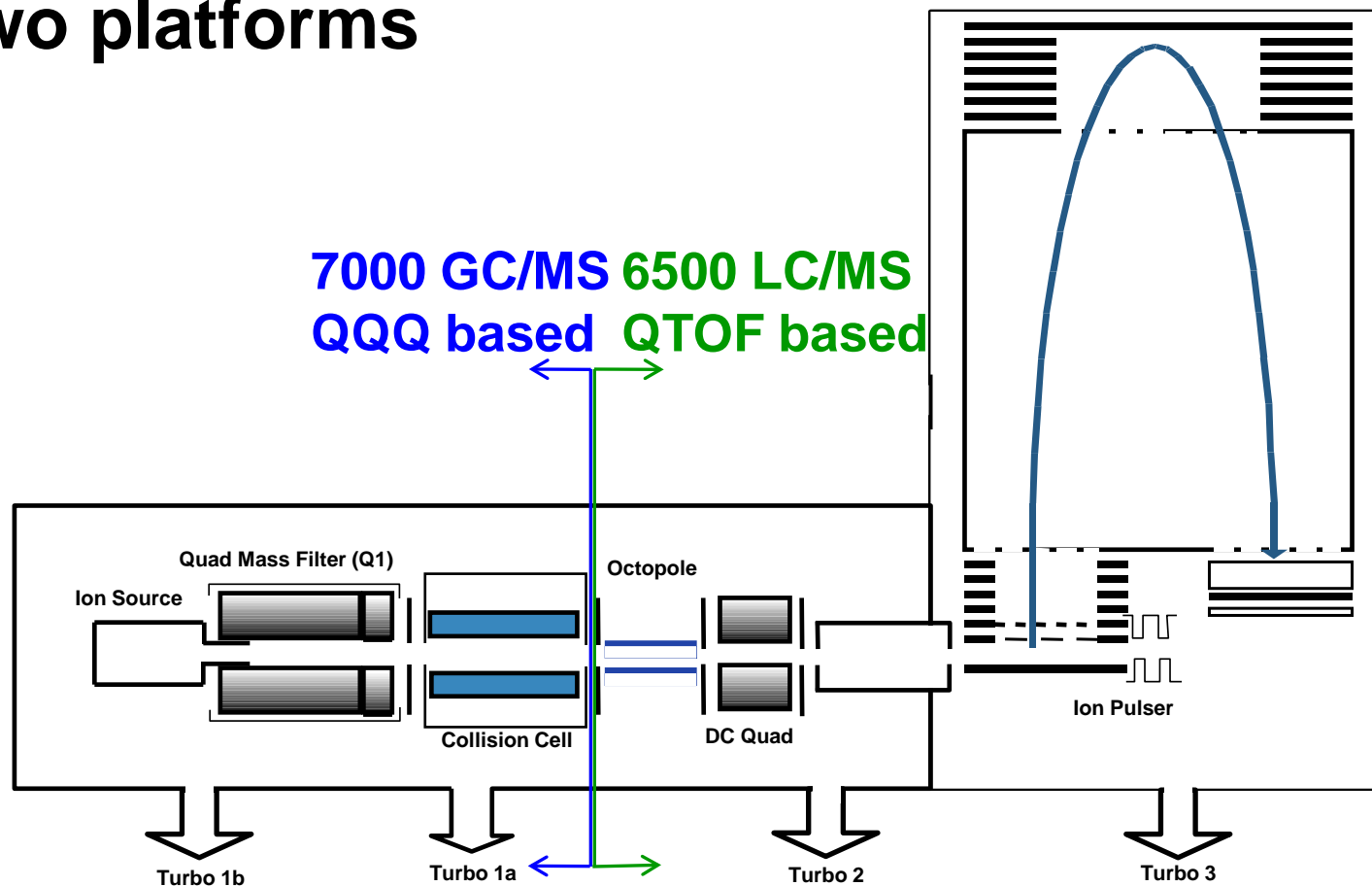
## TEQ (upper bound) $\sim < 3$ pg/g



