EU Compliant Routine Quantitative Dioxin and Dioxin-like compounds in food and feed by GC-MS/MS with the Advanced Ionization Source

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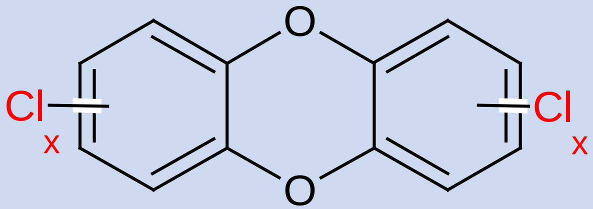
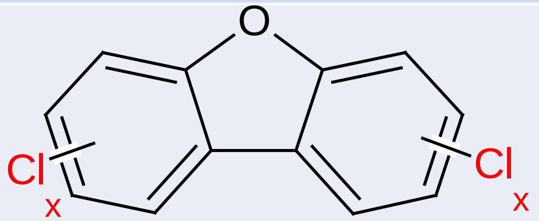
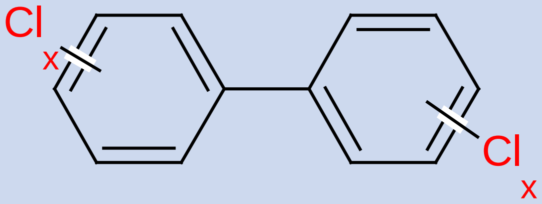
GCMS

The world leader in serving science

Introduction

- Polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzo-p-furans (PCDFs) commonly referred to as dioxins, and polychlorinated biphenyls (PCBs) are highly toxic substances classed as persistent organic pollutants (POPs).
- High fat-solubility and accumulate in the fatty tissues of animals. More than 90% of exposure from diet.
- In 2014 a change in European Commission regulations, permitted the use of GC-MS/MS as an alternative GC-HRMS for confirmatory analysis and for the control of maximum levels (MLs) and action levels (ALs) in certain food and feed samples.

Structure	Abbreviation	# Toxic Congeners
	PCDD	7
	PCDF	10
	PCB	12

Results are reported as Toxic Equivalence (TEQ) in the sample

Challenges and Objectives

- Current EU legislation requires GC-MS/MS analytical methods to demonstrate compliance at 1/5th of the maximum levels (MLs), the methods must also be able to demonstrate:

Separation of isomers shall be < 25 % peak to peak between **1,2,3,4,7,8-HxCDF** and **1,2,3,6,7,8-HxCDF**.

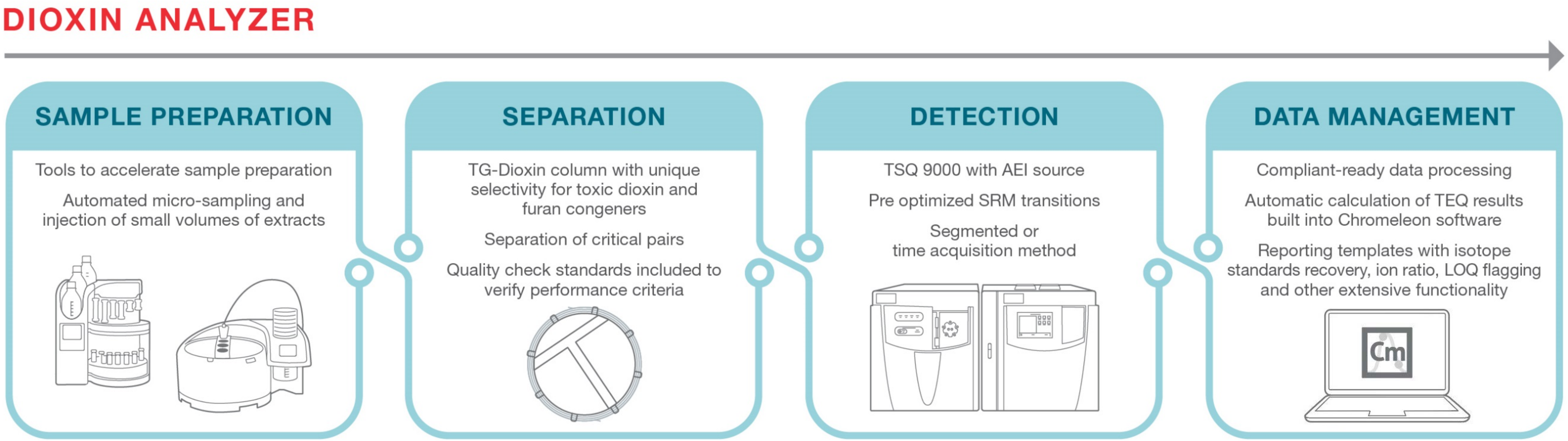
2 specific precursor and one specific corresponding transition product ion for all labelled and native congeners.

Maximum permitted tolerance of relative ion intensities of ± 15 % for selected transition product ions in comparison to calculated or measured values.

Resolution for each quadrupole to be set **equal to or better than unit mass resolution** (unit mass resolution: sufficient resolution to separate two peaks one mass unit apart).

- Analysis method must be stable over a long period of time and be easy to implement in a routine lab
- Objectives:
  - Demonstrate that the Dioxin analyzer meet regulatory requirements for analysis of Dioxins in food
  - Evaluated performance of the Dioxin analyzer across geographical locations

The Dioxin Analyzer Product



DIOXIN ANALYZER

SAMPLE PREPARATION

Tools to accelerate sample preparation

Automated micro-sampling and injection of small volumes of extracts

SEPARATION

TG-Dioxin column with unique selectivity for toxic dioxin and furan congeners

Separation of critical pairs

Quality check standards included to verify performance criteria

DETECTION

TSQ 9000 with AEI source

Pre optimized SRM transitions

Segmented or time acquisition method

DATA MANAGEMENT

Compliant-ready data processing

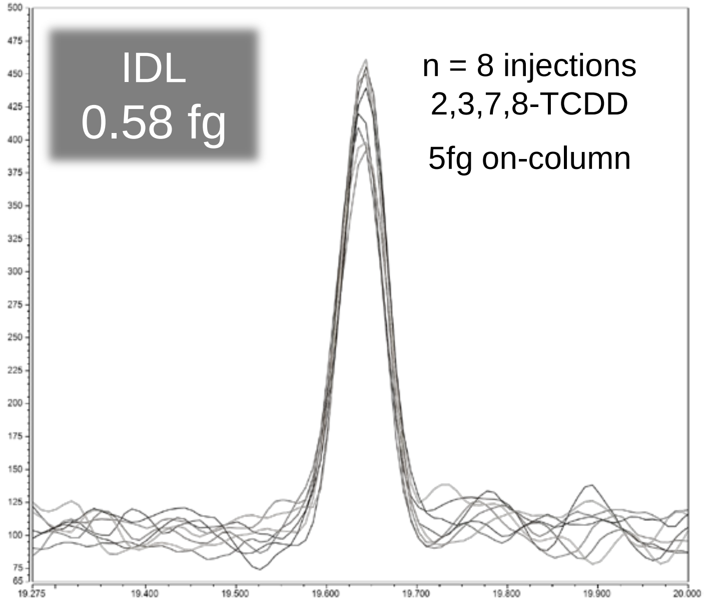
Automatic calculation of TEQ results built into Chromeleon software

Reporting templates with isotope standards recovery, ion ratio, LOQ flagging and other extensive functionality

- ✓ Comprehensive user deployment guide for out-of-the box implementation
- ✓ Quality check standards for performance checking at the installation
- ✓ Pre-loaded acquisition method, data processing and reporting templates for immediate productivity
- ✓ Complete consumable package for 6 months continuous operation

TSQ 9000 GC-MS/MS

Advanced Electron Ionization (AEI) source


IDL
0.58 fg

n = 8 injections
2,3,7,8-TCDD

5fg on-column

Thermo Scientific™ TSQ 9000 triple quadrupole GC-MS/MS system with AEI source

Feature	Benefit
Highly efficient ionization	A greater ion flux reaching the detector
A more tightly focused ion beam	Less ion burn and a higher degree of robustness

Instant connect modules

Fully user-exchangeable:

- **No service engineers**
- **No special tools**
- **No special training**

GC and Injector conditions

TRACE 1310 GC PTV Parameters

Operating Mode:	Large Volume
Injection Volume (µL):	4
Initial Inlet temperature (°C):	75
Carrier Gas, Flow (mL/min):	Helium, 1.2
Splitless Time (min)	1
Split Flow (mL/min)	100
Septum Purge (mL/min)	5 (constant)

PTV Ramp Settings

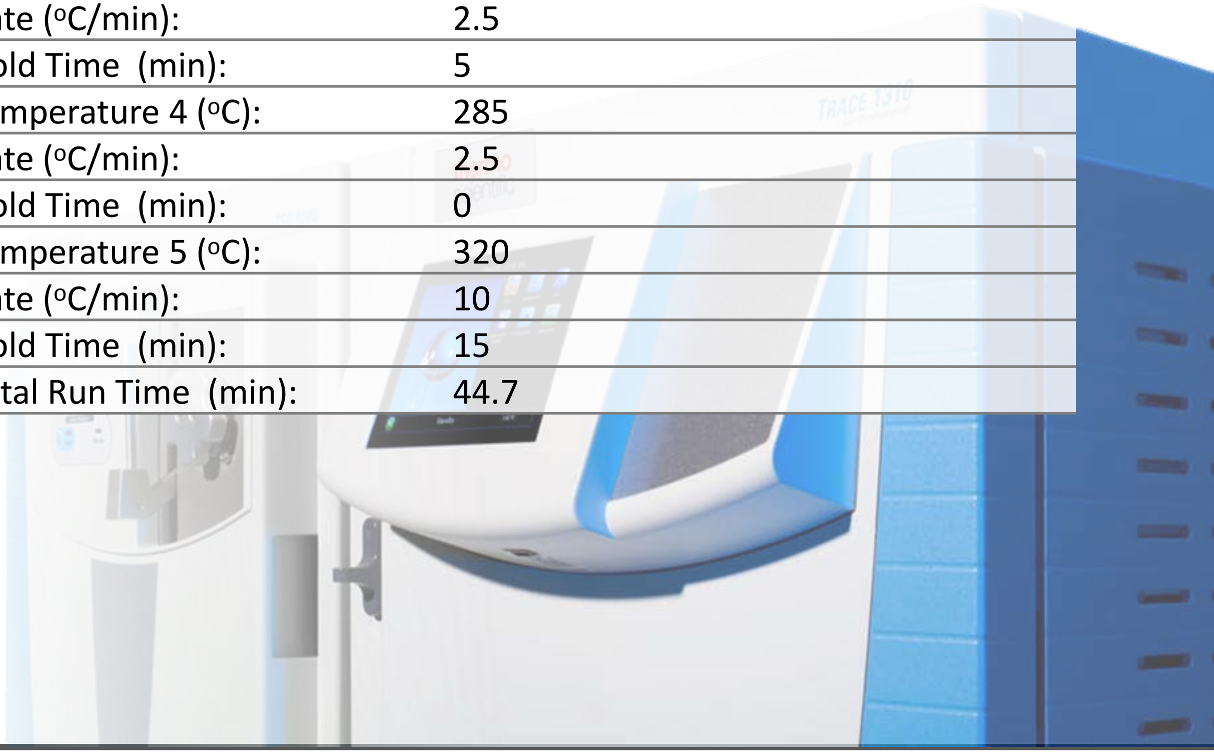
	Pressure (Psi)	Rate (°C/s)	Temperature (°C)	Time (min)	Flow (mL/min)
Injection:	-	-	-	0.2	100.0
Transfer:	-	5	300.0	1.0	-
Cleaning:	-	14.5	330.0	5.0	200.0

Autosampler settings

Injection Depth (mm)	45
Penetration Speed (mm/s)	100
Injection Speed (µL/s)	1

TRACE 1310 GC Parameters

Oven Temperature Program:	
Temperature 1 (°C):	120 (initial)
Hold Time (min):	2
Temperature 2 (°C):	250
Rate (°C/min):	25
Hold Time (min):	0
Temperature 3 (°C):	260
Rate (°C/min):	2.5
Hold Time (min):	5
Temperature 4 (°C):	285
Rate (°C/min):	2.5
Hold Time (min):	0
Temperature 5 (°C):	320
Rate (°C/min):	10
Hold Time (min):	15
Total Run Time (min):	44.7

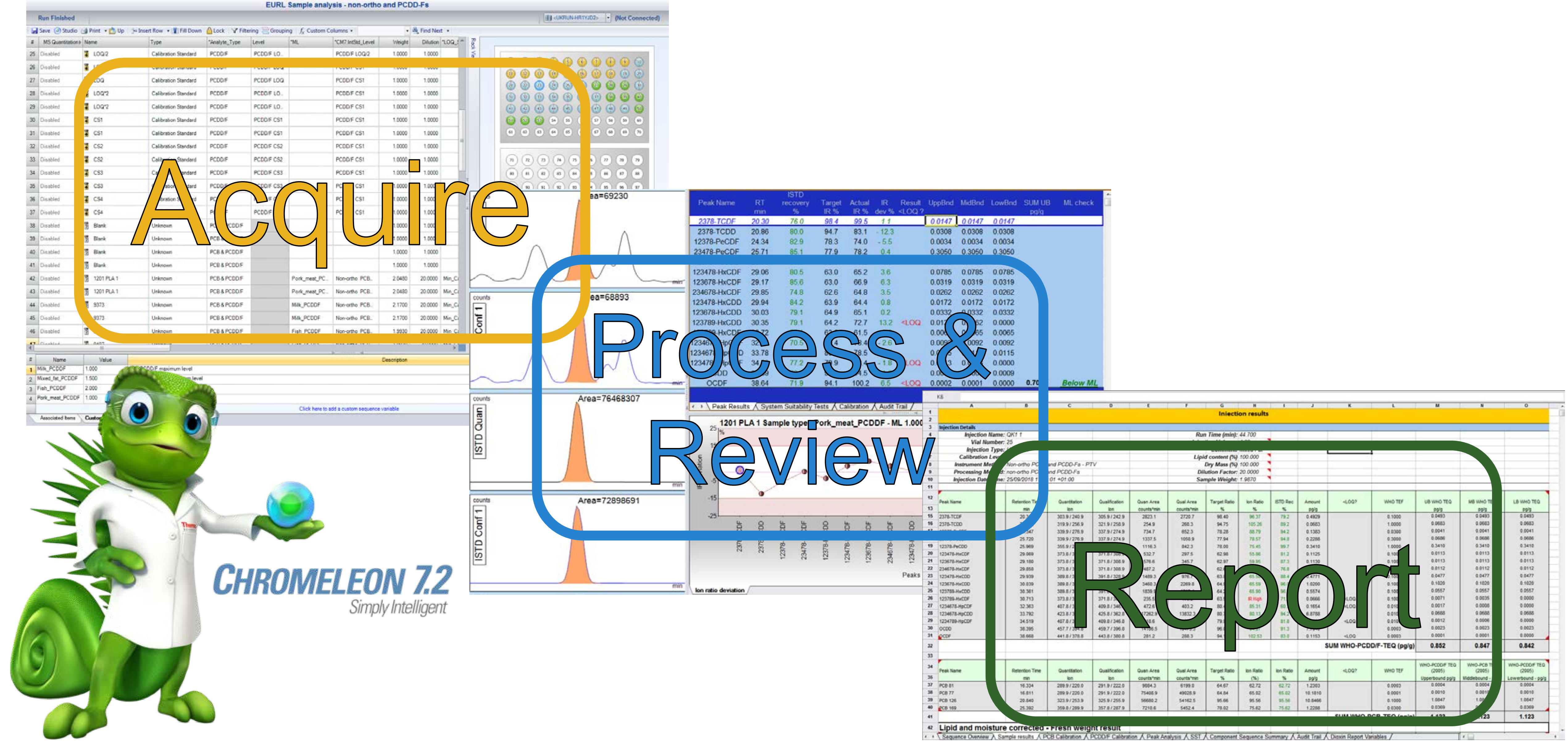


MS conditions

TSQ 9000 Mass Spectrometer Parameters	
Transfer Line (°C):	300
Ionization Type:	EI – with Advanced EI source
Ion Source (°C):	350
Electron Energy (eV):	50
Acquisition Mode:	Timed SRM with Dwell Time Prioritization (x10 – natives HIGH, labelled LOW)
Tuning parameters:	AEI Smart Tune
Collision gas and pressure (psi):	Argon, 70
Resolution :	0.7 (both Q1 and Q3)

Resolution for each quadrupole to be set **equal to or better than unit mass resolution** (unit mass resolution: sufficient resolution to separate two peaks one mass unit apart).

