食品中二噁英及其类似物GC-MS/MS检测方法的验证

Validation of GC-MS/MS Analysis of Dioxins and Dioxin-like Polychlorobiphenyls in Food

吕冰
Bing Lyu
国家食品安全风险评估中心
China National Center for Food Safety Risk Assessment
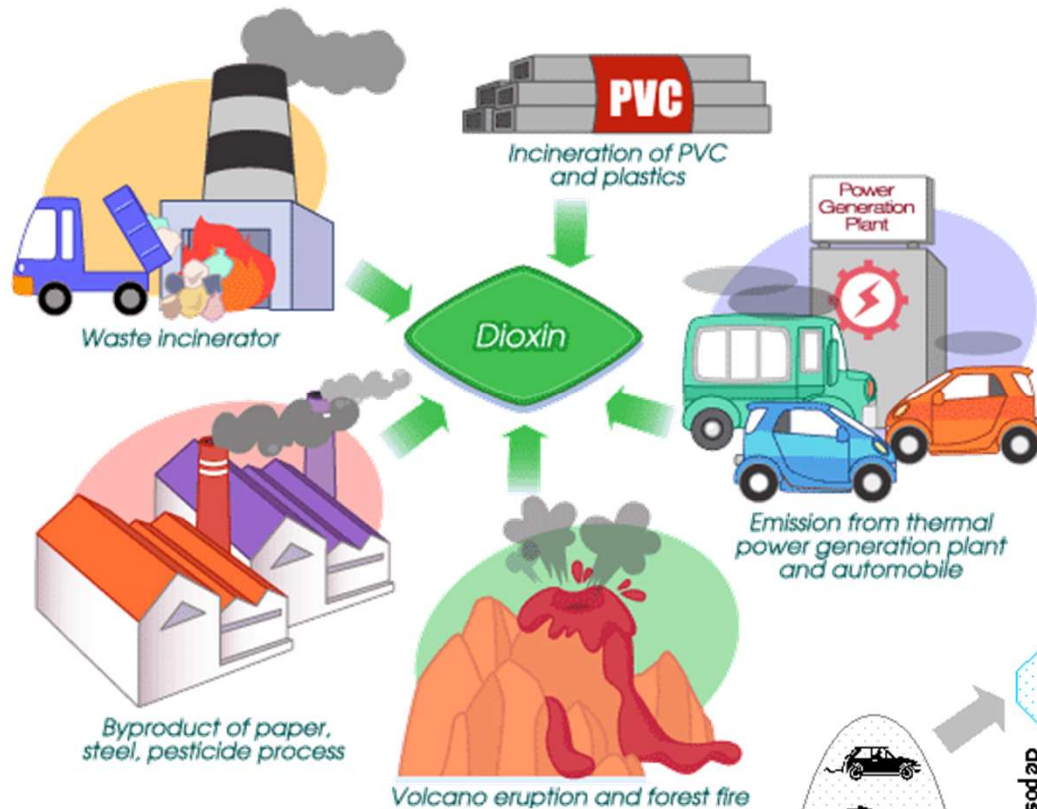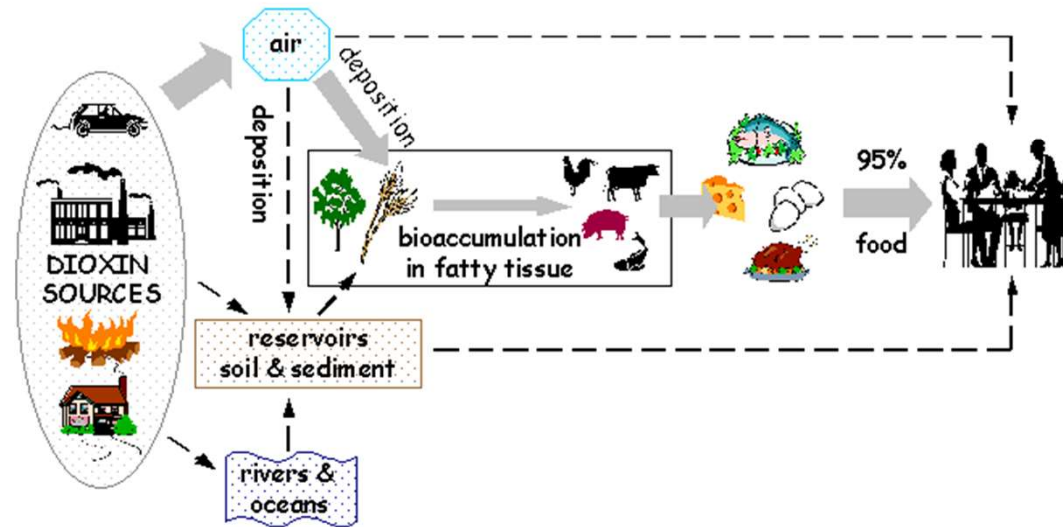
EU-China Safe-Setting up RL2020

Setting up RL2020:

Based on the EU legislation, validation of GC-MS/MS Analysis of Dioxins and Dioxin-like Polychlorobiphenyls in Food. Explore its applicability and the possibility of technology promotion. Comparing the method between the Chinese National Reference Laboratory (CNRL) and the EU National Reference Laboratory (NRL), and convert it to Chinese national standards.

Human exposure to dioxins

Waste incinerator

Incineration of PVC and plastics

Power Generation Plant

Dioxin

Byproduct of paper, steel, pesticide process

Volcano eruption and forest fire

Emission from thermal power generation plant and automobile

Polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzo-*p*-furans (PCDFs), more commonly referred to as *dioxins,* are a group of chemically-related compounds that are persistent environmental pollutants (POPs).

air

deposition

deposition

DIOXIN SOURCES

bioaccumulation in fatty tissue

95% food

reservoirs soil & sediment

rivers & oceans

REGULATIONS

COMMISSION REGULATION (EU) No 709/2014

of 20 June 2014

amending Regulation (EC) No 152/2009 as regards the determination of the levels of dioxins and polychlorinated biphenyls
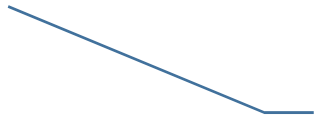
COMMISSION REGULATION (EU) No 589/2014

of 2 June 2014

laying down methods of sampling and analysis for the control of levels of dioxins, dioxin-like PCBs and non-dioxin-like PCBs in certain foodstuffs and repealing Regulation (EU) No 252/2012

COMMISSION REGULATION (EU) 2017/644

of 5 April 2017

laying down methods of sampling and analysis for the control of levels of dioxins, dioxin-like PCBs and non-dioxin-like PCBs in certain foodstuffs and repealing Regulation (EU) No 589/2014
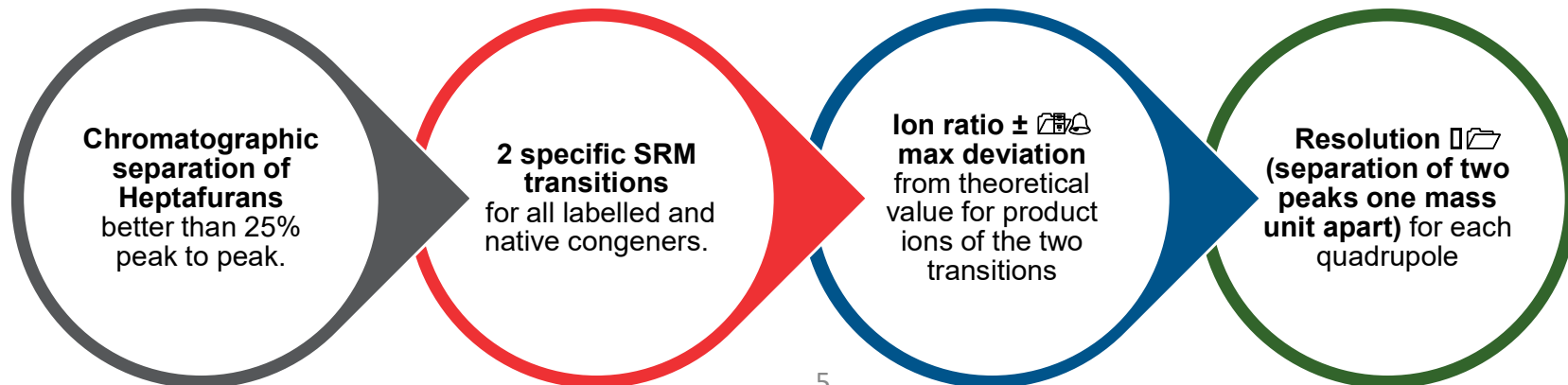
GC-MS/MS: confirmatory method