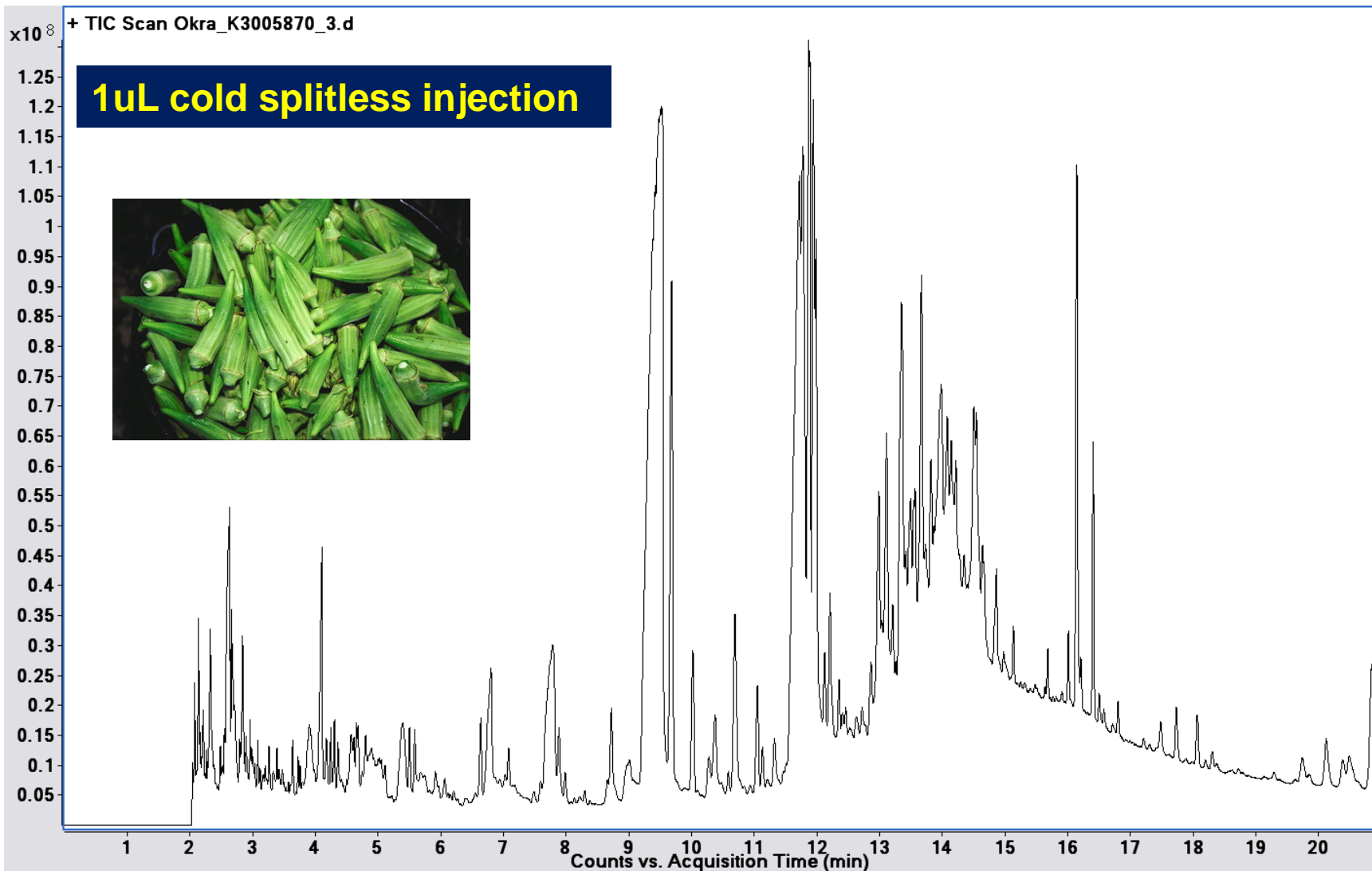
**LOD animal feed: GC-HRMS: 0.01-0.06 pg/g; GC-MS/MS: 0.02-0.08 pg/g**