Thermo Scientific™ Chromeleon™ acquisition, processing and reporting



ThermoFisher SCIENTIFIC

Standards and samples

- Food and feedstuff samples (including PT samples) were provided by the EURL for Halogenated POPs in Feed and Food, Freiburg, Germany. A nominal sample intake weight of 2 grams (fat) was used for the samples unless indicated otherwise

- European method EN:1948 standard solutions were utilised for the extraction, calibration and quantitation of PCDD/Fs, dioxin-like PCBs and indicator PCBs.
  - PCDD/Fs
    - EN-1948CVS (calibration and quantitation)
    - EN-1948ES, EN-1948IS (extraction)
  - PCBs
    - WM48-CVS (calibration and quantitation),
    - P48-W-ES, P48-M-ES and P48-RS (extraction)

- All standards were obtained from Wellington Laboratories Inc., Canada.

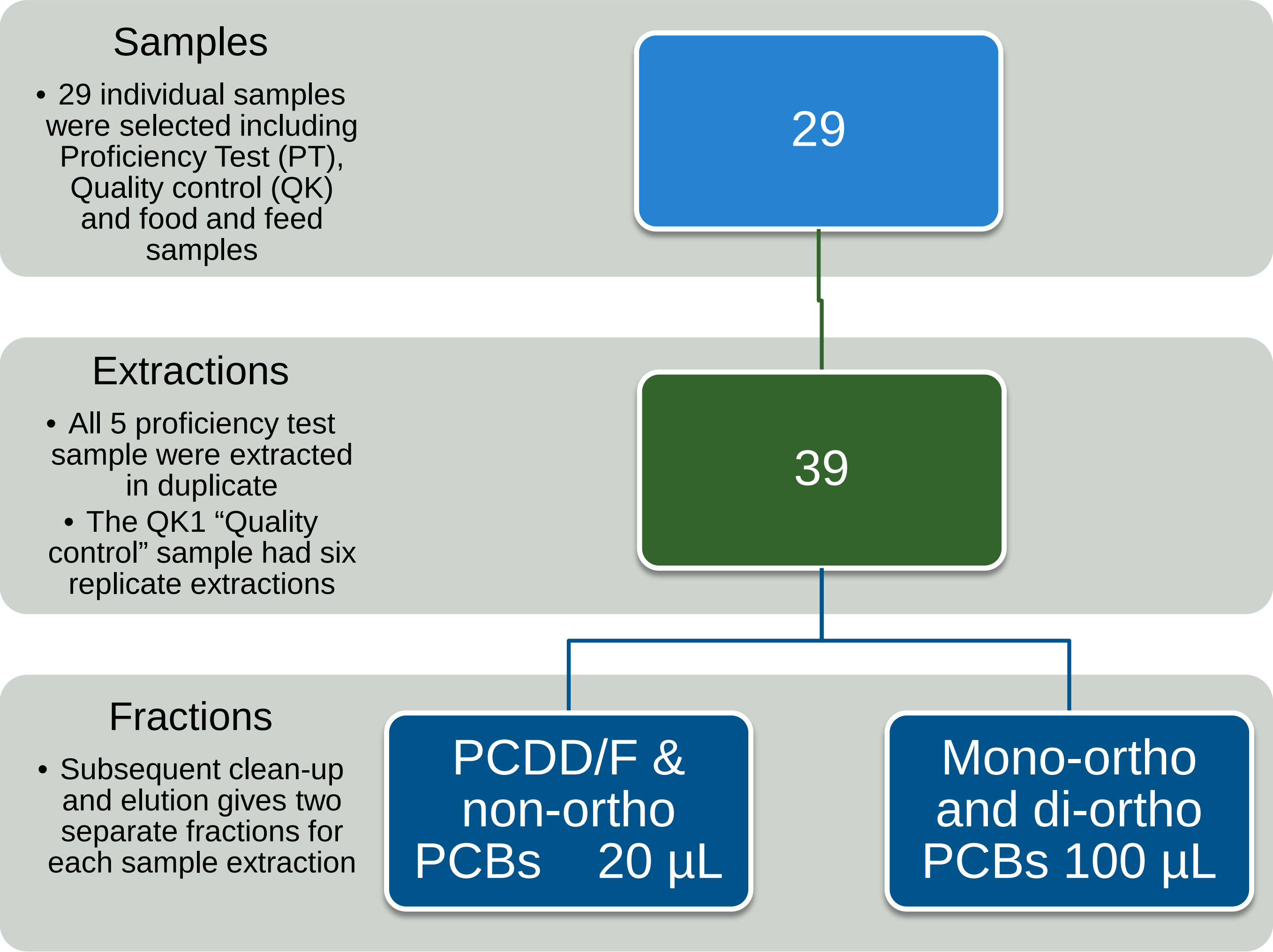
Sample type	Matrix	Nominal weight taken (g)	Number of replicates	Basis
PT	Pork sausage	2	2	Fat
PT	Whole egg	2	2	Fat
PT	Milk powder	2	2	Fat
PT	Halibut fillet	2	2	Fat
PT	Sugar beet pulp	20	2	Product
QK1	Mixed fat	2	6	Fat
Food	Meat	2	5 (individual)	Fat
Food	Milk	2	4 (individual)	Fat
Food	Fish	2	4 (individual)	Fat
Food	Eggs	2	5 (individual)	Fat
Feed	Fish meal	2	1	Fat
Feed	Grass meal	20	1	Product
Feed	Sepiolite	20	1	Product
Feed	Palm fatty acid distillate (PFAD)	2	1	Product
Feed	Feed fat	2	1	Fat

EURL
European Union Reference Laboratory
Halogenated POPs

WELLINGTON
LABORATORIES
Standards for Environmental Testing and Research

Sample extraction

- Sample extraction was performed by Twisselmann hot extraction (comparable to Soxhlet) or pressurized liquid extraction.
- Automated clean-up of extracts was performed using a three column (multi-layered acidic silica, alumina, and carbon columns) setup on the DEXTech™ Plus system (LCTech GmbH).



Samples

- 29 individual samples were selected including Proficiency Test (PT), Quality control (QK) and food and feed samples

29

Extractions

- All 5 proficiency test sample were extracted in duplicate
- The QK1 “Quality control” sample had six replicate extractions

39

Fractions

- Subsequent clean-up and elution gives two separate fractions for each sample extraction

PCDD/F & non-ortho PCBs 20 µL

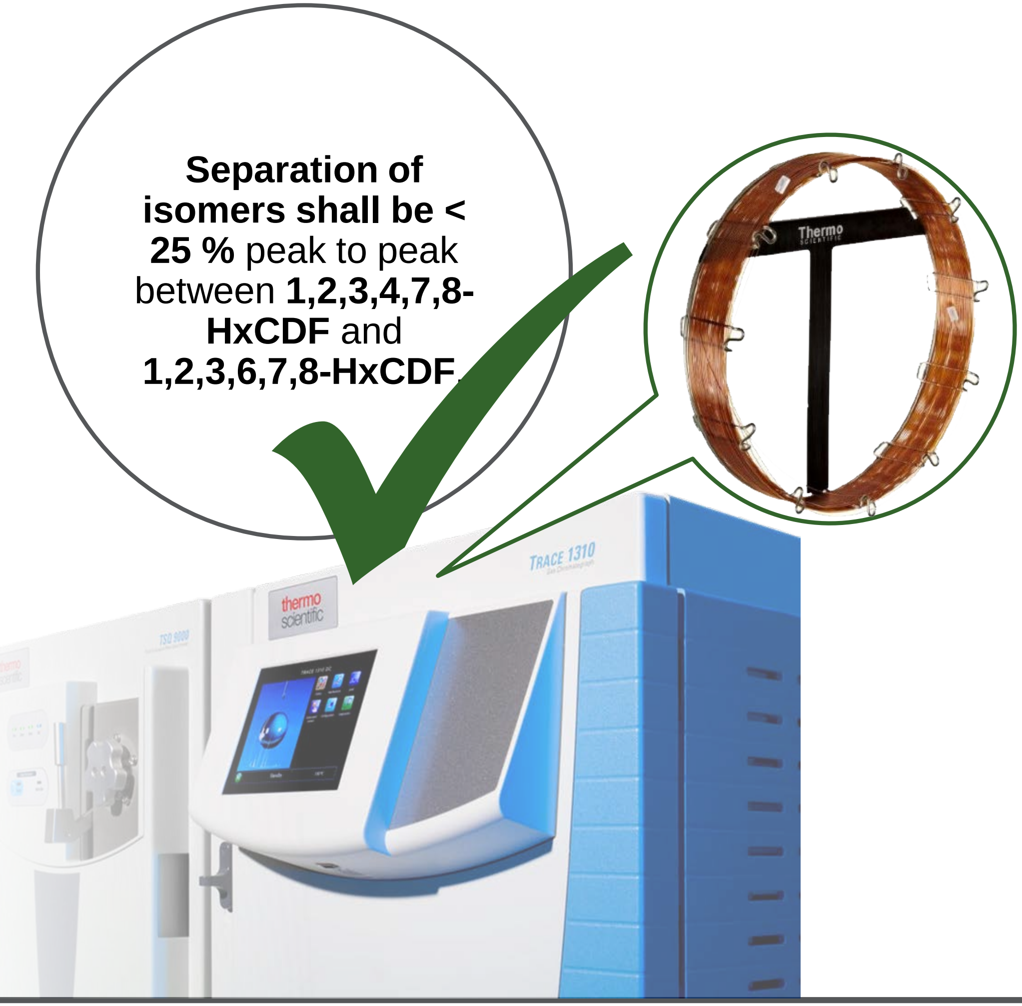
Mono-ortho and di-ortho PCBs 100 µL

Thermo Scientific™ Dionex™ ASE™ 350 Accelerated Solvent Extractor

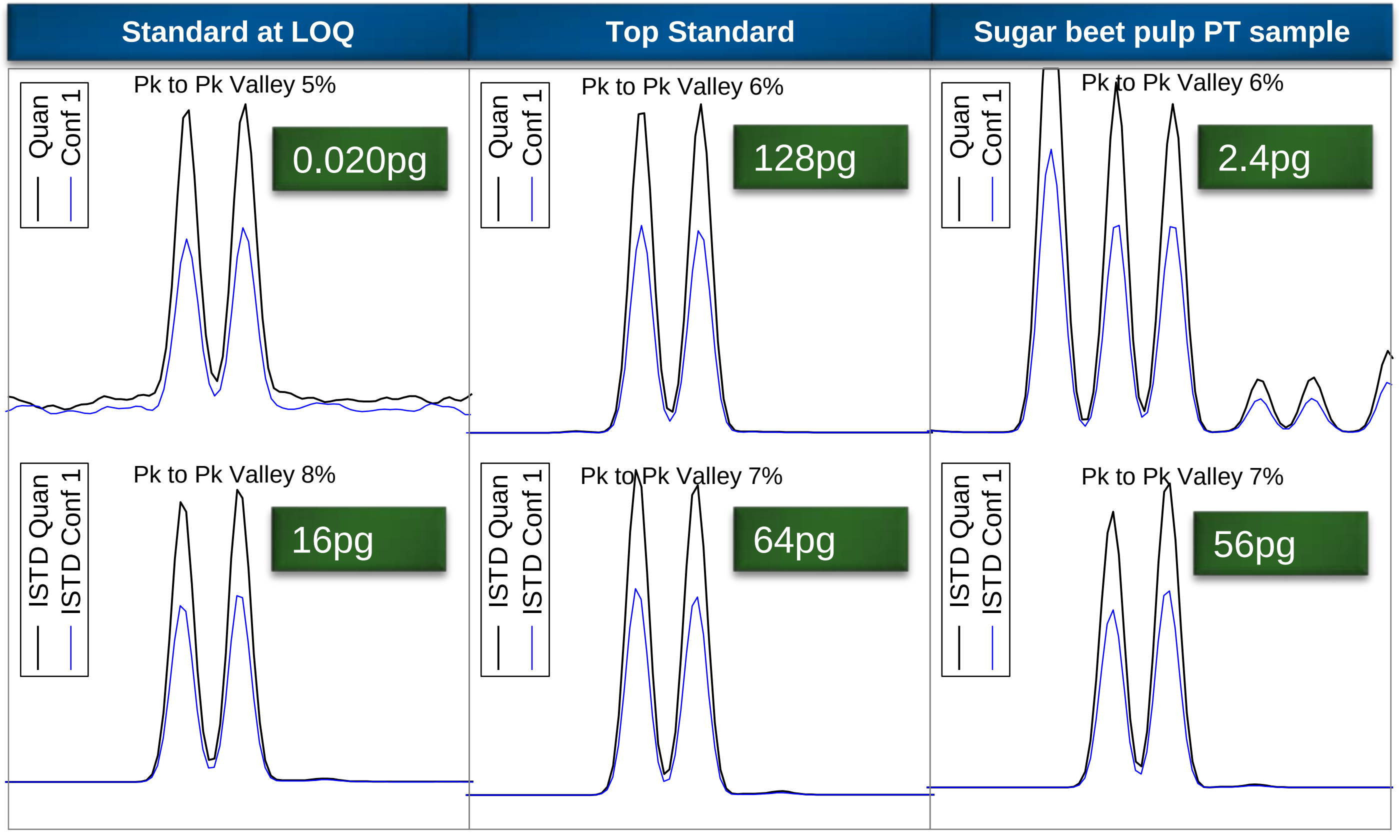
Thermo Scientific™ Rocket™ Evaporator System

Chromatography

EU regulations specify that the separation of the 1,2,3,4,7,8 and 1,2,3,6,7,8 HxCDF isomers shall be less than 25% peak to peak.