COMMISSION REGULATION (EU)

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

- Gas-chromatographic 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.
- Monitoring of at least 2 specific precursor ions, each with one specific corresponding transition product ion for all labelled and unlabelled analytes in the scope of analysis.
- Maximum permitted tolerance of relative ion intensities of $\pm$ 15 % for selected transition product ions in comparison to calculated or measured values (average from calibration standards), applying identical MS/MS conditions, in particular collision energy and collision gas pressure, for each transition of an analyte.
- 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) in order to minimise possible interferences on the analytes of interest.

Chromatographic separation of Heptafurans better than 25% peak to peak.

2 specific SRM transitions for all labelled and native congeners.

Ion ratio ± max deviation from theoretical value for product ions of the two transitions

Resolution (separation of two peaks one mass unit apart) for each quadrupole

Instrument

1

Thermo TSQ9000

2

Agilent 7693GC-7010B

3

APGC-TQS

GC-MS/MS conditions(Dioxins)

GC Parameters

Injection Volume (μL):	2
Inlet (°C):	280
Carrier Gas, (mL/min):	He(>99.999%), 0.8
Inlet Mode:	Splitless
Column	DB-5MS UI(60m x 0.25mm, 0.25μm)

Oven Temperature Program:

Temperature 1 (°C):	120(1 min)
Temperature 2 (°C):	220(Rate: 43 °C/min; Hold: 15 min)
Temperature 3 (°C):	250(Rate: 2.3 °C/min; Hold: 0 min)
Temperature 4 (°C):	260(Rate: 0.9 °C/min; Hold: min)
Temperature 4 (°C):	310(Rate: 20 °C/min; Hold: 9 min)

Mass Spectrometer Parameters

Transfer Line (°C):	300
Ionization Type:	EI(APGC+)
Ion Source(°C):	280
Electron Energy (eV):	70
Acquisition Mode:	MRM
Collision gas and pressure (psi)	Argon, 70
Resolution	0.7 (both Q1 and Q3)

Resolution ≤1 ✓

GC-MS/MS conditions(DL-PCBs)

CFSA 国家食品安全风险评估中心
China National Center for Food Safety Risk Assessment

GC Parameters

Injection Volume (μL):	2
Inlet (°C):	290
Carrier Gas, (mL/min):	He(>99.999%), 0.8
Inlet Mode:	Splitless
Column	DB-5MS UI(60m x 0.25mm, 0.25μm)

Oven Temperature Program:

Temperature 1 (°C):	80(2 min)
Temperature 2 (°C):	220(Rate: 70 °C/min; Hold: 15 min)
Temperature 3 (°C):	250(Rate: 2 °C/min; Hold: 0 min)
Temperature 4 (°C):	260(Rate: 1 °C/min; Hold: min)
Temperature 4 (°C):	310(Rate: 20 °C/min; Hold: 11 min)
Total Run Time (min):	56 min

Mass Spectrometer Parameters

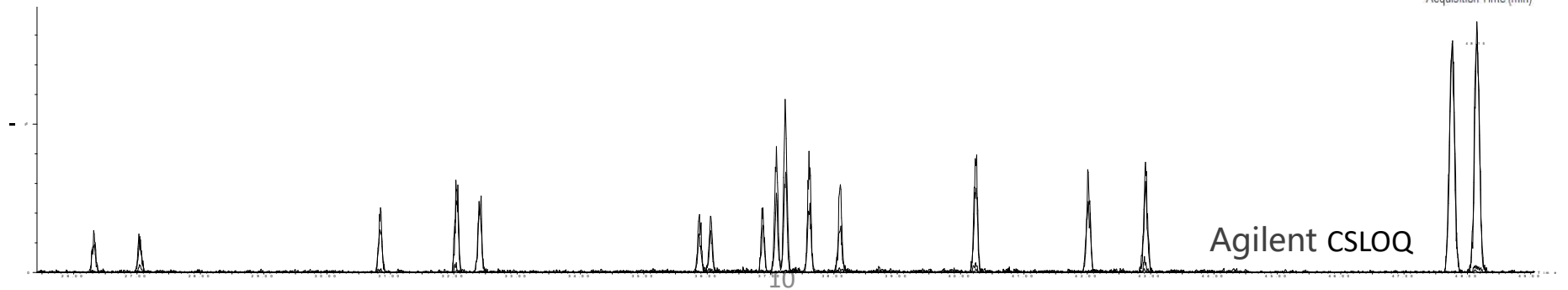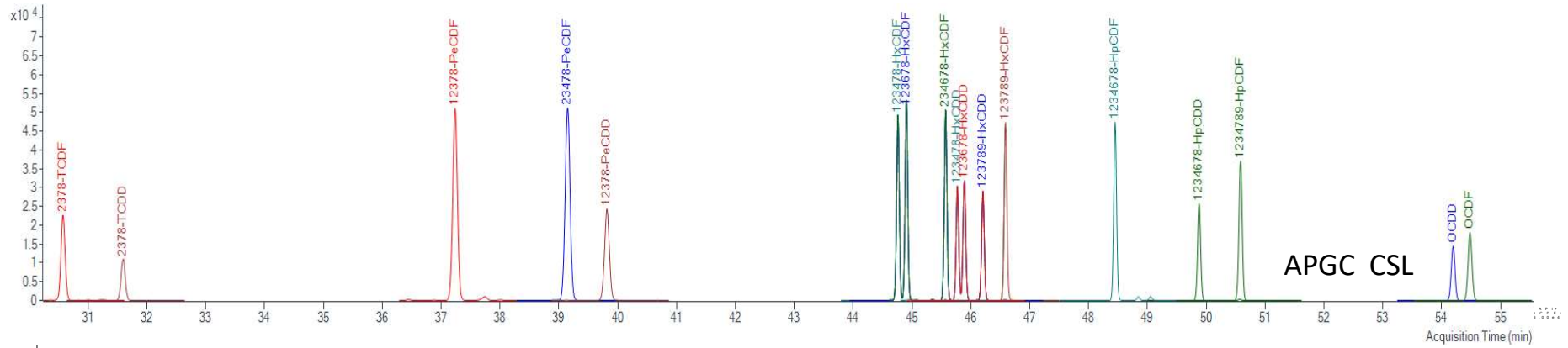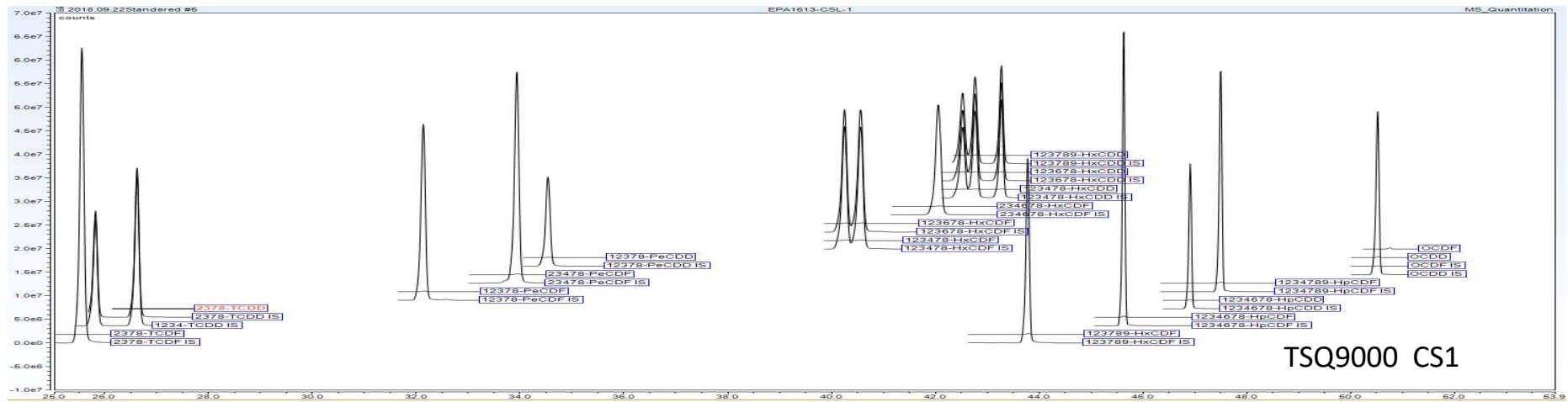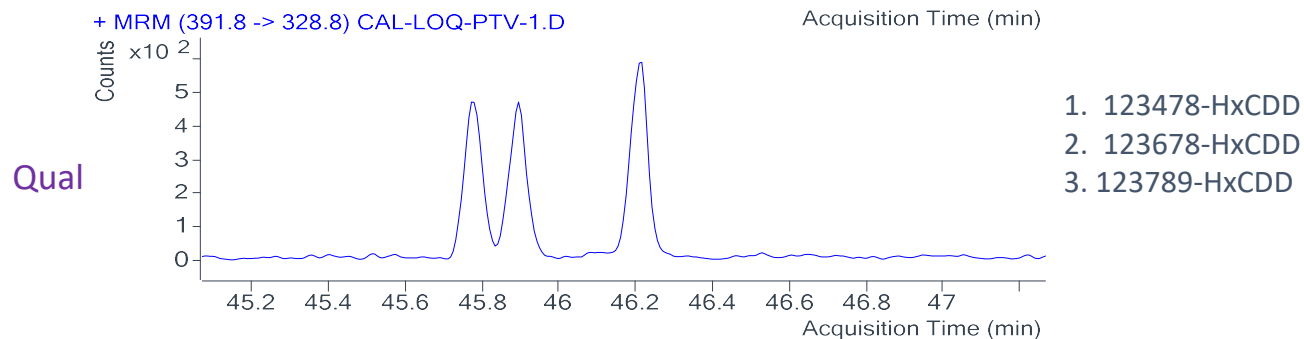|	
Transfer Line (°C):	300
Ionization Type:	EI(APGC+)
Ion Source(°C):	280
Electron Energy (eV):	70
Acquisition Mode:	MRM
Collision gas and pressure (psi)	Argon, 70
Resolution	0.7 (both Q1 and Q3)