# What's Next for Food Safety Analysis?

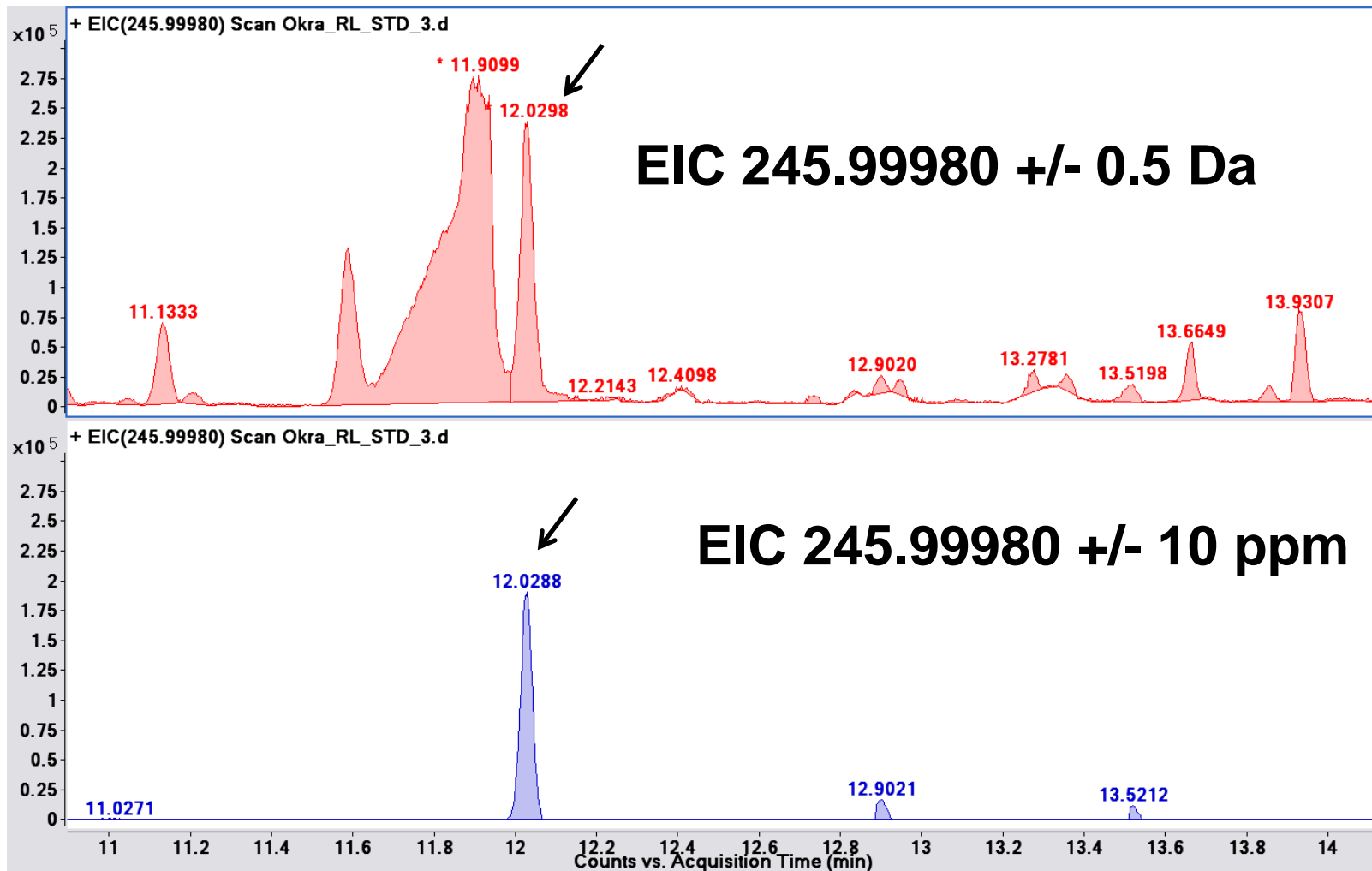
## GC-QTOF - The merging of two platforms