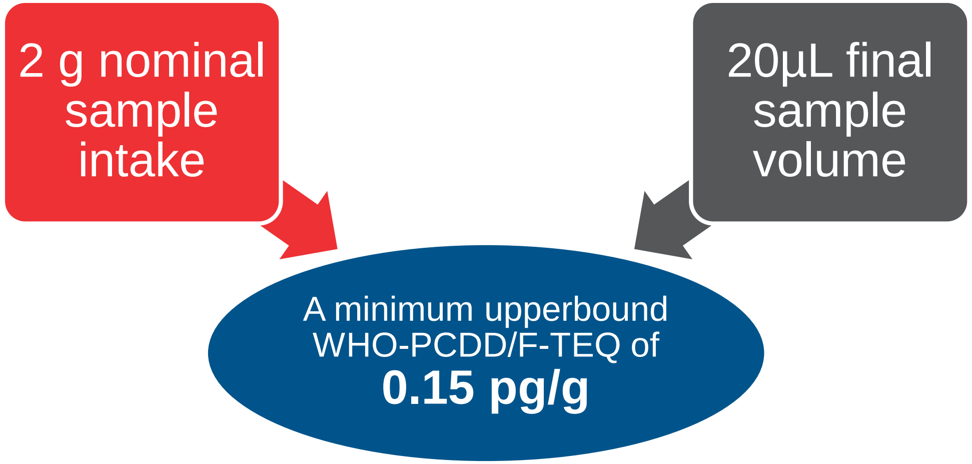


Separation of isomers shall be < 25 % peak to peak between **1,2,3,4,7,8-HxCDF** and **1,2,3,6,7,8-HxCDF**.



LOQ

- Injection of the lowest level calibration point and regular assessment of this ensures:



2 g nominal sample intake

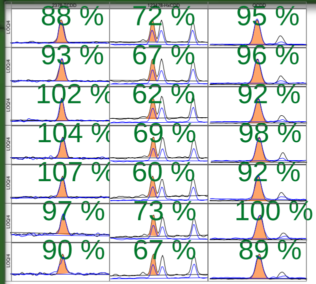
20µL final sample volume

A minimum upperbound WHO-PCDD/F-TEQ of

0.15 pg/g

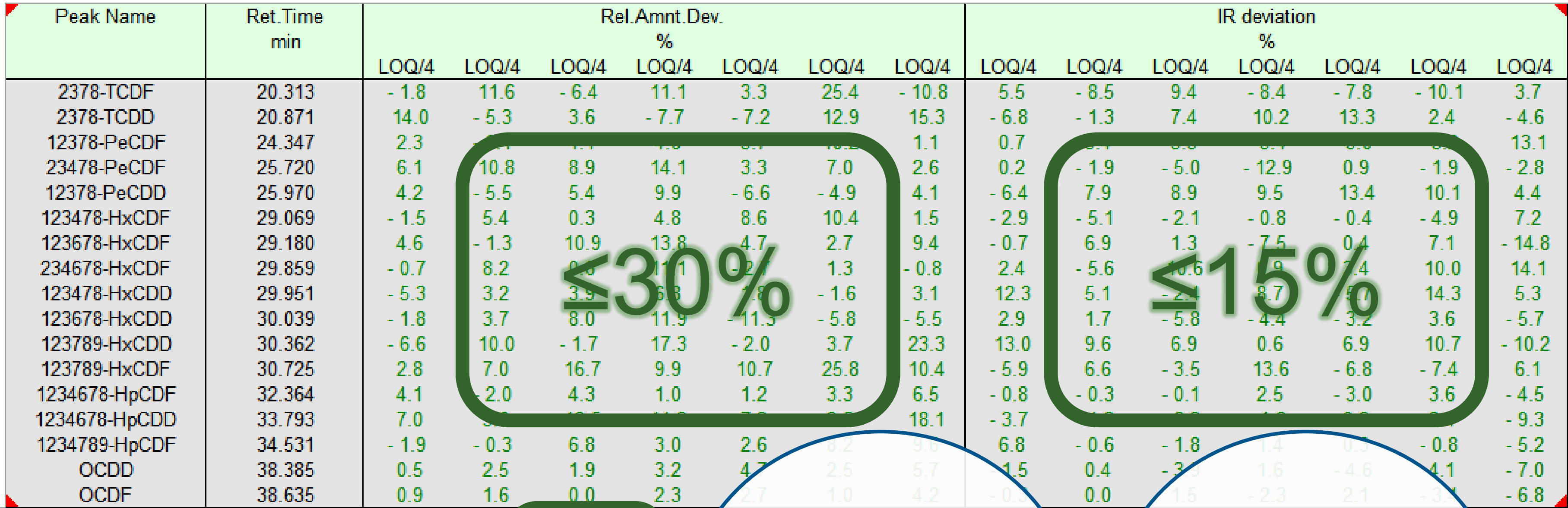
Criteria	**Acceptance**	**Result**
Retention time window (for all monitored ions)	'within window' ± 0.1 min	Pass
Relative ion intensities	± 15 %	Pass
Deviation from the average relative response factor	≤ 30 %	Pass

Injection #	10 fg on-column	40 fg on-column	160 fg on-column
22			
23			
53			
66			
79			
92			
101			



LOQ Data…

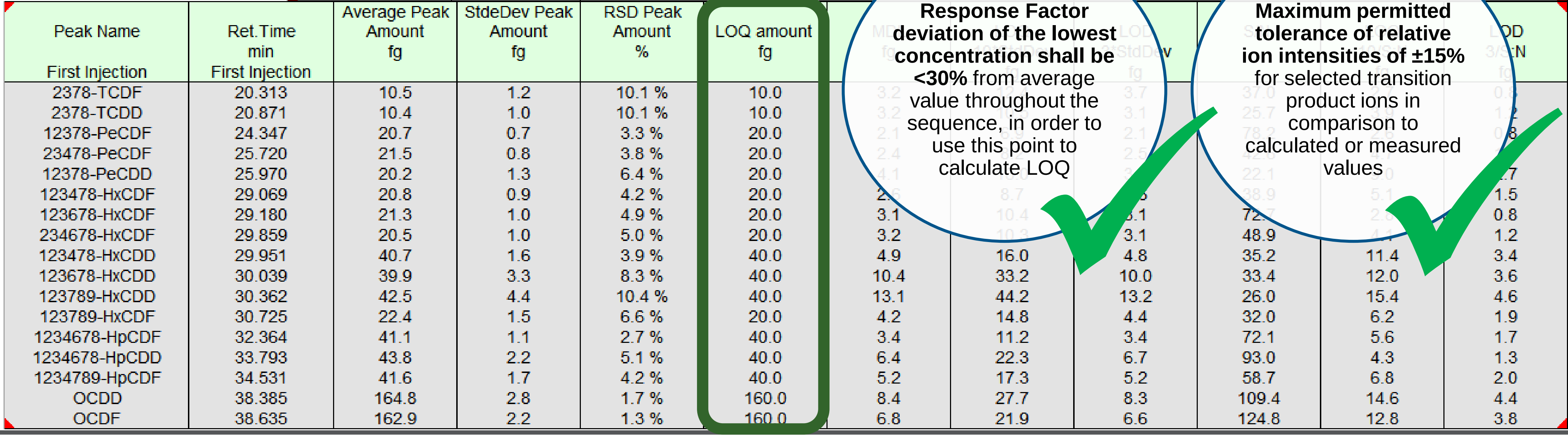
- As displayed, the deviation from the Response Factor and Ion Ratio are within tolerance for all LOQ injections…



Peak Name	Ret.Time min	Rel.Amnt.Dev. % LOQ/4	LOQ/4	LOQ/4	LOQ/4	LOQ/4	LOQ/4	LOQ/4	IR deviation % LOQ/4	LOQ/4	LOQ/4	LOQ/4	LOQ/4	LOQ/4	LOQ/4
2378-TCDF	20.313	- 1.8	11.6	- 6.4	11.1	3.3	25.4	- 10.8	5.5	- 8.5	9.4	- 8.4	- 7.8	- 10.1	3.7
2378-TCDD	20.871	14.0	- 5.3	3.6	- 7.7	- 7.2	12.9	15.3	- 6.8	- 1.3	7.4	10.2	13.3	2.4	- 4.6
12378-PeCDF	24.347	2.3	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	1.1	0.7	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	13.1
23478-PeCDF	25.720	6.1	10.8	8.9	14.1	3.3	7.0	2.6	0.2	- 1.9	- 5.0	- 12.9	0.9	- 1.9	- 2.8
12378-PeCDD	25.970	4.2	- 5.5	5.4	9.9	- 6.6	- 4.9	4.1	- 6.4	7.9	8.9	9.5	13.4	10.1	4.4
123478-HxCDF	29.069	- 1.5	5.4	0.3	4.8	8.6	10.4	1.5	- 2.9	- 5.1	- 2.1	- 0.8	- 0.4	- 4.9	7.2
123678-HxCDF	29.180	4.6	- 1.3	10.9	13.8	4.7	2.7	9.4	- 0.7	6.9	1.3	- 7.5	0.4	7.1	- 14.8
234678-HxCDF	29.859	- 0.7	8.2	[illegible]	11.1	- 2.4	1.3	- 0.8	2.4	- 5.6	[illegible]	[illegible]	[illegible]	10.0	14.1
123478-HxCDD	29.951	- 5.3	3.2	3.9	6.8	1.8	- 1.6	3.1	12.3	5.1	- 2.4	8.7	[illegible]	14.3	5.3
123678-HxCDD	30.039	- 1.8	3.7	8.0	11.9	- 11.3	- 5.8	- 5.5	2.9	1.7	- 5.8	- 4.4	- 3.2	3.6	- 5.7
123789-HxCDD	30.362	- 6.6	10.0	- 1.7	17.3	- 2.0	3.7	23.3	13.0	9.6	6.9	0.6	6.9	10.7	- 10.2
123789-HxCDF	30.725	2.8	7.0	16.7	9.9	10.7	25.8	10.4	- 5.9	6.6	- 3.5	13.6	- 6.8	- 7.4	6.1
1234678-HpCDF	32.364	4.1	- 2.0	4.3	1.0	1.2	3.3	6.5	- 0.8	- 0.3	- 0.1	2.5	- 3.0	3.6	- 4.5
1234678-HpCDD	33.793	7.0	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	18.1	- 3.7	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	- 9.3
1234789-HpCDF	34.531	- 1.9	- 0.3	6.8	3.0	2.6	8.2	9.6	6.8	- 0.6	- 1.8	1.4	0.5	- 0.8	- 5.2
OCDD	38.385	0.5	2.5	1.9	3.2	4.7	2.5	5.7	- 1.5	0.4	- 3.9	1.6	- 4.6	4.1	- 7.0
OCDF	38.635	0.9	1.6	0.0	2.3	2.7	1.0	4.2	- 0.3	0.0	1.5	- 2.3	2.1	- 3.4	- 6.8

≤30%

≤15%



Peak Name First Injection	Ret.Time min First Injection	Average Peak Amount fg	StdeDev Peak Amount fg	RSD Peak Amount %	LOQ amount fg	MDL fg	LOQ 10*StdDev fg	LOD 3*StdDev fg	S/N	LOQ 10/S:N fg	LOD 3/S:N fg
2378-TCDF	20.313	10.5	1.2	10.1 %	10.0	3.2	12.4	3.7	37.0	2.7	0.8
2378-TCDD	20.871	10.4	1.0	10.1 %	10.0	3.2	10.5	3.1	25.7	3.9	1.2
12378-PeCDF	24.347	20.7	0.7	3.3 %	20.0	2.1	6.9	2.1	78.2	2.6	0.8
23478-PeCDF	25.720	21.5	0.8	3.8 %	20.0	2.4	8.2	2.5	42.6	4.7	[illegible]
12378-PeCDD	25.970	20.2	1.3	6.4 %	20.0	4.1	13.0	[illegible]	22.1	9.0	[illegible]
123478-HxCDF	29.069	20.8	0.9	4.2 %	20.0	2.6	8.7	[illegible]	38.9	5.1	1.5
123678-HxCDF	29.180	21.3	1.0	4.9 %	20.0	3.1	10.4	3.1	72.7	2.8	0.8
234678-HxCDF	29.859	20.5	1.0	5.0 %	20.0	3.2	10.3	3.1	48.9	4.1	1.2
123478-HxCDD	29.951	40.7	1.6	3.9 %	40.0	4.9	16.0	4.8	35.2	11.4	3.4
123678-HxCDD	30.039	39.9	3.3	8.3 %	40.0	10.4	33.2	10.0	33.4	12.0	3.6
123789-HxCDD	30.362	42.5	4.4	10.4 %	40.0	13.1	44.2	13.2	26.0	15.4	4.6
123789-HxCDF	30.725	22.4	1.5	6.6 %	20.0	4.2	14.8	4.4	32.0	6.2	1.9
1234678-HpCDF	32.364	41.1	1.1	2.7 %	40.0	3.4	11.2	3.4	72.1	5.6	1.7
1234678-HpCDD	33.793	43.8	2.2	5.1 %	40.0	6.4	22.3	6.7	93.0	4.3	1.3
1234789-HpCDF	34.531	41.6	1.7	4.2 %	40.0	5.2	17.3	5.2	58.7	6.8	2.0
OCDD	38.385	164.8	2.8	1.7 %	160.0	8.4	27.7	8.3	109.4	14.6	4.4
OCDF	38.635	162.9	2.2	1.3 %	160.0	6.8	21.9	6.6	124.8	12.8	3.8

Response Factor deviation of the lowest concentration shall be <30% from average value throughout the sequence, in order to use this point to calculate LOQ

Maximum permitted tolerance of relative ion intensities of ±15% for selected transition product ions in comparison to calculated or measured values