Resolution ≤1 ✓

MS Parameters

Compound	MS-Quantitation Peak	MA-Confirming Peak	Compound	MS-Quantitation Peak	MA-Confirming Peak
2378-TCDF	303.9 / 240.9	305.9 / 242.9	PCB 77	289.9/219.9	291.9/221.9
2378-TCDD	319.9 / 256.9	321.9 / 258.9	PCB 81	289.9/219.9	291.9/221.9
12378-PeCDF	339.9 / 276.9	337.9 / 274.9			
23478-PeCDF	339.9 / 276.9	337.9 / 274.9	PCB 105	323.9/253.9	325.9/255.9
12378-PeCDD	355.9 / 292.9	353.9 / 290.9	PCB 114	323.9/253.9	325.9/255.9
123478-HxCDF	373.8 / 310.9	371.8 / 308.9	PCB 118	323.9/253.9	325.9/255.9
123678-HxCDF	373.8 / 310.9	371.8 / 308.9			
234678-HxCDF	373.8 / 310.9	371.8 / 308.9	PCB 123	323.9/253.9	325.9/255.9
123478-HxCDD	389.8 / 326.9	391.8 / 328.9	PCB 126	323.9/253.9	325.9/255.9
123678-HxCDD	389.8 / 326.9	391.8 / 328.9			
123789-HxCDD	389.8 / 326.9	391.8 / 328.9	PCB 156	359.9/289.9	357.8/287.9
123789-HxCDF	373.8 / 310.9	371.8 / 308.9	PCB 157	359.9/289.9	357.8/287.9
1234678-HpCDF	407.8 / 344.8	409.8 / 346.8	PCB 167	359.9/289.9	357.8/287.9
1234678-HpCDD	423.8 / 360.8	425.8 / 362.8			
1234789-HpCDF	407.8 / 344.8	409.8 / 346.8	PCB 169	359.9/289.9	357.8/287.9
OCDD	457.7 / 394.8	459.7 / 396.8			
OCDF	441.8 / 378.8	443.8 / 380.8	PCB 189	393.8/323.8	395.8/325.8

2 specific SRM transtions ✓

Chromatography

Separation

+ MRM (373.8 -> 310.9)

Quant — HxCDF_0.02 pg/uL@5uL

Peaks: 1, 2, 3, 4

+ MRM (375.8 -> 312.9) CAL-LOQ-PTV-1.D

Qual

1. 123478-HxCDF
2. 123678-HxCDF
3. 234678-HxCDF
4. 123789-HxCDF

+ MRM (389.8 -> 326.9)