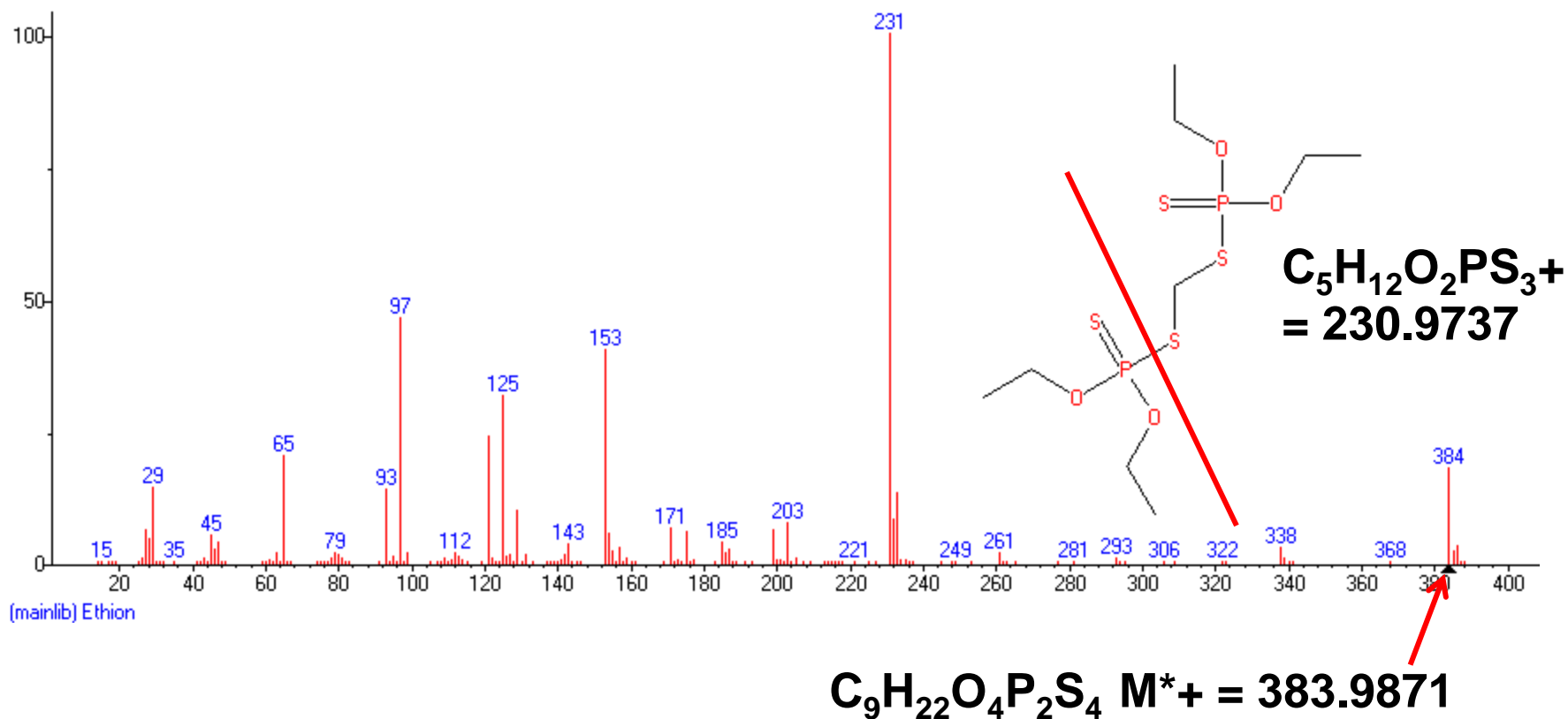
# GC-QTOF – Okra Sample K3005870



# GC-QTOF – Okra RL Standard pp'-DDE [M-<sup>35</sup>Cl<sub>2</sub>]<sup>+</sup>



# Ethion Spectrum



# Ethion @ 5 ppb in Ginseng Extract

## Extracted Ions = 230.9737 and 383.9871 +/- 10 ppm

Full Scale

1uL cold splitless injection

x10<sup>8</sup> +ESI TIC Scan Frag=80.0V JW Ginseng LS3\_3.d

200,000,000

x10<sup>5</sup> +ESI EIC(230.9737) Scan Frag=80.0V JW Ginseng LS3\_3.d

200,000

230.9737 +/- 10 ppm

x10<sup>3</sup> +ESI EIC(383.9871) Scan Frag=80.0V JW Ginseng LS3\_3.d

5000

383.9871 +/- 10 ppm

Counts vs. Acquisition Time (min)

# Conclusions

## Needle Finding by Haystack Removal

- **GC-Tandem Quadrupole Mass Spec**

- Sensitive and selective
- Comparable to HR MS for dioxin analysis in food at levels of interest

- **GC-Quadrupole Time-of-Flight MS**

- Accurate Mass provides high selectivity
- Available later this year





**48th ANNUAL FLORIDA  
PESTICIDE  
RESIDUE WORKSHOP  
July 17-20, 2011  
TradeWinds Island Resort  
St. Pete Beach, Florida**

Info and online registration at [www.FLworkshop.com](http://www.FLworkshop.com)  
May 1 deadline for talks and June 1 for posters

**LC/MS/MS Short Course on Sunday, July 17<sup>th</sup>  
(8:30 am – 4:30 pm)  
Dr. Robert Voyksner, Instructor**





**Portrait with Vegetables (*The Greengrocer*)**  
**Artist: Giuseppe Arcimboldo**  
**b. 1527 d. 1593, Milan, Italy**

**Thank You**