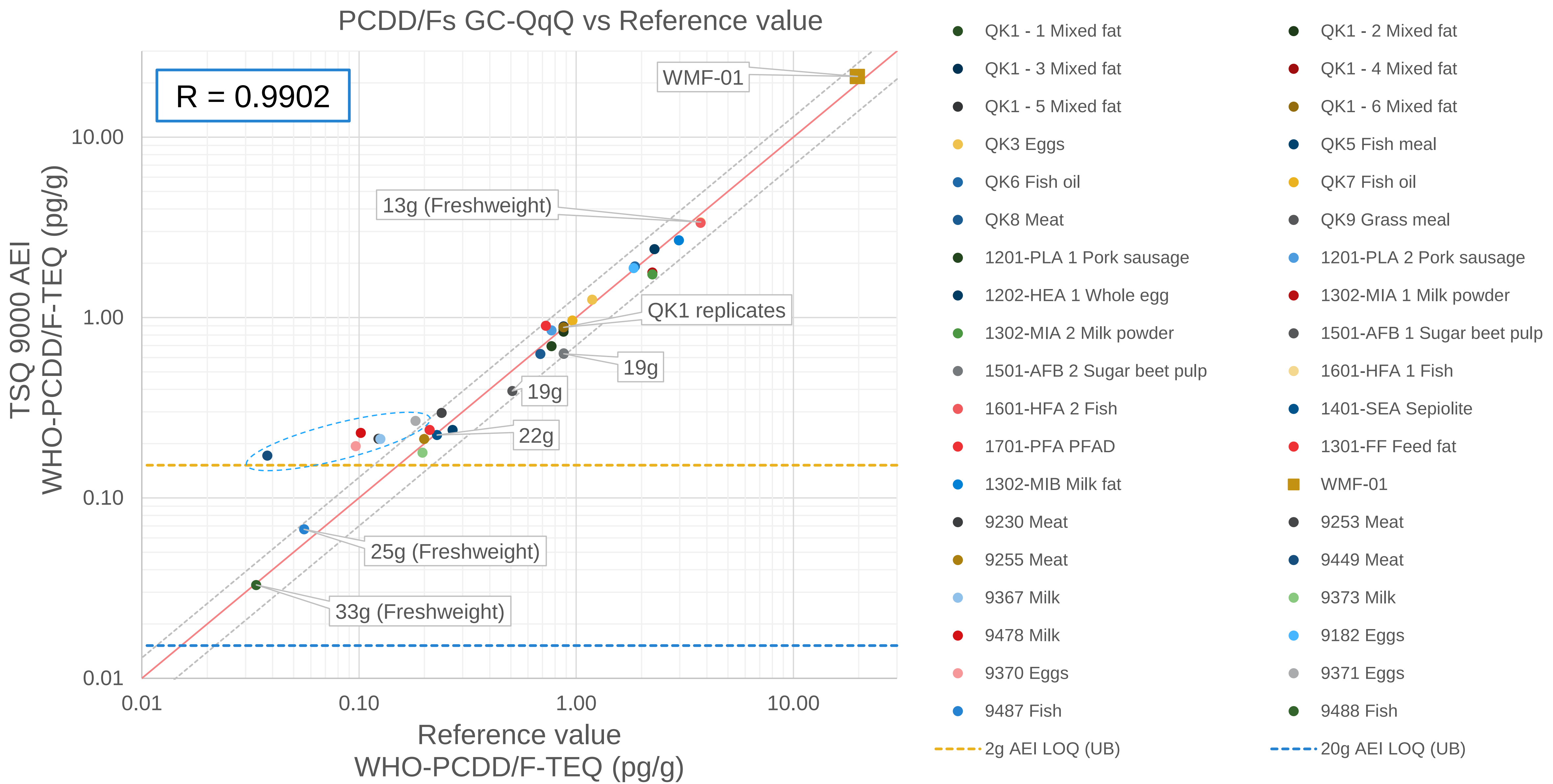
Calibration range

Peak Name	Ret.Time (min)	Number of Points	RF RSD (%)	Coeff.of Determination (R2)	Average RF (Slope)	Range (pg)
2378-TCDF	20.30	16	3.87	0.9995	0.96	0.01 – 64
2378-TCDD	20.86	16	4.72	0.9996	1.04	0.01 – 64
12378-PeCDF	24.34	16	1.66	0.9999	0.93	0.02 – 128
23478-PeCDF	25.71	16	5.36	0.9977	1.03	0.02 – 128
12378-PeCDD	25.96	16	3.60	0.9999	1.05	0.02 – 128
123478-HxCDF	29.06	16	2.98	0.9996	1.02	0.02 – 128
123678-HxCDF	29.17	16	1.95	0.9998	1.00	0.02 – 128
234678-HxCDF	29.86	16	2.83	0.9993	1.02	0.02 – 128
123478-HxCDD	29.94	16	2.49	0.999	1.12	0.04 – 128
123678-HxCDD	30.04	16	2.01	0.9991	1.12	0.04 – 128
123789-HxCDD	30.35	16	3.82	0.9987	1.09	0.04 – 128
123789-HxCDF	30.71	16	3.52	0.9997	0.95	0.02 – 128
1234678-HpCDF	32.35	16	1.78	0.9999	1.03	0.04 – 256
1234678-HpCDD	33.78	16	5.99	0.9968	1.09	0.04 – 256
1234789-HpCDF	34.52	16	1.88	0.9998	1.04	0.04 – 256
OCDD	38.39	16	1.64	1.0000	1.12	0.16 – 256
OCDF	38.64	16	1.34	0.9997	0.94	0.16 – 256
		Max	**5.99**	**1.0000**		
		Min	**1.34**	**0.9968**		

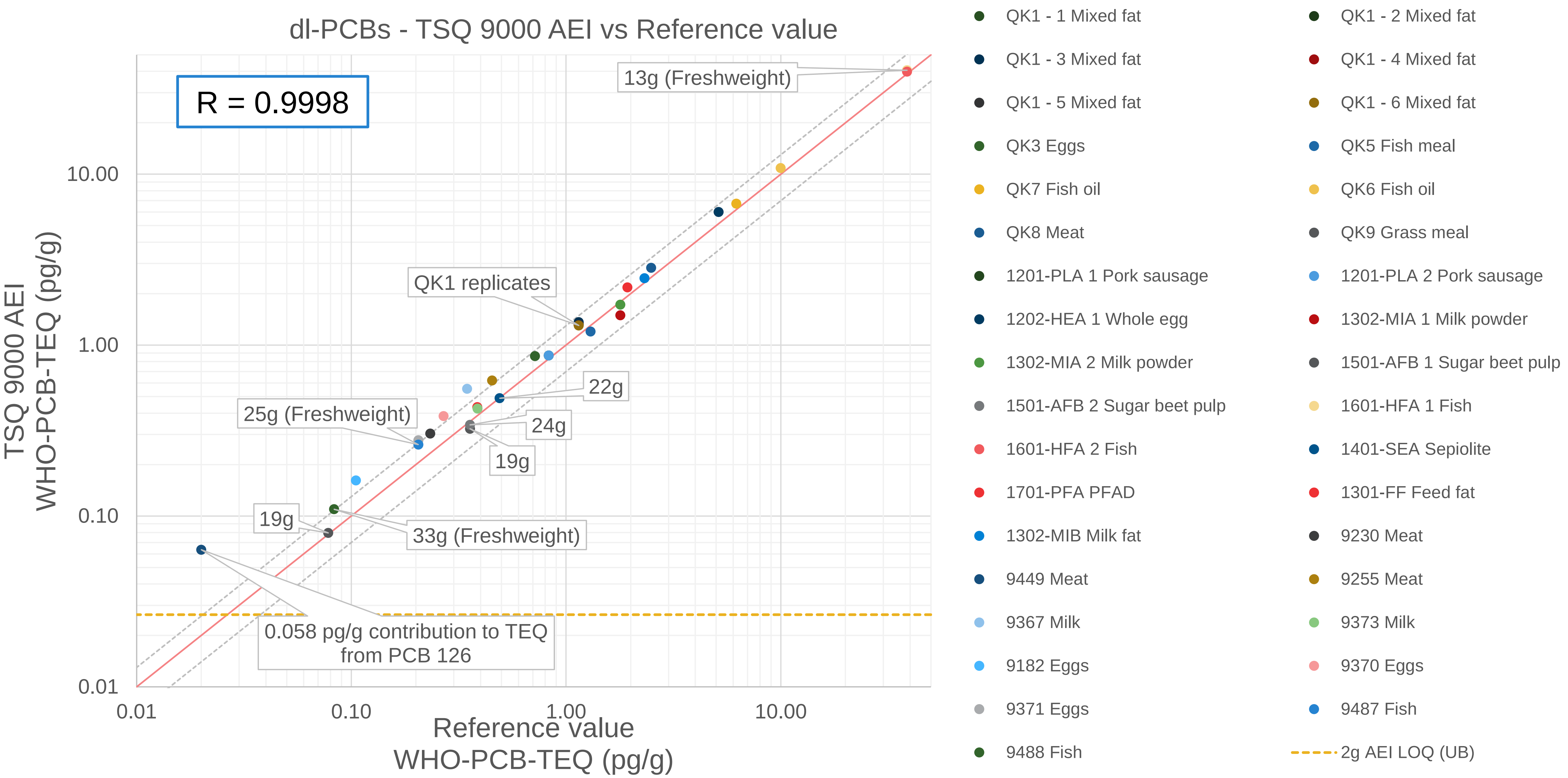
Peak Name	Ret.Time (min)	Number of Points	RF RSD (%)	Coeff.of Determination (R2)	Average RF (Slope)	Range (pg)
PCB 28	11.91	14	2.23	0.9989	1.01	0.1 – 1000
PCB 52	12.49	14	1.81	0.9993	1.06	0.1 – 1000
PCB 101	14.89	14	1.00	0.9999	1.02	0.1 – 1000
PCB 81	16.38	14	1.49	0.9997	1.06	0.04 – 160
PCB 77	16.86	14	1.08	0.9997	1.00	0.04 – 160
PCB 123	17.40	14	2.66	0.9998	0.92	0.02 – 200
PCB 123	17.40	14	2.66	0.9998	0.92	0.02 – 200
PCB 118	17.64	14	1.46	0.9999	0.96	0.1 – 1000
PCB 118	17.64	14	1.46	0.9999	0.96	0.1 – 1000
PCB 114	18.18	14	3.02	0.9989	1.04	0.02 – 200
PCB 114	18.18	14	3.02	0.9989	1.04	0.02 – 200
PCB 153	18.37	14	3.31	0.9996	1.12	0.1 – 1000
PCB 105	18.96	14	5.95	0.9947	0.96	0.02 – 200
PCB 105	18.96	14	5.95	0.9947	0.96	0.02 – 200
PCB 138	19.80	14	1.95	0.9986	1.08	0.1 – 1000
PCB 126	20.90	14	5.69	0.9985	0.95	0.04 – 160
PCB 167	21.52	14	1.74	0.9998	1.15	0.02 – 200
PCB 167	21.52	14	1.74	0.9998	1.15	0.02 – 200
PCB 156	22.90	14	1.98	0.9998	1.14	0.02 – 200
PCB 156	22.91	14	1.97	0.9998	1.14	0.02 – 200
PCB 157	23.12	14	2.41	0.9999	1.11	0.02 – 200
PCB 157	23.12	14	2.41	0.9999	1.11	0.02 – 200
PCB 180	23.43	14	2.33	0.9997	1.03	0.1 – 1000
PCB 169	25.48	14	4.00	0.9999	1.08	0.04 – 160
PCB 189	27.28	14	1.96	0.9989	0.99	0.02 – 200
PCB 189	27.28	14	1.96	0.9989	0.99	0.02 – 200
		Max	**5.95**	**0.9999**		
		Min	**1.00**	**0.9947**		

- Calibration range of over 5 orders for PCBs
  - All RF RSD <6 % for native congeners
- Duplicate injection per level (8 levels for PCDD/Fs, 7 levels for PCBs)