Quant — HxCDD_0.04 pg/uL@5uL

Peaks: 1, 2, 3

+ MRM (391.8 -> 328.8) CAL-LOQ-PTV-1.D

Qual

1. 123478-HxCDD
2. 123678-HxCDD
3. 123789-HxCDD
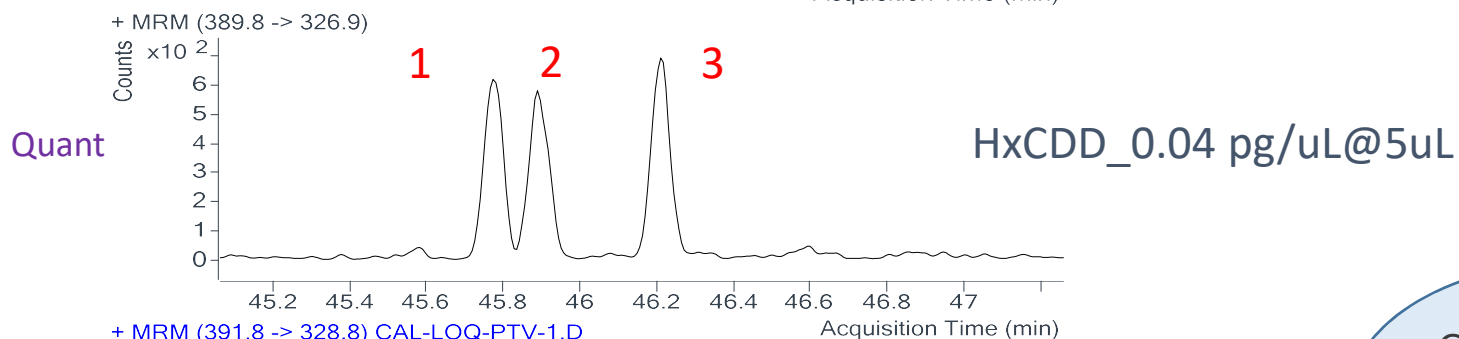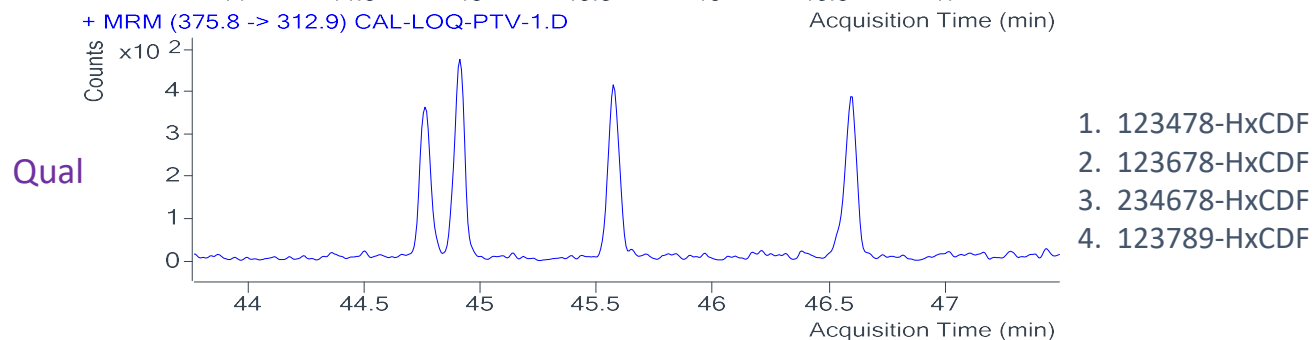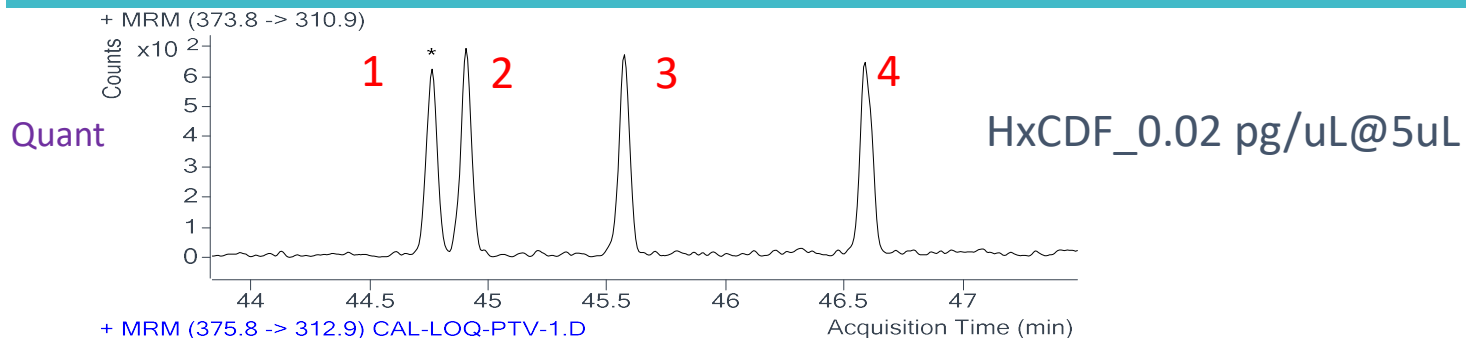
GC separation of isomers < 25 % peak to peak
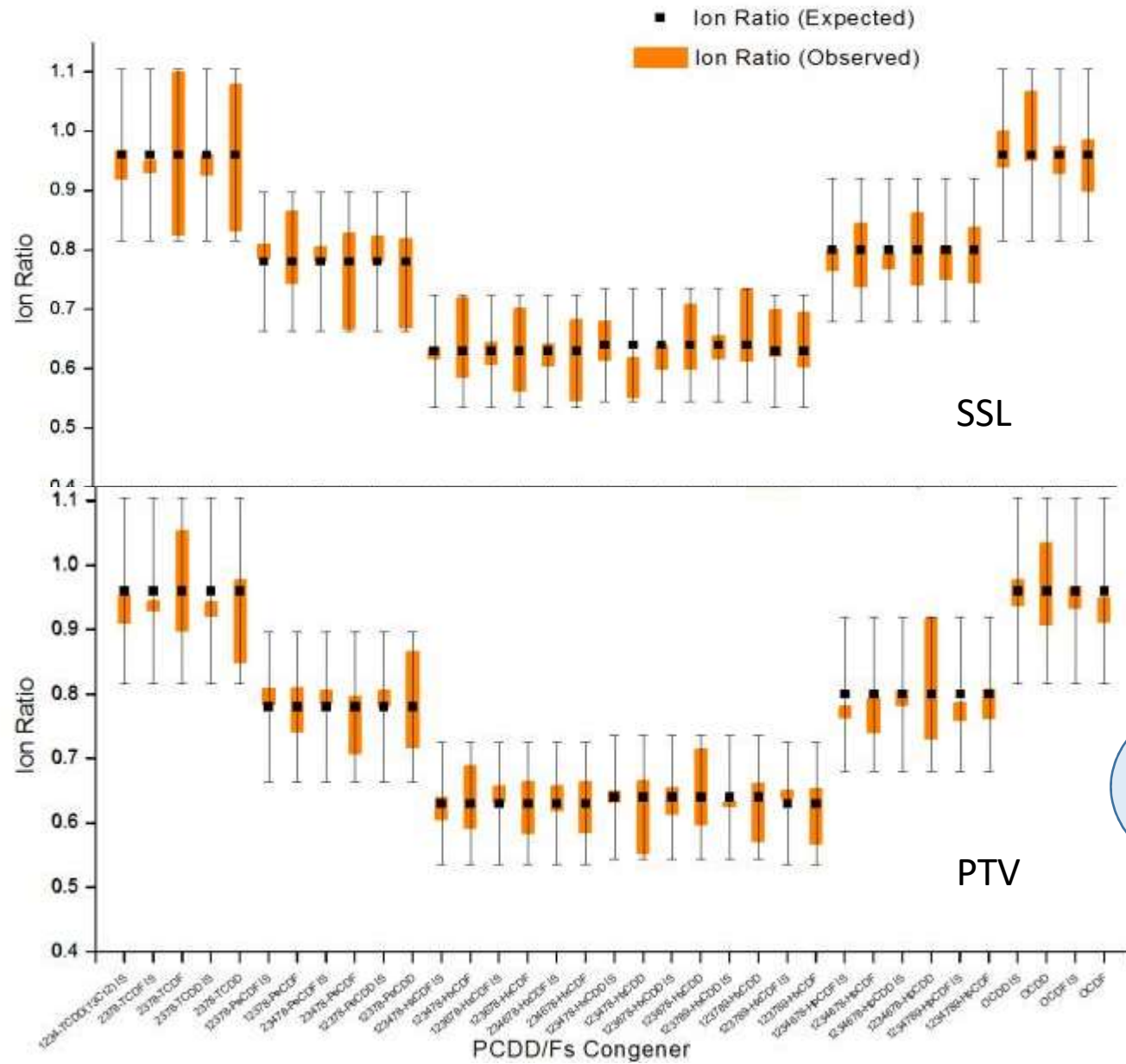
Instrument sensitivity

Congener	LOQ(ng/ml)
2,3,7,8 TCDD	0.01
1,2,3,7,8 PeCDD	0.02
1,2,3,4,7,8 HxCDD	0.04
1,2,3,6,7,8 HxCDD	0.04
1,2,3,7,8,9 HxCDD	0.04
1,2,3,4,6,7,8 HpCDD	0.04
OCDD	0.16
2,3,7,8 TCDF	0.01
1,2,3,7,8 PeCDF	0.02
2,3,4,7,8 PeCDF	0.02
1,2,3,6,7,8 HxCDF	0.02
2,3,4,6,7,8 HxCDF	0.02
1,2,3,4,7,8 HxCDF	0.02
1,2,3,7,8,9 HxCDF	0.02
1,2,3,4,6,7,8 HpCDF	0.04
1,2,3,4,7,8,9 HpCDF	0.04
OCDF	0.16
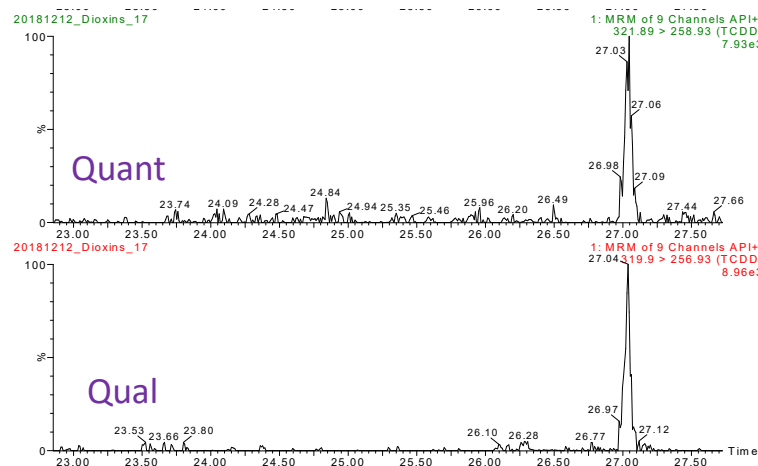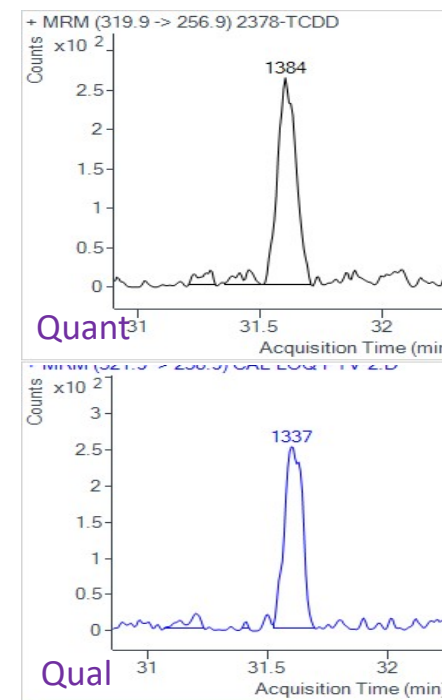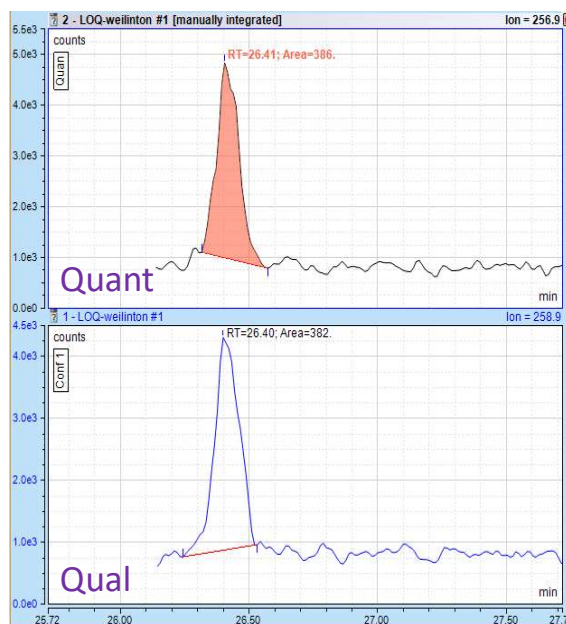
Instrument sensitivity

Congener	Con.（ng/mL）	Average (Intraday)（ng/mL）	RSD (Intraday)	Average (Interday)（ng/mL）	RSD (Interday)
2378-TCDD	0.01	0.0102	6.2%	0.0107	5.5%
2378-TCDF	0.01	0.0101	5.2%	0.0100	4.0%
12378-PeCDD	0.02	0.0200	5.1%	0.0184	10.9%
123478-HxCDD	0.04	0.0387	3.9%	0.0368	3.8%
123678-HxCDD	0.04	0.0392	4.9%	0.0385	6.6%
123789-HxCDD	0.04	0.0408	6.3%	0.0402	7.4%
123478-HxCDF	0.02	0.0211	9.3%	0.0203	15.0%
123678-HxCDF	0.02	0.0206	7.6%	0.0208	4.1%
234678-HxCDF	0.02	0.0198	5.6%	0.0199	8.5%
123789-HxCDF	0.02	0.0197	4.7%	0.0184	4.8%
1234678-HpCDD	0.04	0.0434	5.1%	0.0433	4.7%
1234678-HpCDF	0.04	0.0406	5.3%	0.0388	4.5%
1234789-HpCDF	0.04	0.0401	2.9%	0.0404	6.3%
OCDD	0.16	0.1598	4.6%	0.1580	2.2%
OCDF	0.16	0.1603	4.5%	0.1687	1.7%
PCB-77	0.1	0.0987	8.5%	0.1010	2.9%
PCB-126	0.1	0.1005	7.3%	0.1003	1.3%
PCB-169	0.1	0.1022	7.9%	0.1026	3.4%
PCB-81	0.1	0.0978	9.4%	0.0979	3.0%
PCB-105	0.5	0.4725	6.8%	0.4864	0.7%
PCB-114	0.1	0.0976	7.9%	0.1015	7.1%
PCB-118	0.1	0.0981	6.0%	0.1021	3.3%
PCB-123	0.1	0.0993	5.7%	0.1032	4.3%
PCB-156	0.1	0.1025	4.4%	0.1011	3.7%
PCB-157	0.1	0.1011	4.3%	0.1014	1.5%
PCB-167	0.1	0.1002	6.3%	0.1014	2.9%
PCB-189	0.1	0.0984	5.9%	0.1056	9.4%

"The limit of quantification of an individual congener may be defined as…

the lowest concentration point on a calibration curve that gives an acceptable(≤ 30 %) and consistent (measured at least at the start and at the end of an analytical series of samples) deviation to the average relative response factor calculated for all points on the calibration curve in each series of samples (The LOQ is calculated from the lowest concentration point taking into account the recovery of internal standards and sample intake.)."

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

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本方法选择0.01 ng/ml TCDD作为最低浓度点并代入标准曲线各浓度点，计算的相对响应因子（RRF）的相对标准偏差不高于30%。将此最低浓度点折算样品最低回收率（50%），样品平均取样量（50g）及定容体积（20μL），计算方法定量限