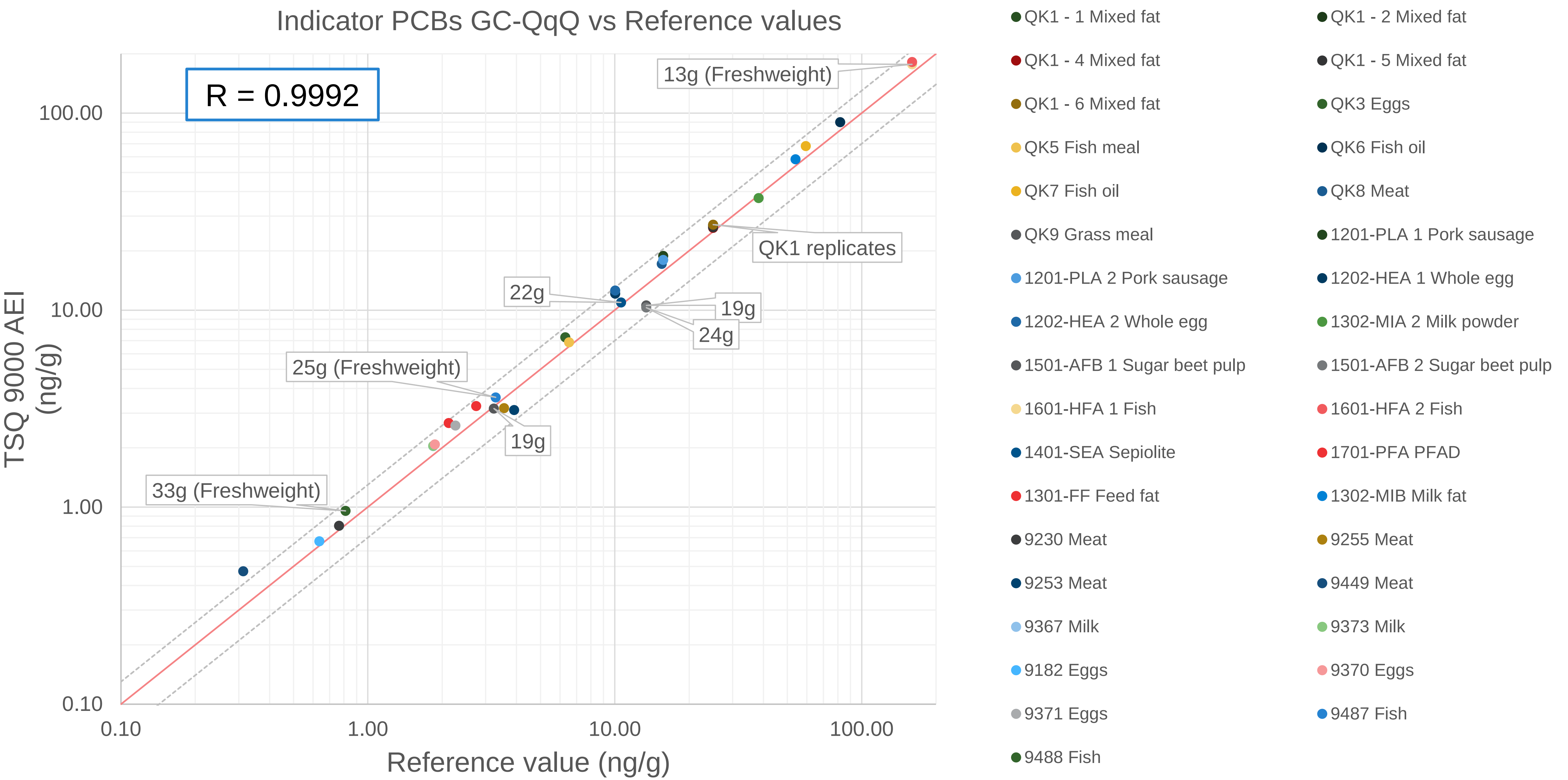
Sample analysis – PCDD/Fs



Sample analysis – dl-PCBs



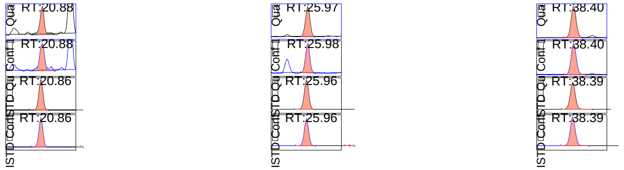
Sample analysis – Indicator PCBs

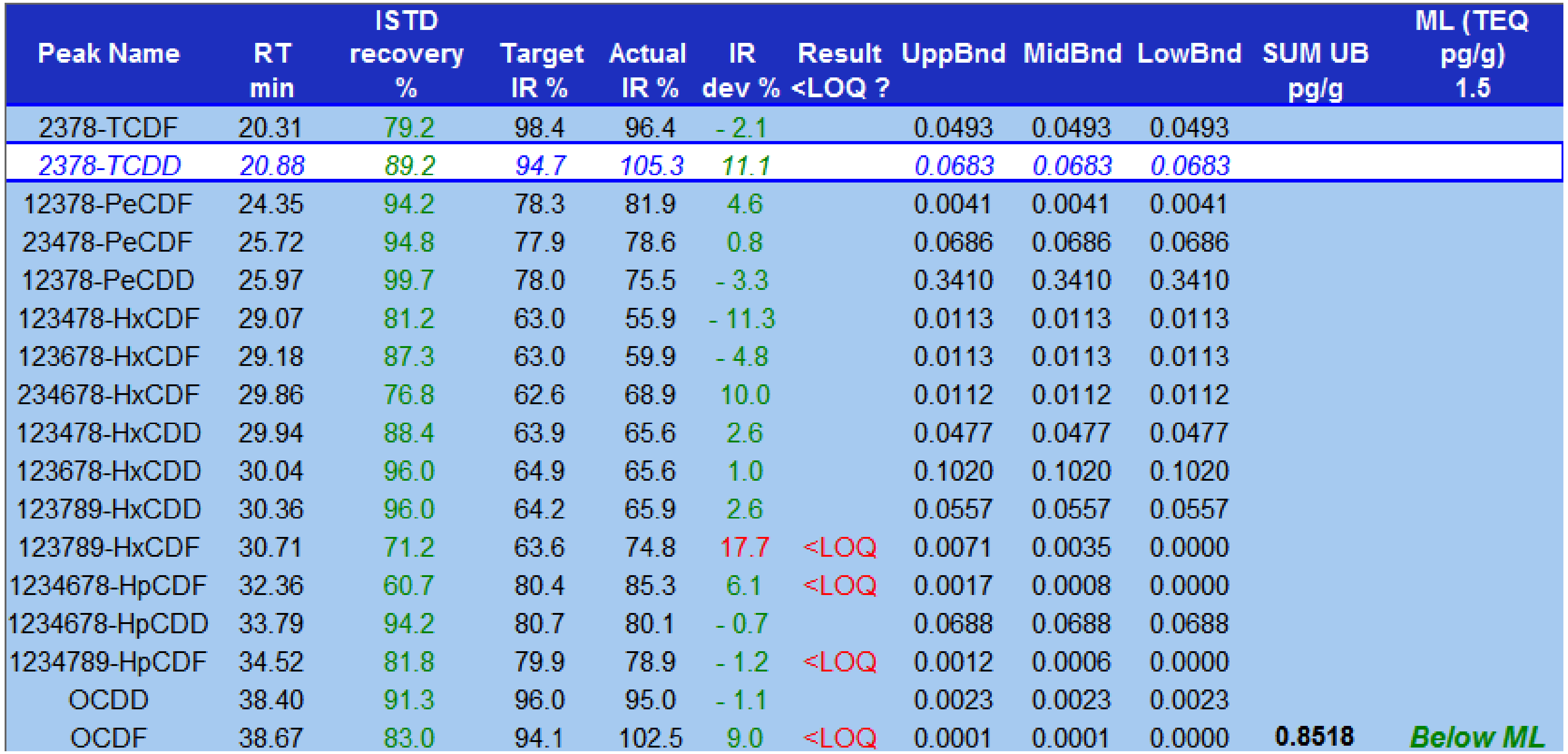


Results – quality control

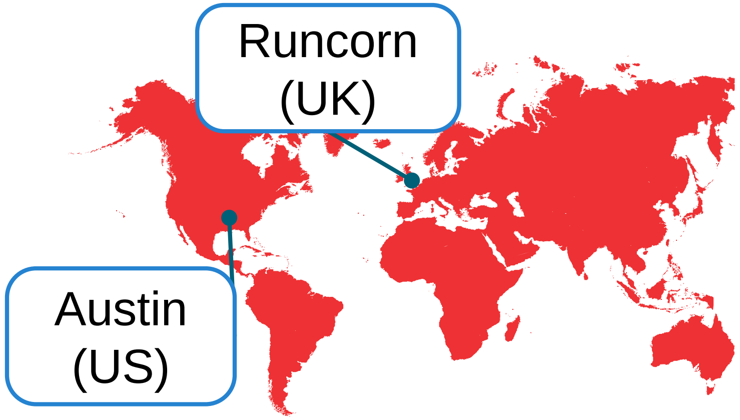
- Six replicate extractions of a mixed fat quality control sample
  - **QK1** – reference value: 0.87 pg sum WHO-PCDD/F-TEQ
  - split between the UK and USA sites
  - Analysed at regular intervals

2,3,7,8-TCDD – 0.03 pg on-column	1,2,3,7,8-PeCDD – 0.14 pg on-column	OCDD – 3.1 pg on-column



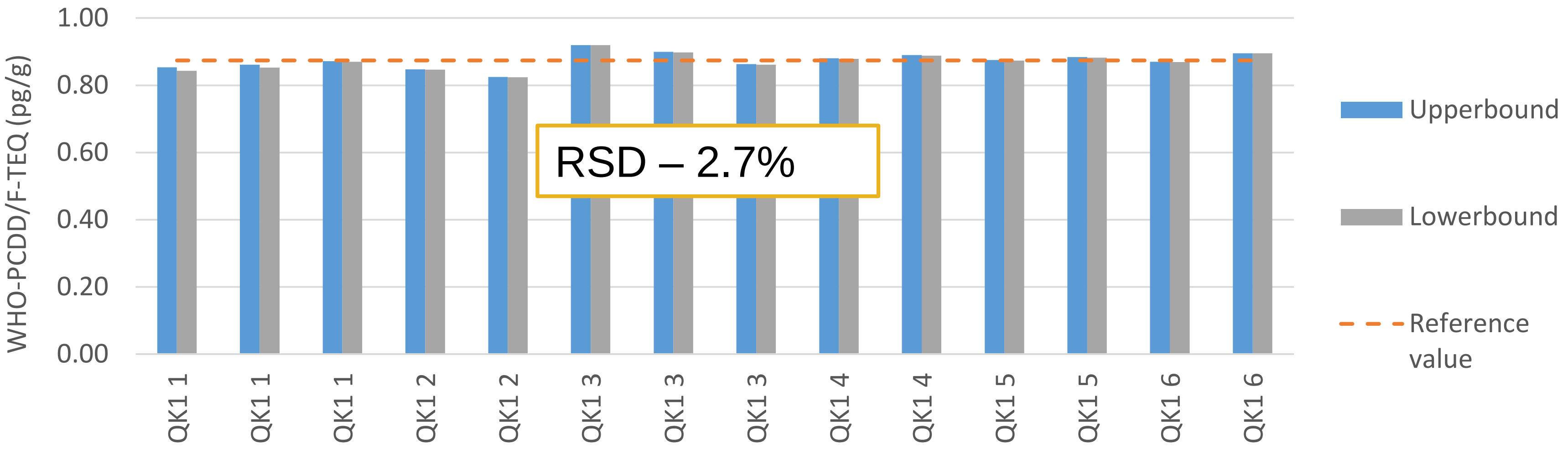


Peak Name	RT min	ISTD recovery %	Target IR %	Actual IR %	IR dev %	Result <LOQ ?	UppBnd	MidBnd	LowBnd	SUM UB pg/g	ML (TEQ pg/g) 1.5
2378-TCDF	20.31	79.2	98.4	96.4	- 2.1		0.0493	0.0493	0.0493		
2378-TCDD	*20.88*	*89.2*	*94.7*	*105.3*	*11.1*		*0.0683*	*0.0683*	*0.0683*		
12378-PeCDF	24.35	94.2	78.3	81.9	4.6		0.0041	0.0041	0.0041		
23478-PeCDF	25.72	94.8	77.9	78.6	0.8		0.0686	0.0686	0.0686		
12378-PeCDD	25.97	99.7	78.0	75.5	- 3.3		0.3410	0.3410	0.3410		
123478-HxCDF	29.07	81.2	63.0	55.9	- 11.3		0.0113	0.0113	0.0113		
123678-HxCDF	29.18	87.3	63.0	59.9	- 4.8		0.0113	0.0113	0.0113		
234678-HxCDF	29.86	76.8	62.6	68.9	10.0		0.0112	0.0112	0.0112		
123478-HxCDD	29.94	88.4	63.9	65.6	2.6		0.0477	0.0477	0.0477		
123678-HxCDD	30.04	96.0	64.9	65.6	1.0		0.1020	0.1020	0.1020		
123789-HxCDD	30.36	96.0	64.2	65.9	2.6		0.0557	0.0557	0.0557		
123789-HxCDF	30.71	71.2	63.6	74.8	17.7	<LOQ	0.0071	0.0035	0.0000		
1234678-HpCDF	32.36	60.7	80.4	85.3	6.1	<LOQ	0.0017	0.0008	0.0000		
1234678-HpCDD	33.79	94.2	80.7	80.1	- 0.7		0.0688	0.0688	0.0688		
1234789-HpCDF	34.52	81.8	79.9	78.9	- 1.2	<LOQ	0.0012	0.0006	0.0000		
OCDD	38.40	91.3	96.0	95.0	- 1.1		0.0023	0.0023	0.0023		
OCDF	38.67	83.0	94.1	102.5	9.0	<LOQ	0.0001	0.0001	0.0000	**0.8518**	***Below ML***


Runcorn (UK)

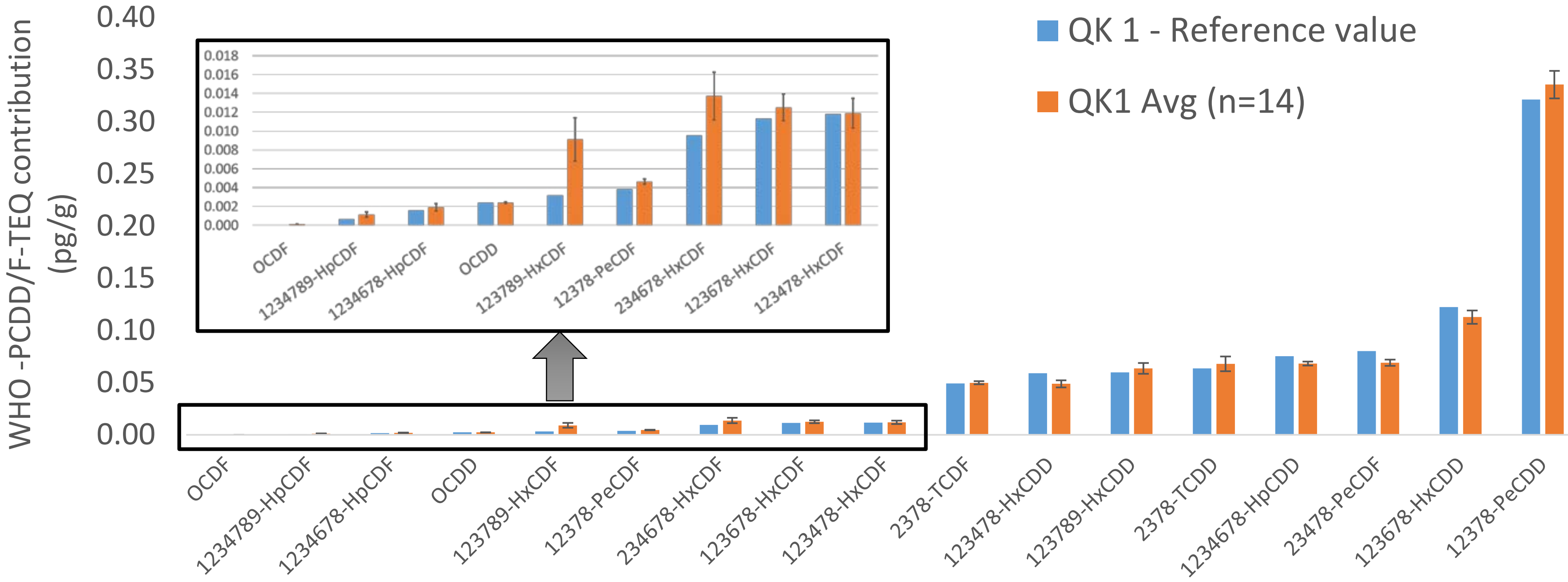
Austin (US)

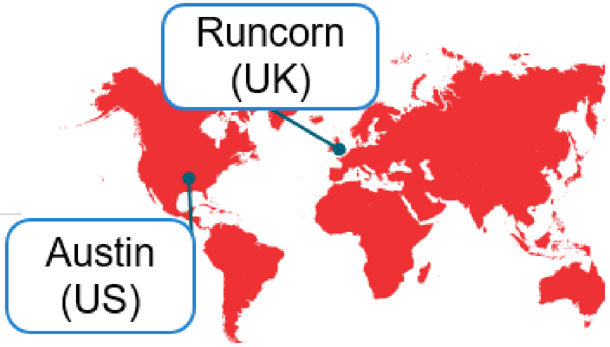
Quality control - precision



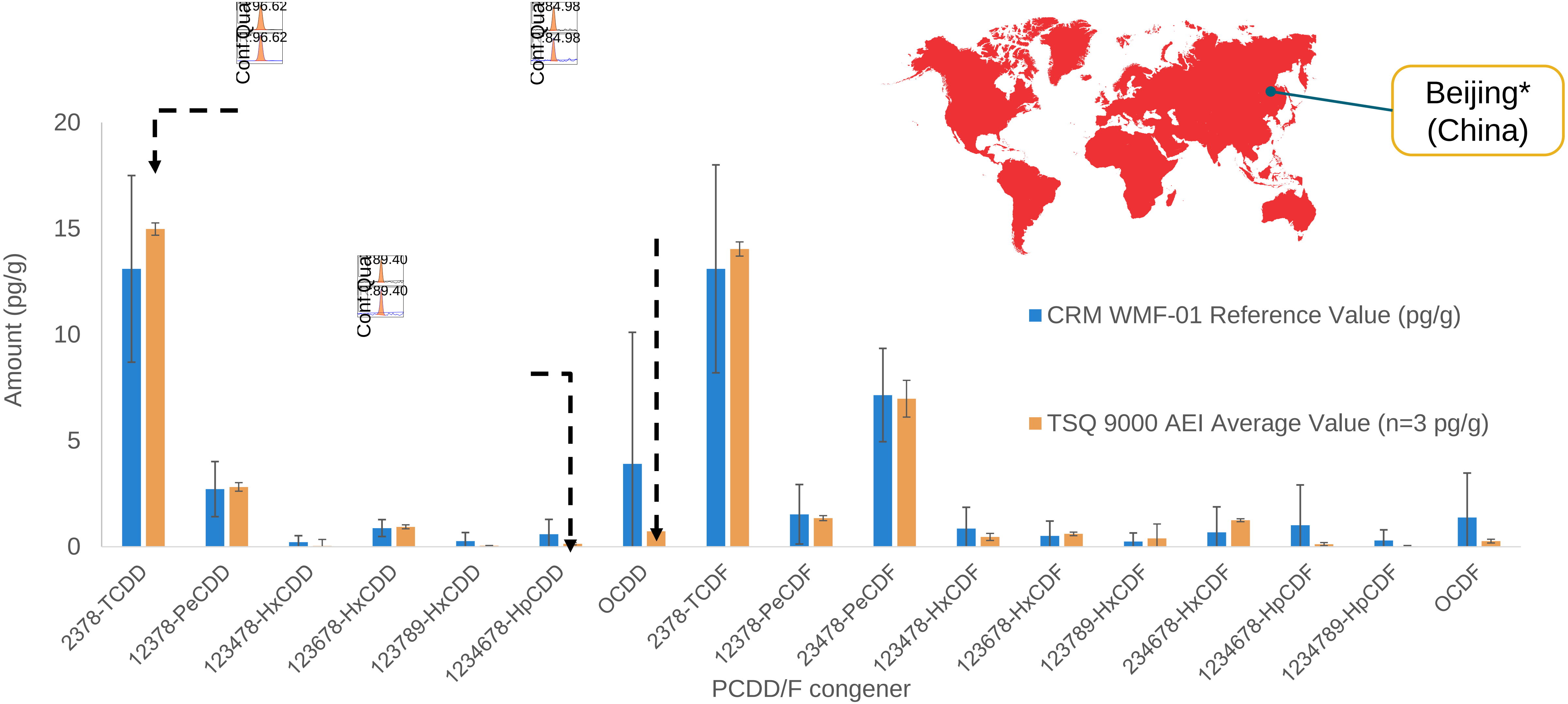
RSD – 2.7%

- Replicate analysis of the QK 1 sample over the two sequences on two separate instruments showed excellent repeatability and sensitivity.
- Deviation between the upper and lowerbound was no more than 1.2% (for confirmation of exceeding the ML, less than 20% deviation is required)