LOQ(relative response factor)
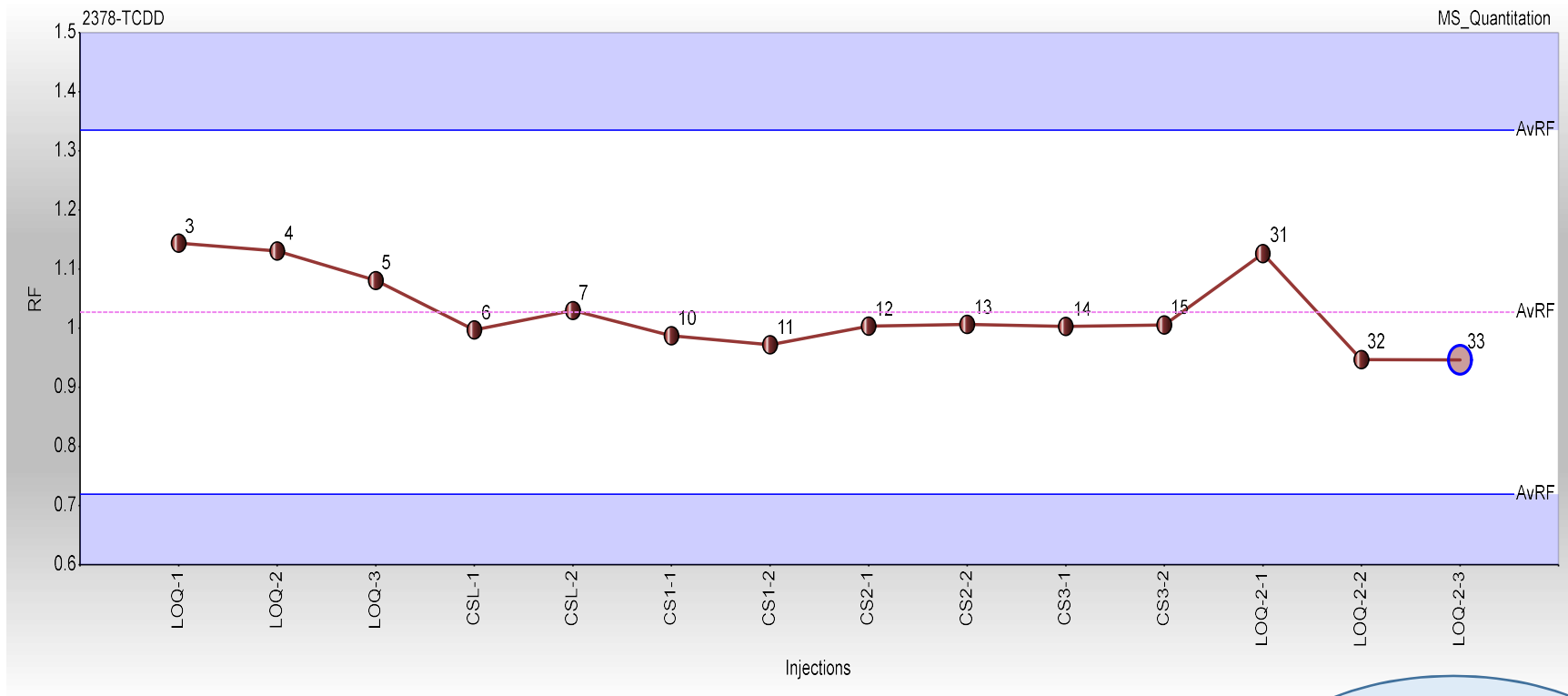
RRF ≤ *30 %* deviation

LOQ

Congener	LOQ（pg/g）
2378-TCDD	0.008
12378-PeCDD	0.02
123478-HxCDD	0.03
123678-HxCDD	0.03
123789-HxCDD	0.03
1234678-HpCDD	0.03
OCDD	0.10
2378-TCDF	0.008
12378-PeCDF	0.02
23478-PeCDF	0.02
123478-HxCDF	0.02
123678-HxCDF	0.02
234678-HxCDF	0.02
123789-HxCDF	0.02
1234678-HpCDF	0.03
1234789-HpCDF	0.03
OCDF	0.10
PCB-77	0.08
PCB-126	0.08
PCB-169	0.08
PCB-81	0.08
PCB-105	0.08
PCB-114	0.08
PCB-118	0.08
PCB-123	0.08
PCB-156	0.08
PCB-157	0.08
PCB-167	0.08
PCB-189	0.08

Linearity

Congener	浓度范围（μg/L）	线性方程	R²	RRF	RSD%
2378-TCDD	0.1-200	y =1.3037x -0.0039	0.9999	1.19	4.96
2378-TCDF	0.1-200	y =1.6485x -0.0032	0.9999	1.07	6.03
12378-PeCDD	0.5-1000	y =1.1347x -0.0161	0.9999	1.06	4.65
12378-PeCDF	0.5-1000	y =1.1491x -0.0147	0.9999	1.07	4.70
23478-PeCDF	0.5-1000	y =1.2664x -0.0189	0.9999	1.17	5.70
123478-HxCDD	0.5-1000	y =1.1762x -0.0136	0.9999	1.10	4.42
123678-HxCDD	0.5-1000	y =1.1691x -0.0199	0.9999	1.07	7.37
123789-HxCDD	0.5-1000	y =0.9910x -0.0103	0.9999	0.94	4.22
123478-HxCDF	0.5-1000	y =1.1842x -0.0192	0.9999	1.08	6.14
123678-HxCDF	0.5-1000	y =1.1418x -0.0138	0.9999	1.08	3.60
234678-HxCDF	0.5-1000	y =1.1808x -0.0132	0.9999	1.11	4.55
123789-HxCDF	0.5-1000	y =1.0569x -0.0003	0.9999	1.02	3.65
1234678-HpCDD	0.5-1000	y =1.1292x -0.0180	0.9999	1.07	3.22
1234678-HpCDF	0.5-1000	y =1.0703x -0.0115	0.9999	1.01	4.22
1234789-HpCDF	0.5-1000	y =1.0579x -0.0143	0.9999	0.99	4.27
OCDD	1.0-2000	y =1.1135x -0.0131	0.9999	1.07	4.36
OCDF	1.0-2000	y =1.6907x -0.0228	0.9999	1.59	3.65
PCB-77	0.1-200	y =1.2332x -0.06515	0.9999	1.15	3.39
PCB-81	0.1-200	y =1.3090x -0.0739	0.9998	1.23	3.09
PCB-105	0.1-200	y =1.2259x -0.0499	0.9999	1.17	3.02
PCB-114	0.1-200	y =1.3261x -0.0797	0.9998	1.23	4.16
PCB-118	0.5-1000	y =1.2699x -0.3013	0.9999	1.18	4.36
PCB-123	0.1-200	y =1.1899x -0.0730	0.9998	1.10	4.15
PCB-126	0.1-200	y =1.2479x -0.0565	0.9999	1.19	2.52
PCB-156	0.1-200	y =1.2599x -0.0952	0.9998	1.17	5.16
PCB-157	0.1-200	y =1.2190x -0.0639	0.9999	1.15	3.75
PCB-167	0.1-200	y =1.2676x -0.0697	0.9999	1.18	3.86
PCB-169	0.1-200	y =1.1843x -0.0817	0.9997	1.12	3.22
PCB-189	0.1-200	y =1.2889x -0.1229	0.9995	1.23	9.10

Intraday Precision

Congener	Pork（No.09026143）		Fish（No.13059483）		Dark Egg（No.15092370）	
	Average	RSD(%)	Average	RSD(%)	Average	RSD(%)
2378-TCDD	0.008	-	0.078	7.5%	0.037	6.8%
12378-PeCDD	0.016	-	0.376	8.3%	0.147	10.4%
123478-HxCDD	0.032	-	0.096	14.0%	0.140	8.0%
123678-HxCDD	0.032	-	0.162	13.4%	0.238	12.0%
123789-HxCDD	0.041	7.4%	0.111	8.2%	0.168	7.8%
1234678-HpCDD	0.204	12.0%	0.209	6.8%	0.670	6.9%
OCDD	1.623	6.4%	0.427	13.3%	4.062	5.3%
2378-TCDF	0.013	10.0%	3.007	1.0%	0.240	5.1%
12378-PeCDF	0.040	10.4%	0.456	2.9%	0.249	4.4%
23478-PeCDF	0.590	3.3%	1.248	1.8%	0.328	10.0%
123478-HxCDF	0.283	4.4%	0.133	7.4%	0.246	5.9%
123678-HxCDF	0.104	5.8%	0.105	7.1%	0.168	5.8%
234678-HxCDF	0.083	3.6%	0.153	7.1%	0.189	7.6%
123789-HxCDF	0.079	6.7%	0.108	8.9%	0.135	10.7%
1234678-HpCDF	0.326	8.3%	0.127	10.9%	0.330	12.4%
1234789-HpCDF	0.055	13.2%	0.095	15.4%	0.114	5.7%
OCDF	0.273	13.6%	0.216	9.0%	0.337	18.2%
TEQ-PCDD/Fs	**0.245**	**2.4%**	**1.234**	**3.5%**	**0.455**	**5.0%**
TEQ-PCBs	**0.006**	**20.2%**	**3.157**	**3.3%**	**0.146**	**3.7%**
总TEQs	**0.251**	**2.4%**	**4.392**	**2.3%**	**0.601**	**3.9%**

Interday Precision

Congener	Pork (No.09026143)		Fish (No.13059483)		Duck Egg (No.15092370)	
	Average	RSD(%)	Average	RSD(%)	Average	RSD(%)
2378-TCDD	0.008	-	0.068	17.2%	0.028	21.7%
12378-PeCDD	0.016	-	0.361	8.4%	0.151	18.9%
123478-HxCDD	0.032	-	0.082	17.0%	0.137	16.1%
123678-HxCDD	0.032	-	0.155	17.2%	0.217	14.2%
123789-HxCDD	0.029	23.5%	0.096	23.4%	0.120	19.9%
1234678-HpCDD	0.200	13.5%	0.190	18.8%	0.627	3.9%
OCDD	1.571	3.1%	0.408	10.7%	3.950	6.6%
2378-TCDF	0.013	23.1%	3.028	1.2%	0.228	5.6%
12378-PeCDF	0.035	20.8%	0.449	5.3%	0.252	6.3%
23478-PeCDF	0.590	3.5%	1.243	1.5%	0.306	9.0%
123478-HxCDF	0.261	6.4%	0.128	12.5%	0.235	4.5%
123678-HxCDF	0.098	16.1%	0.104	19.8%	0.177	17.4%
234678-HxCDF	0.089	4.9%	0.141	22.8%	0.188	16.9%
123789-HxCDF	0.063	13.7%	0.091	16.3%	0.104	5.1%
1234678-HpCDF	0.266	10.3%	0.136	23.1%	0.278	10.5%
1234789-HpCDF	0.047	15.1%	0.082	18.4%	0.096	16.1%
OCDF	0.220	17.9%	0.188	18.5%	0.220	23.9%
TEQ-PCDD/Fs	**0.239**	**3.3%**	**1.203**	**4.0%**	**0.430**	**6.0%**
TEQ-PCBs	**0.005**	**14.2%**	**3.074**	**5.6%**	**0.152**	**5.43%**
总TEQs	**0.244**	**3.3%**	**4.276**	**5.1%**	**0.582**	**5.22%**

Accuracy

According to the EU's limit requirements, 6 different substrates of interlabrotary comparison study samples were selected, and 4 categories of samples were tested, including beef, fish ,Salmon, herring, cheese, and eggs, analysis and testing by this method , use the Z-score method to evaluate the difference between the measured value and the reference value.

	Egg			Beef		
	Reference value (pg/g)	Measured value (pg/g)	Z-score	Reference value (pg/g)	Measured value (pg/g)	Z-score
TEQ-PCDD/Fs	0.290	0.281	-0.2	0.074	0.074	0.0
TEQ-PCBs	0.219	0.297	1.8	0.340	0.355	0.2
总TEQs	0.510	0.578	0.7	0.420	0.429	0.1
	Salmon			Herring1		
	Reference value (pg/g)	Measured value (pg/g)	Z-score	Reference value (pg/g)	Measured value (pg/g)	Z-score
TEQ-PCDD/Fs	0.380	0.377	0.0	0.940	0.973	0.2
TEQ-PCBs	0.638	0.747	0.9	1.140	1.054	-0.4
总TEQs	1.000	1.124	0.6	2.100	2.027	-0.2
	Cheese			Herring2		
	Reference value (pg/g)	Measured value (pg/g)	Z-score	Reference value (pg/g)	Measured value (pg/g)	Z-score
TEQ-PCDD/Fs	0.030	0.047	2.9	1.300	1.328	0.1
TEQ-PCBs	0.026	0.036	1.8	0.974	1.292	1.6
总TEQs	0.054	0.083	2.7	2.300	2.620	0.7

Method comparison(GC-MS/MS&GC-HRMS)

Congener	value(pg/g)				ANOVA（P Value）			
	Egg	Beef	Cheese	Fish	Egg	Beef	Cheese	Fish
2378-TCDD	0.005	0.009	0.006	0.089	/	0.797	/	0.131
12378-PeCDD	0.029	0.021	0.009	0.190	0.418	0.781	0.283	0.069
123478-HxCDD	0.021	0.013	0.013	0.035	0.817	0.517	0.233	0.756
123678-HxCDD	1.600	0.039	0.014	0.120	0.555	0.081	0.865	0.858
123789-HxCDD	0.440	0.011	0.014	0.032	0.429	0.361	0.259	0.411
1234678-HpCDD	2.000	0.075	0.030	0.066	0.652	0.402	0.352	0.411
OCDD	1.100	0.100	0.094	0.059	0.995	0.307	0.735	0.431
2378-TCDF	0.058	0.008	0.010	1.800	0.052	0.840	0.484	0.146
12378-PeCDF	0.027	0.005	0.008	0.250	0.412	0.299	0.557	0.541
23478-PeCDF	0.049	0.086	0.018	0.870	0.007	0.886	0.940	0.855
123478-HxCDF	0.033	0.037	0.009	0.077	0.919	0.717	0.795	0.152
123678-HxCDF	0.020	0.028	0.009	0.077	0.250	0.680	0.514	0.782
234678-HxCDF	0.019	0.028	0.008	0.092	0.250	0.975	0.183	0.401
123789-HxCDF	0.016	0.005	0.007	0.007	0.136	0.501	0.923	0.239
1234678-HpCDF	0.053	0.020	0.012	0.055	0.520	0.725	0.386	0.392
1234789-HpCDF	0.014	0.005	0.014	0.014	/	0.369	0.804	0.369
OCDF	0.032	0.094	0.094	0.094	/	0.369	0.401	/
TEQ-PCDD/Fs	0.290	0.074	0.030	0.770	0.781	0.605	0.453	0.854

Method comparison(GC-MS/MS&GC-HRMS)

Congener	value(pg/g)				ANOVA（P Value）			
	Egg	Beef	Cheese	Fish	Egg	Beef	Cheese	Fish
PCB-77	2.600	1.800	0.820	32.000	0.608	0.266	0.403	0.431
PCB-126	2.000	3.000	0.220	7.600	0.114	0.428	0.389	0.748
PCB-169	0.250	0.440	0.080	1.900	0.215	0.316	0.160	0.877
PCB-81	0.130	0.130	0.080	0.880	0.468	0.311	0.179	0.380
PCB-105	54.000	87.000	8.600	335.000	0.601	0.193	0.841	0.602
PCB-114	1.700	12.000	1.000	14.000	0.297	0.176	0.877	0.061
PCB-118	189.000	630.000	36.000	1119.000	0.832	0.974	0.619	0.350
PCB-123	2.400	6.700	0.550	12.000	0.112	0.775	0.991	0.418
PCB-156	75.000	85.000	3.100	115.000	0.979	0.841	0.867	0.678
PCB-157	10.000	17.000	0.620	31.000	0.784	0.909	0.608	0.388
PCB-167	39.000	40.000	1.500	77.000	0.824	0.678	0.838	0.659
PCB-189	12.000	8.100	0.240	11.000	0.459	0.784	0.079	0.516
总TEQs	0.219	0.340	0.026	0.872	0.194	0.371	0.265	0.875

Interlaboratory Validation(China)