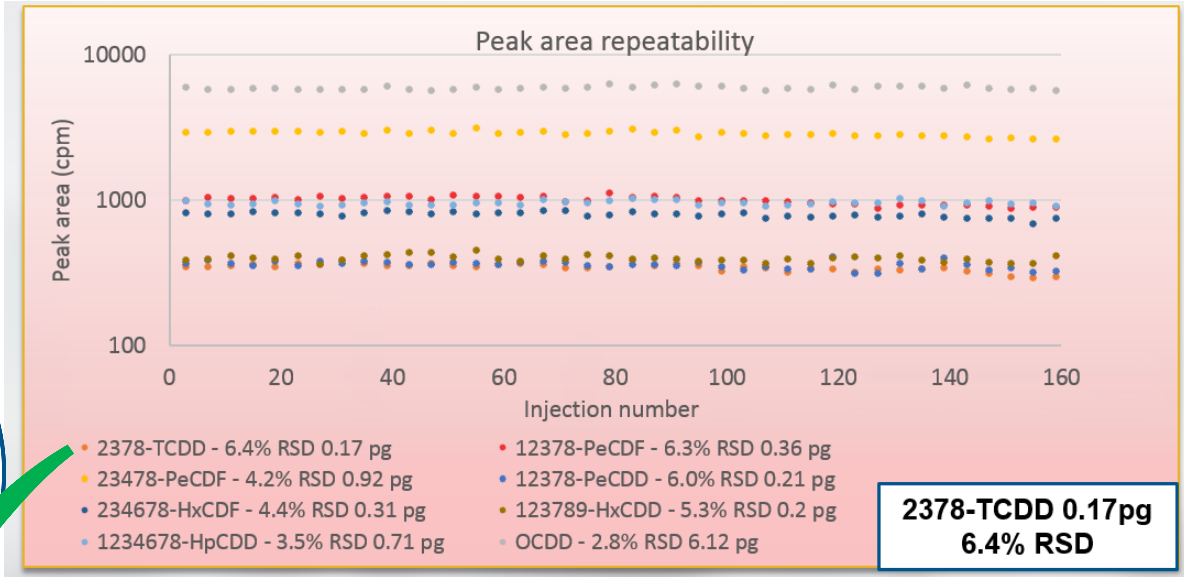
WMF-01 replicate analysis



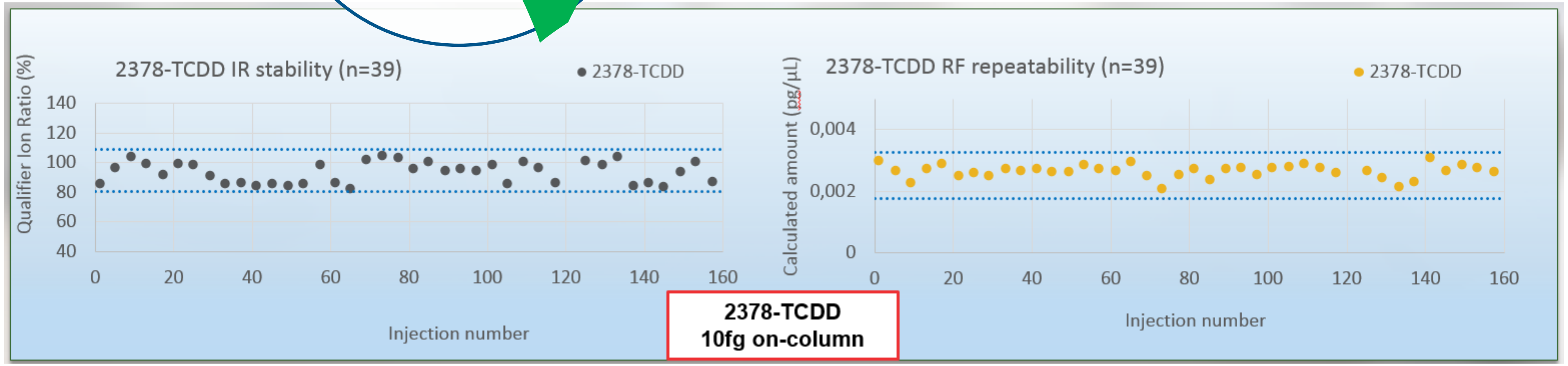
Method Robustness

- The remaining extract from the UK PCDD/F analysis was combined to give a pooled, mixed matrix sample
- A **160 injection sequence** (39 LOQ standard + 40 matrix QC + 80 solvent blank) carried out **over two weeks** of acquisition with **no tuning** or **maintenance** performed

Maximum permitted tolerance of relative ion intensities of ±15% for selected transition product ions in comparison to calculated or measured values ✓



2378-TCDD 0.17pg
6.4% RSD



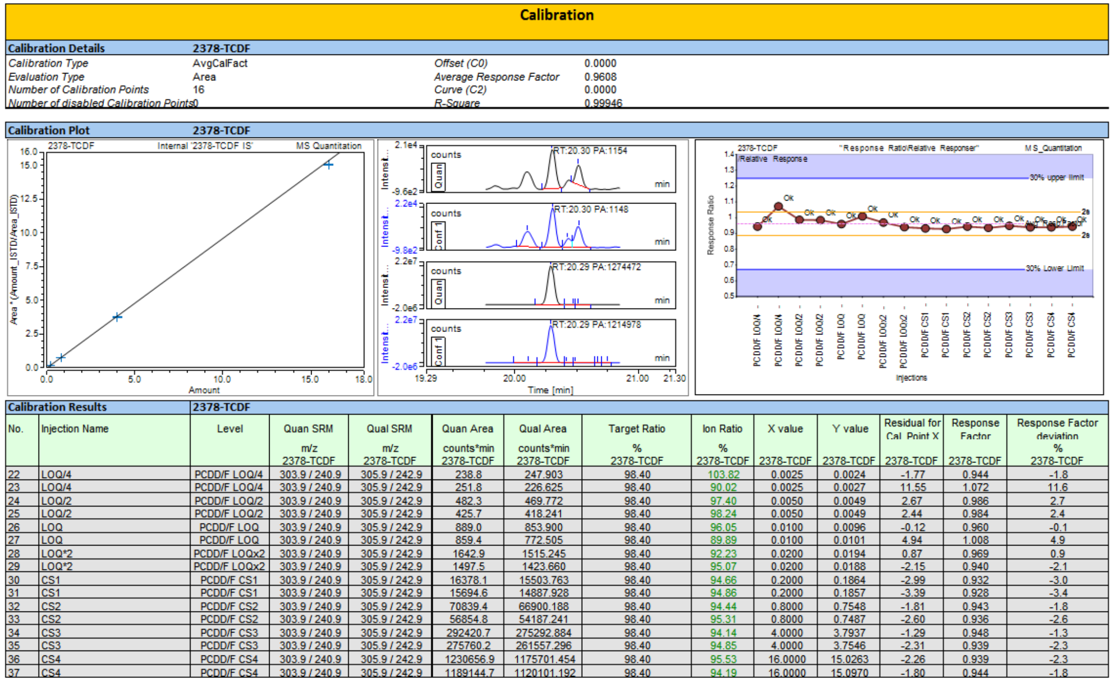
2378-TCDD
10fg on-column

Method robustness validated over a large variety of samples

Operational Simplicity Expanded Through Chromeleon CDS

Comprehensive suite of Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS) productivity tools with **pre-loaded calculation template** for isotope dilution quantification and **reporting** as required by regulations

Calibration/Sample reports for dioxin and PCBs



Calibration

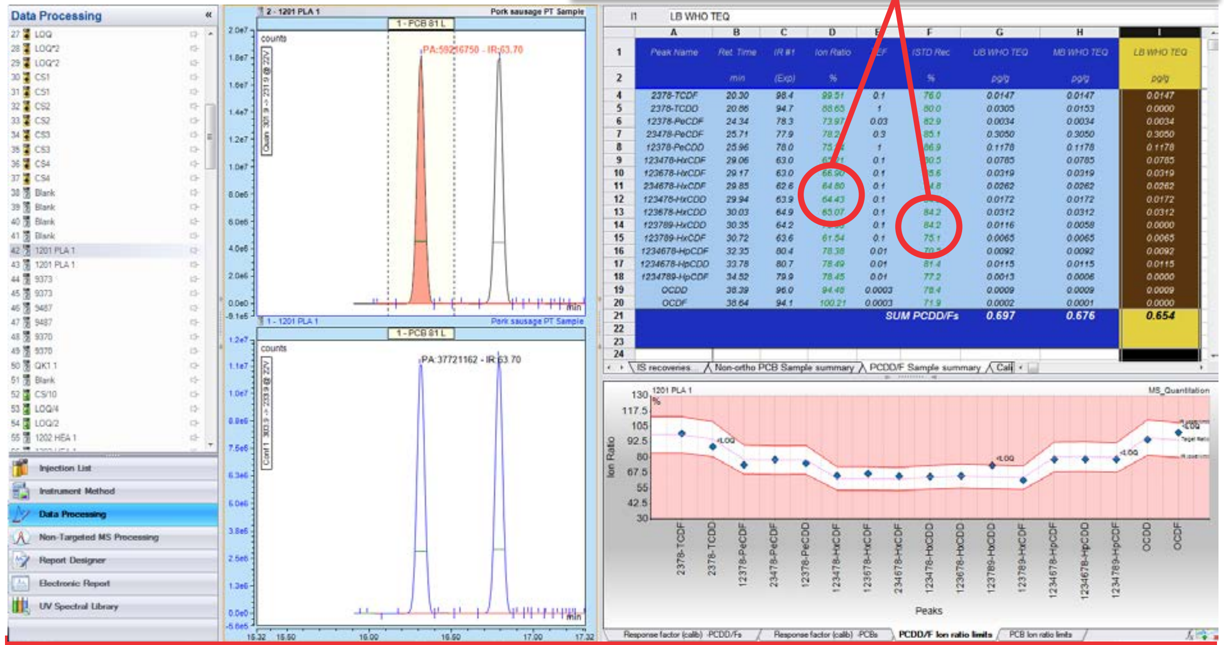
Calibration Details	**2378-TCDF**		
Calibration Type	AvgCalFact	*Offset (C0)*	0.0000
Evaluation Type	Area	*Average Response Factor*	0.9608
Number of Calibration Points	16	*Curve (C2)*	0.0000
Number of disabled Calibration Points	0	*R-Square*	0.99946

Calibration Plot **2378-TCDF**

Calibration Results		**2378-TCDF**											
No.	Injection Name	Level	Quan SRM m/z 2378-TCDF	Qual SRM m/z 2378-TCDF	Quan Area counts*min 2378-TCDF	Qual Area counts*min 2378-TCDF	Target Ratio % 2378-TCDF	Ion Ratio % 2378-TCDF	X value 2378-TCDF	Y value 2378-TCDF	Residual for Cal. Point X 2378-TCDF	Response Factor 2378-TCDF	Response Factor deviation % 2378-TCDF
22	LOQ/4	PCDD/F LOQ/4	303.9 / 240.9	305.9 / 242.9	238.8	247.903	98.40	103.82	0.0025	0.0024	-1.77	0.944	-1.8
23	LOQ/4	PCDD/F LOQ/4	303.9 / 240.9	305.9 / 242.9	251.8	226.625	98.40	90.02	0.0025	0.0027	11.55	1.072	11.6
24	LOQ/2	PCDD/F LOQ/2	303.9 / 240.9	305.9 / 242.9	482.3	469.772	98.40	97.40	0.0050	0.0049	2.67	0.986	2.7
25	LOQ/2	PCDD/F LOQ/2	303.9 / 240.9	305.9 / 242.9	425.7	418.241	98.40	98.24	0.0050	0.0049	2.44	0.984	2.4
26	LOQ	PCDD/F LOQ	303.9 / 240.9	305.9 / 242.9	889.0	853.900	98.40	96.05	0.0100	0.0096	-0.12	0.960	-0.1
27	LOQ	PCDD/F LOQ	303.9 / 240.9	305.9 / 242.9	859.4	772.505	98.40	89.89	0.0100	0.0101	4.94	1.008	4.9
28	LOQ*2	PCDD/F LOQx2	303.9 / 240.9	305.9 / 242.9	1642.9	1515.245	98.40	92.23	0.0200	0.0194	0.87	0.969	0.9
29	LOQ*2	PCDD/F LOQx2	303.9 / 240.9	305.9 / 242.9	1497.5	1423.660	98.40	95.07	0.0200	0.0188	-2.15	0.940	-2.1
30	CS1	PCDD/F CS1	303.9 / 240.9	305.9 / 242.9	16378.1	15503.763	98.40	94.66	0.2000	0.1864	-2.99	0.932	-3.0
31	CS1	PCDD/F CS1	303.9 / 240.9	305.9 / 242.9	15694.6	14887.928	98.40	94.86	0.2000	0.1857	-3.39	0.928	-3.4
32	CS2	PCDD/F CS2	303.9 / 240.9	305.9 / 242.9	70839.4	66900.188	98.40	94.44	0.8000	0.7548	-1.81	0.943	-1.8
33	CS2	PCDD/F CS2	303.9 / 240.9	305.9 / 242.9	56854.8	54187.241	98.40	95.31	0.8000	0.7487	-2.60	0.936	-2.6
34	CS3	PCDD/F CS3	303.9 / 240.9	305.9 / 242.9	292420.7	275292.884	98.40	94.14	4.0000	3.7937	-1.29	0.948	-1.3
35	CS3	PCDD/F CS3	303.9 / 240.9	305.9 / 242.9	275760.2	261557.296	98.40	94.85	4.0000	3.7546	-2.31	0.939	-2.3
36	CS4	PCDD/F CS4	303.9 / 240.9	305.9 / 242.9	1230656.9	1175701.454	98.40	95.53	16.0000	15.0263	-2.26	0.939	-2.3
37	CS4	PCDD/F CS4	303.9 / 240.9	305.9 / 242.9	1189144.7	1120101.192	98.40	94.19	16.0000	15.0970	-1.80	0.944	-1.8

All templates can be exported as pdf/excel

Automatic flagging of results



Interactive studio screen shot showing all calculation results

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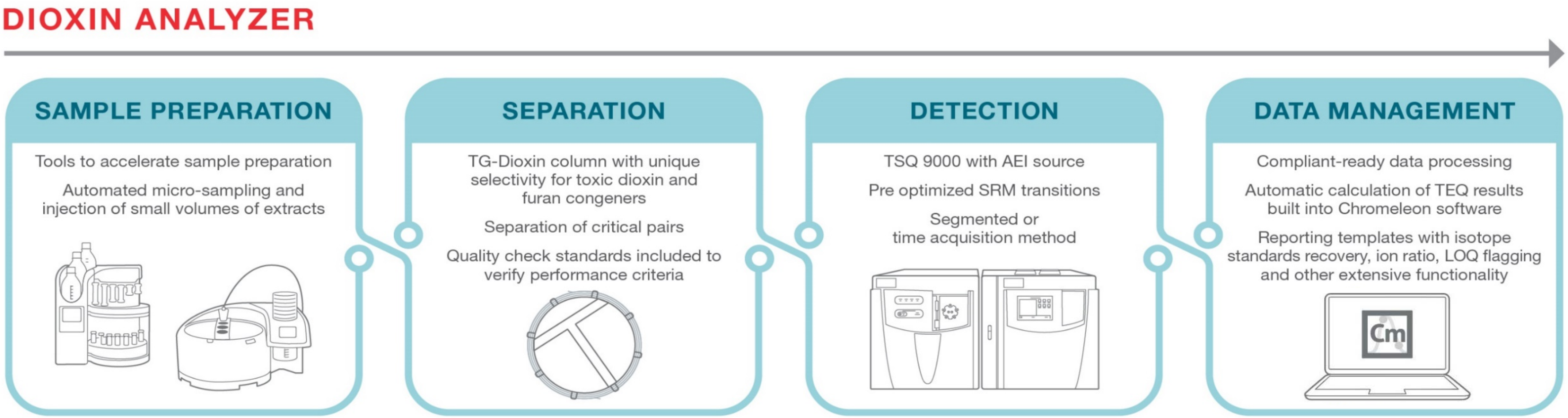
Conclusions

- The new Dioxin Analyzer delivers:
  - Compliance with all EU requirements for Dioxin/PCBs in food and feed
  - Operational simplicity and out-of-box implementation
  - Comprehensive suite of Chromeleon CDS productivity tools with pre-loaded calculation and reporting templates as required by regulations
  - Method robustness validated over a large variety of samples
  - Unmatched uptime via the new ultra-robustness source designed for high matrix tolerance



DIOXIN ANALYZER

SAMPLE PREPARATION

Tools to accelerate sample preparation

Automated micro-sampling and injection of small volumes of extracts

SEPARATION

TG-Dioxin column with unique selectivity for toxic dioxin and furan congeners

Separation of critical pairs

Quality check standards included to verify performance criteria

DETECTION

TSQ 9000 with AEI source

Pre optimized SRM transitions

Segmented or time acquisition method

DATA MANAGEMENT

Compliant-ready data processing

Automatic calculation of TEQ results built into Chromeleon software

Reporting templates with isotope standards recovery, ion ratio, LOQ flagging and other extensive functionality

Thank You for Your Attention!

Questions?

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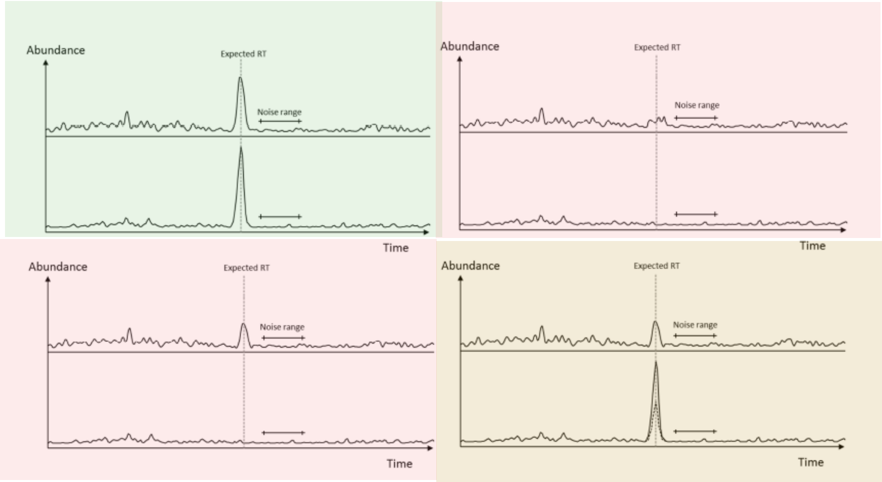
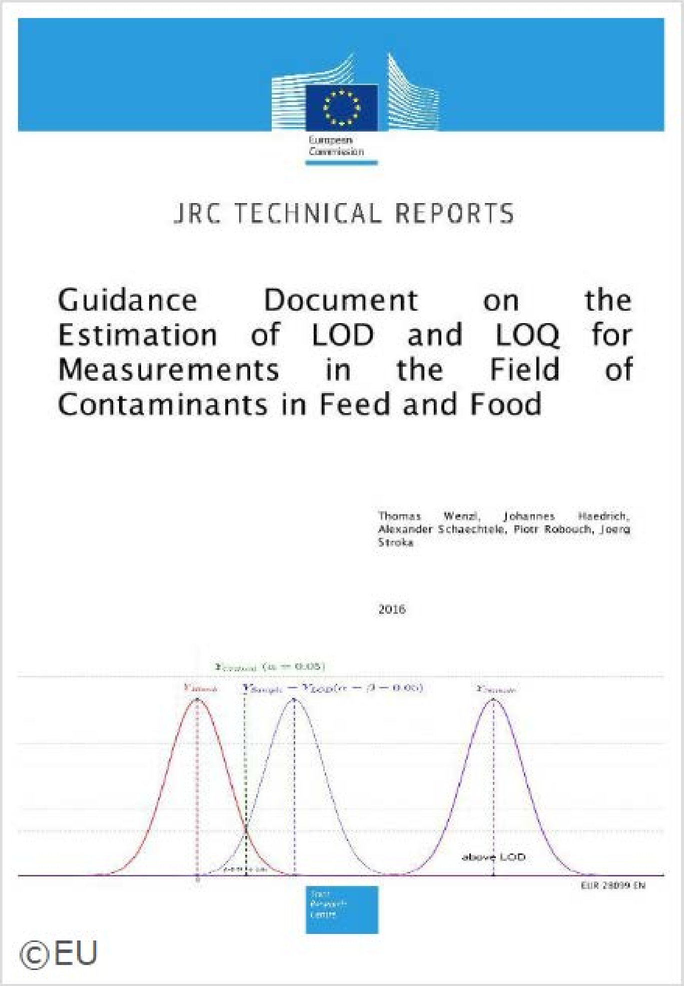
BACK UP

LOQ Definition

- Traditionally, when using magnetic sector instruments, LOQ was calculated using the signal-to-noise value for a low level standard



- This can be problematic when using GC-MS/MS, as in many instances there can be inconsistent or little to no noise
- With this in mind, the European Commission produced a technical guidance document to address this
- In these experiments, European Union Reference Laboratories guidance was followed and a calibration based approached was used.
- To demonstrate the sensitivity required to routine achieve the LOQs applied, a low level standard, at the LOQ, was included in the calibration curve and also injected at regular intervals throughout the batch.



European Commission

JRC TECHNICAL REPORTS

Guidance Document on the Estimation of LOD and LOQ for Measurements in the Field of Contaminants in Feed and Food

Thomas Wenzl, Johannes Haedrich, Alexander Schaechtele, Piotr Robouch, Joerg Stroka

2016

EUR 28099 EN

Joint Research Centre

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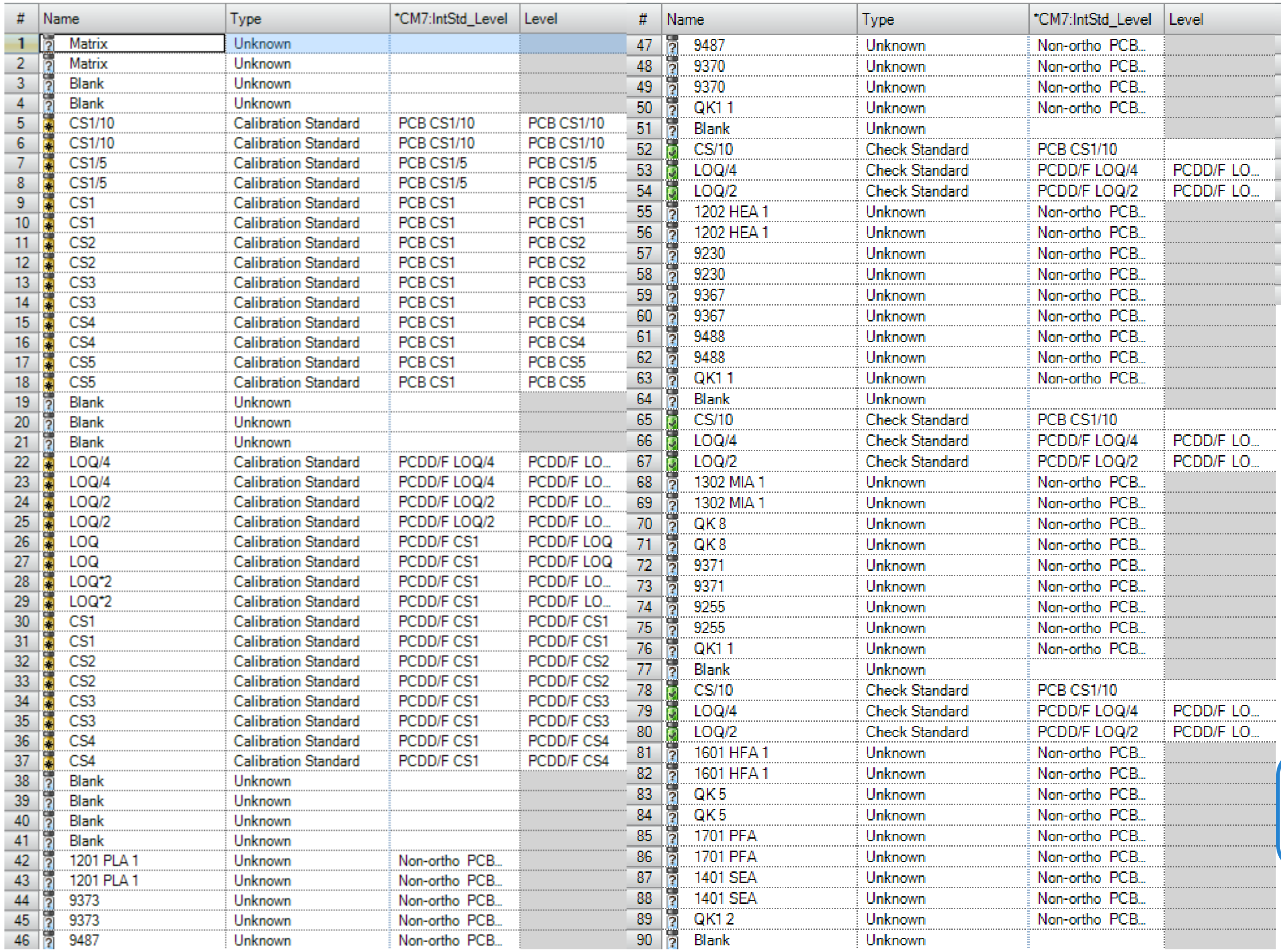
Sample List



#	Name	Type	*CM7:IntStd_Level	Level
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3	Blank	Unknown		
4	Blank	Unknown		
5	CS1/10	Calibration Standard	PCB CS1/10	PCB CS1/10
6	CS1/10	Calibration Standard	PCB CS1/10	PCB CS1/10
7	CS1/5	Calibration Standard	PCB CS1/5	PCB CS1/5
8	CS1/5	Calibration Standard	PCB CS1/5	PCB CS1/5
9	CS1	Calibration Standard	PCB CS1	PCB CS1
10	CS1	Calibration Standard	PCB CS1	PCB CS1
11	CS2	Calibration Standard	PCB CS1	PCB CS2
12	CS2	Calibration Standard	PCB CS1	PCB CS2
13	CS3	Calibration Standard	PCB CS1	PCB CS3
14	CS3	Calibration Standard	PCB CS1	PCB CS3
15	CS4	Calibration Standard	PCB CS1	PCB CS4
16	CS4	Calibration Standard	PCB CS1	PCB CS4
17	CS5	Calibration Standard	PCB CS1	PCB CS5
18	CS5	Calibration Standard	PCB CS1	PCB CS5
19	Blank	Unknown		
20	Blank	Unknown		
21	Blank	Unknown		
22	LOQ/4	Calibration Standard	PCDD/F LOQ/4	PCDD/F LO...
23	LOQ/4	Calibration Standard	PCDD/F LOQ/4	PCDD/F LO...
24	LOQ/2	Calibration Standard	PCDD/F LOQ/2	PCDD/F LO...
25	LOQ/2	Calibration Standard	PCDD/F LOQ/2	PCDD/F LO...
26	LOQ	Calibration Standard	PCDD/F CS1	PCDD/F LOQ
27	LOQ	Calibration Standard	PCDD/F CS1	PCDD/F LOQ
28	LOQ*2	Calibration Standard	PCDD/F CS1	PCDD/F LO...
29	LOQ*2	Calibration Standard	PCDD/F CS1	PCDD/F LO...
30	CS1	Calibration Standard	PCDD/F CS1	PCDD/F CS1
31	CS1	Calibration Standard	PCDD/F CS1	PCDD/F CS1
32	CS2	Calibration Standard	PCDD/F CS1	PCDD/F CS2
33	CS2	Calibration Standard	PCDD/F CS1	PCDD/F CS2
34	CS3	Calibration Standard	PCDD/F CS1	PCDD/F CS3
35	CS3	Calibration Standard	PCDD/F CS1	PCDD/F CS3
36	CS4	Calibration Standard	PCDD/F CS1	PCDD/F CS4
37	CS4	Calibration Standard	PCDD/F CS1	PCDD/F CS4
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39	Blank	Unknown		
40	Blank	Unknown		
41	Blank	Unknown		
42	1201 PLA 1	Unknown	Non-ortho PCB...	
43	1201 PLA 1	Unknown	Non-ortho PCB...	
44	9373	Unknown	Non-ortho PCB...	
45	9373	Unknown	Non-ortho PCB...	
46	9487	Unknown	Non-ortho PCB...	
47	9487	Unknown	Non-ortho PCB...	
48	9370	Unknown	Non-ortho PCB...	
49	9370	Unknown	Non-ortho PCB...	
50	QK1 1	Unknown	Non-ortho PCB...	
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53	LOQ/4	Check Standard	PCDD/F LOQ/4	PCDD/F LO...
54	LOQ/2	Check Standard	PCDD/F LOQ/2	PCDD/F LO...
55	1202 HEA 1	Unknown	Non-ortho PCB...	
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59	9367	Unknown	Non-ortho PCB...	
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61	9488	Unknown	Non-ortho PCB...	
62	9488	Unknown	Non-ortho PCB...	
63	QK1 1	Unknown	Non-ortho PCB...	
64	Blank	Unknown		
65	CS/10	Check Standard	PCB CS1/10	
66	LOQ/4	Check Standard	PCDD/F LOQ/4	PCDD/F LO...
67	LOQ/2	Check Standard	PCDD/F LOQ/2	PCDD/F LO...
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70	QK 8	Unknown	Non-ortho PCB...	
71	QK 8	Unknown	Non-ortho PCB...	
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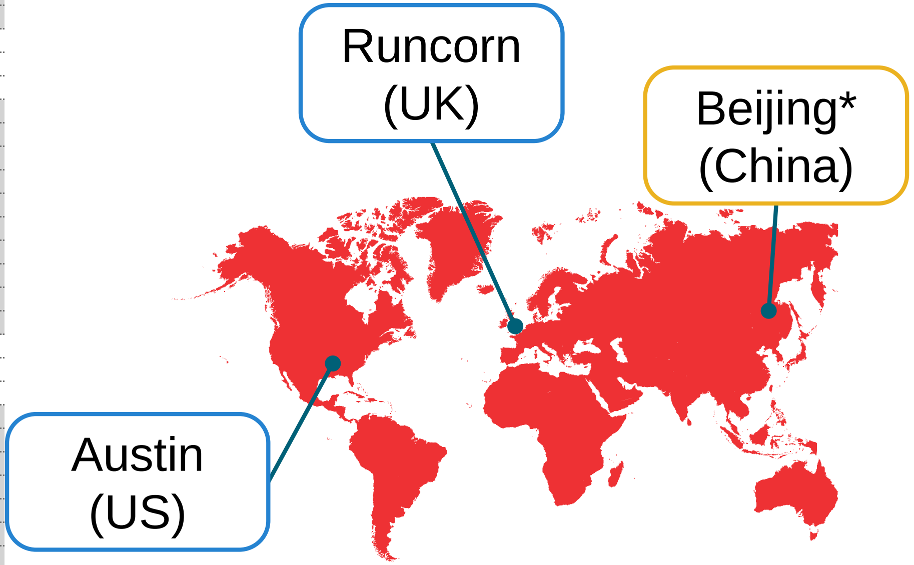
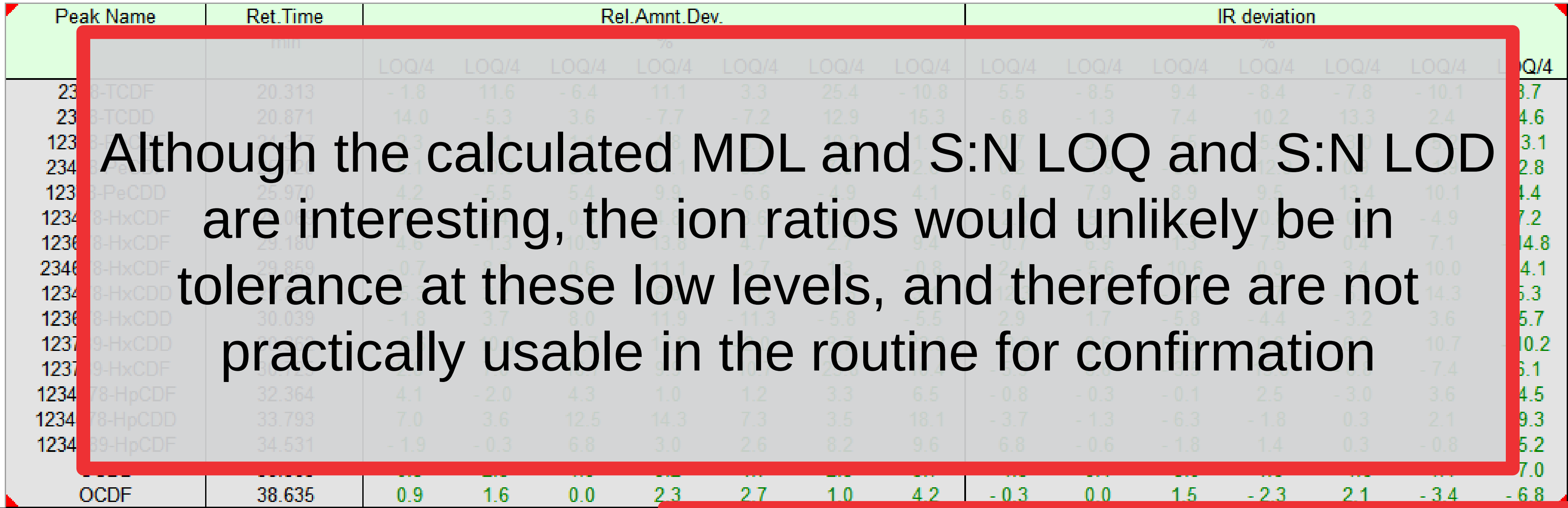
74	9255	Unknown	Non-ortho PCB...	
75	9255	Unknown	Non-ortho PCB...	
76	QK1 1	Unknown	Non-ortho PCB...	
77	Blank	Unknown		
78	CS/10	Check Standard	PCB CS1/10	
79	LOQ/4	Check Standard	PCDD/F LOQ/4	PCDD/F LO...
80	LOQ/2	Check Standard	PCDD/F LOQ/2	PCDD/F LO...
81	1601 HFA 1	Unknown	Non-ortho PCB...	
82	1601 HFA 1	Unknown	Non-ortho PCB...	
83	QK 5	Unknown	Non-ortho PCB...	
84	QK 5	Unknown	Non-ortho PCB...	
85	1701 PFA	Unknown	Non-ortho PCB...	
86	1701 PFA	Unknown	Non-ortho PCB...	
87	1401 SEA	Unknown	Non-ortho PCB...	
88	1401 SEA	Unknown	Non-ortho PCB...	
89	QK1 2	Unknown	Non-ortho PCB...	
90	Blank	Unknown		
90	Blank	Unknown		
91	CS/10	Check Standard	PCB CS1/10	
92	LOQ/4	Check Standard	PCDD/F LOQ/4	PCDD/F LO...
93	LOQ/2	Check Standard	PCDD/F LOQ/2	PCDD/F LO...
94	1501 AFB 1	Unknown	Non-ortho PCB...	
95	1501 AFB 1	Unknown	Non-ortho PCB...	
96	9182	Unknown	Non-ortho PCB...	
97	9182	Unknown	Non-ortho PCB...	
98	QK1 2	Unknown	Non-ortho PCB...	
99	Blank	Unknown		
100	CS/10	Check Standard	PCB CS1/10	
101	LOQ/4	Check Standard	PCDD/F LOQ/4	PCDD/F LO...
102	LOQ/2	Check Standard	PCDD/F LOQ/2	PCDD/F LO...



Extended testing and validation across multiple sites with different sample types

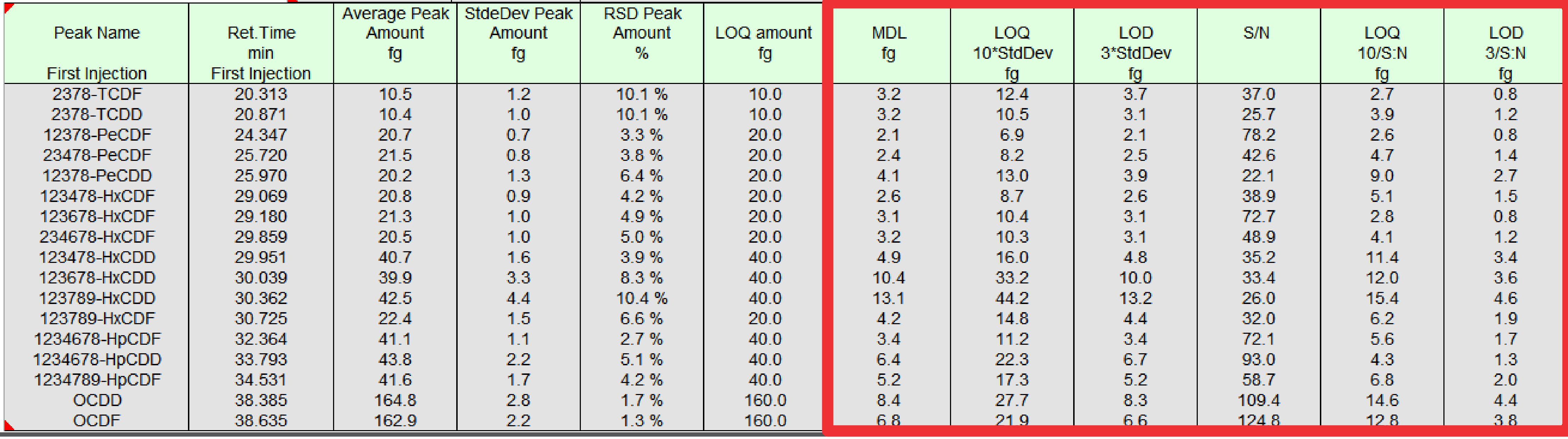
LOQ Data…

- What about concentrations below the LOQ standard?



Peak Name	Ret.Time min	Rel.Amnt.Dev. % LOQ/4	LOQ/4	LOQ/4	LOQ/4	LOQ/4	LOQ/4	LOQ/4	IR deviation % LOQ/4	LOQ/4	LOQ/4	LOQ/4	LOQ/4	LOQ/4	Q/4
23 8-TCDF	20.313	- 1.8	11.6	- 6.4	11.1	3.3	25.4	- 10.8	5.5	- 8.5	9.4	- 8.4	- 7.8	- 10.1	3.7
23 8-TCDD	20.871	14.0	- 5.3	3.6	- 7.7	- 7.2	12.9	15.3	- 6.8	- 1.3	7.4	10.2	13.3	2.4	4.6
123	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	3.1
234	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	2.8
123 8-PeCDD	25.970	4.2	- 5.5	5.4	9.9	- 6.6	- 4.9	4.1	- 6.4	7.9	8.9	9.5	13.4	10.1	4.4
1234 8-HxCDF	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	- 4.9	7.2
1236 8-HxCDF	29.180	4.6	- 1.3	10.5	13.8	4.7	2.7	9.4	- 0.7	6.5	1.5	- 7.5	0.4	7.1	14.8
2346 8-HxCDF	29.859	- 0.7	[illegible]	0.6	11.1	2.7	[illegible]	- 0.8	[illegible]	- 5.6	10.6	0.9	3.4	10.0	4.1
1234 8-HxCDD	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	14.3	5.3
1236 8-HxCDD	30.039	- 1.8	3.7	8.0	11.9	- 11.3	- 5.8	- 5.5	2.9	1.7	- 5.8	- 4.4	- 3.2	3.6	5.7
1237 9-HxCDD	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	10.7	10.2
1237 9-HxCDF	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	- 7.4	6.1
1234 78-HpCDF	32.364	4.1	- 2.0	4.3	1.0	1.2	3.3	6.5	- 0.8	- 0.3	- 0.1	2.5	- 3.0	3.6	4.5
1234 78-HpCDD	33.793	7.0	3.6	12.5	14.3	7.3	3.5	18.1	- 3.7	- 1.3	- 6.3	- 1.8	0.3	2.1	9.3
1234 89-HpCDF	34.531	- 1.9	- 0.3	6.8	3.0	2.6	8.2	9.6	6.8	- 0.6	- 1.8	1.4	0.3	- 0.8	5.2
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	7.0
OCDF	38.635	0.9	1.6	0.0	2.3	2.7	1.0	4.2	- 0.3	0.0	1.5	- 2.3	2.1	- 3.4	- 6.8

Although the calculated MDL and S:N LOQ and S:N LOD are interesting, the ion ratios would unlikely be in tolerance at these low levels, and therefore are not practically usable in the routine for confirmation



Peak Name First Injection	Ret.Time min First Injection	Average Peak Amount fg	StdeDev Peak Amount fg	RSD Peak Amount %	LOQ amount fg	MDL fg	LOQ 10*StdDev fg	LOD 3*StdDev fg	S/N	LOQ 10/S:N fg	LOD 3/S:N fg
2378-TCDF	20.313	10.5	1.2	10.1 %	10.0	3.2	12.4	3.7	37.0	2.7	0.8
2378-TCDD	20.871	10.4	1.0	10.1 %	10.0	3.2	10.5	3.1	25.7	3.9	1.2
12378-PeCDF	24.347	20.7	0.7	3.3 %	20.0	2.1	6.9	2.1	78.2	2.6	0.8
23478-PeCDF	25.720	21.5	0.8	3.8 %	20.0	2.4	8.2	2.5	42.6	4.7	1.4
12378-PeCDD	25.970	20.2	1.3	6.4 %	20.0	4.1	13.0	3.9	22.1	9.0	2.7
123478-HxCDF	29.069	20.8	0.9	4.2 %	20.0	2.6	8.7	2.6	38.9	5.1	1.5
123678-HxCDF	29.180	21.3	1.0	4.9 %	20.0	3.1	10.4	3.1	72.7	2.8	0.8
234678-HxCDF	29.859	20.5	1.0	5.0 %	20.0	3.2	10.3	3.1	48.9	4.1	1.2
123478-HxCDD	29.951	40.7	1.6	3.9 %	40.0	4.9	16.0	4.8	35.2	11.4	3.4
123678-HxCDD	30.039	39.9	3.3	8.3 %	40.0	10.4	33.2	10.0	33.4	12.0	3.6
123789-HxCDD	30.362	42.5	4.4	10.4 %	40.0	13.1	44.2	13.2	26.0	15.4	4.6
123789-HxCDF	30.725	22.4	1.5	6.6 %	20.0	4.2	14.8	4.4	32.0	6.2	1.9
1234678-HpCDF	32.364	41.1	1.1	2.7 %	40.0	3.4	11.2	3.4	72.1	5.6	1.7
1234678-HpCDD	33.793	43.8	2.2	5.1 %	40.0	6.4	22.3	6.7	93.0	4.3	1.3
1234789-HpCDF	34.531	41.6	1.7	4.2 %	40.0	5.2	17.3	5.2	58.7	6.8	2.0
OCDD	38.385	164.8	2.8	1.7 %	160.0	8.4	27.7	8.3	109.4	14.6	4.4
OCDF	38.635	162.9	2.2	1.3 %	160.0	6.8	21.9	6.6	124.8	12.8	3.8