化合物	鸡蛋 参考值	RSD(%)	牛肉 参考值	RSD(%)	奶酪 参考值	RSD(%)	鲱鱼 参考值	RSD(%)
2378-TCDD	0.005	15.1%	0.011	55.7%	0.008	0.0%	0.094	28.8%
12378-PeCDD	0.029	31.2%	0.024	60.6%	0.018	23.9%	0.232	15.2%
123478-HxCDD	0.021	14.4%	0.032	10.9%	0.031	9.4%	0.039	34.8%
123678-HxCDD	1.600	12.2%	0.056	22.3%	0.033	9.1%	0.154	24.0%
123789-HxCDD	0.440	36.9%	0.034	19.4%	0.033	8.1%	0.033	5.4%
1234678-HpCDD	2.000	9.3%	0.094	33.6%	0.050	68.8%	0.060	53.2%
OCDD	1.100	22.5%	0.114	35.3%	0.169	49.7%	0.128	0.0%
2378-TCDF	0.058	17.8%	0.012	65.8%	0.015	29.0%	1.458	5.5%
12378-PeCDF	0.027	48.6%	0.021	44.8%	0.026	65.0%	0.356	29.2%
23478-PeCDF	0.049	28.4%	0.090	18.3%	0.031	58.1%	1.462	16.4%
123478-HxCDF	0.033	51.8%	0.041	29.7%	0.026	49.1%	0.110	23.3%
123678-HxCDF	0.020	60.6%	0.035	40.7%	0.026	40.8%	0.123	25.0%
234678-HxCDF	0.019	27.0%	0.035	63.8%	0.033	0.0%	0.139	24.3%
123789-HxCDF	0.016	54.8%	0.022	48.8%	0.028	71.9%	0.022	59.1%
1234678-HpCDF	0.053	52.8%	0.048	63.1%	0.050	29.7%	0.039	35.4%
1234789-HpCDF	0.014	0.0%	0.035	21.1%	0.034	15.2%	0.032	2.8%
OCDF	0.032	0.0%	0.137	18.5%	0.136	11.0%	0.128	0.0%
TEQ-PCDD/Fs	0.290	11.3%	0.093	34.8%	0.060	38.1%	0.987	10.3%
PCB-77	2.600	21.5%	2.007	18.2%	0.941	60.5%	21.862	15.9%
PCB-126	2.000	24.5%	3.226	11.4%	0.231	55.1%	11.871	28.0%
PCB-169	0.250	47.6%	0.433	13.8%	0.083	14.1%	3.581	17.4%
PCB-81	0.130	49.3%	0.104	19.2%	0.074	24.0%	0.343	54.9%
PCB-105	54.000	19.4%	94.120	15.1%	8.134	18.1%	449.555	16.4%
PCB-114	1.700	13.1%	11.322	11.6%	0.897	21.1%	22.904	16.6%
PCB-118	189.000	10.4%	629.779	10.2%	35.588	23.6%	1,365.341	16.8%
PCB-123	2.400	20.0%	7.133	31.8%	0.403	37.1%	16.397	50.4%
PCB-156	75.000	11.9%	85.456	11.7%	2.965	23.0%	214.132	15.9%
PCB-157	10.000	16.9%	17.099	9.8%	0.557	27.7%	54.044	16.5%
PCB-167	39.000	9.9%	39.986	9.6%	1.471	22.6%	125.026	11.3%
PCB-189	12.000	9.7%	8.320	10.8%	0.228	30.7%	24.772	13.3%
总TEQs	0.510	12.5%	0.429	11.8%	0.087	27.2%	2.328	15.5%

Interlaboratory Validation （EU-China）

	QE-14064614		OE-15053475		MR-13024686	
	RAFA	CFSA	**RAFA**	CFSA	**RAFA**	CFSA
PCDD/F	**0.240**	**0.166**	**1.724**	**1.660**	**0.509**	**0.351**
Sum WHO-TEQ(PCDD/Fs + PCBs)	**0.250**	**0.178**	**2.214**	**2.119**	**1.888**	**1.789**
2,3,7,8-TCDD	0.162	0.117	0.171	0.210	0.050	0.037
1,2,3,7,8-PeCDD	0.053	0.016	0.706	0.676	0.069	0.016
1,2,3,4,7,8-HxCDD	0.013	0.032	0.330	0.339	0.015	0.016
1,2,3,6,7,8-HxCDD	0.031	0.032	0.920	0.772	0.032	0.032
1,2,3,7,8,9-HxCDD	0.018	0.032	0.257	0.233	0.018	0.032
1,2,3,4,6,7,8-HpCDD	0.044	0.032	1.173	1.375	0.052	0.035
OCDD	0.123	0.367	1.498	3.707	0.113	0.044
2,3,7,8-TCDF	0.026	0.008	0.929	0.907	2.456	1.957
1,2,3,7,8-PeCDF	0.022	0.088	0.860	0.765	0.128	0.093
2,3,4,7,8-PeCDF	0.031	0.044	1.357	1.224	0.405	0.272
1,2,3,4,7,8-HxCDF	0.013	0.016	0.569	0.518	0.039	0.040
1,2,3,6,7,8-HxCDF	0.013	0.016	0.496	0.476	0.024	0.021
1,2,3,7,8,9-HxCDF	0.013	0.016	0.056	0.034	0.007	0.017
2,3,4,6,7,8-HxCDF	0.013	0.011	0.428	0.379	0.047	0.013
1,2,3,4,6,7,8-HpCDF	0.022	0.020	0.317	0.285	0.034	0.072
1,2,3,4,7,8,9-HpCDF	0.009	0.032	0.026	0.013	0.007	0.032
OCDF	0.018	0.019	0.021	0.128	0.025	0.128

Interlaboratory Validation （EU-China）

	PM-09026143		DE-15092370		SD-13059483	
	RAFA	CFSA	RAFA	CFSA	RAFA	CFSA
PCDD/F	**0.408**	**0.245**	**0.402**	**0.455**	**1.469**	**1.234**
Sum WHO-TEQ(PCDD/Fs + PCBs)	**0.431**	**0.255**	**0.524**	**0.601**	**5.906**	**4.392**
2,3,7,8-TCDD	0.028	0.008	0.042	0.037	0.109	0.078
1,2,3,7,8-PeCDD	0.008	0.016	0.131	0.147	0.436	0.376
1,2,3,4,7,8-HxCDD	0.008	0.032	0.084	0.140	0.071	0.096
1,2,3,6,7,8-HxCDD	0.008	0.032	0.206	0.238	0.204	0.162
1,2,3,7,8,9-HxCDD	0.024	0.041	0.094	0.168	0.081	0.111
1,2,3,4,6,7,8-HpCDD	0.061	0.204	0.515	0.670	0.119	0.209
OCDD	1.621	1.623	1.554	4.062	0.133	0.427
2,3,7,8-TCDF	0.040	0.013	0.267	0.240	3.749	3.007
1,2,3,7,8-PeCDF	0.033	0.040	0.229	0.249	0.545	0.456
2,3,4,7,8-PeCDF	0.631	0.590	0.328	0.328	1.559	1.248
1,2,3,4,7,8-HxCDF	0.237	0.283	0.183	0.246	0.066	0.133
1,2,3,6,7,8-HxCDF	0.094	0.104	0.154	0.168	0.100	0.105
1,2,3,7,8,9-HxCDF	0.033	0.083	0.019	0.189	0.009	0.153
2,3,4,6,7,8-HxCDF	0.077	0.079	0.168	0.135	0.123	0.108
1,2,3,4,6,7,8-HpCDF	0.094	0.326	0.248	0.330	0.047	0.127
1,2,3,4,7,8,9-HpCDF	0.016	0.055	0.019	0.114	0.005	0.095
OCDF	0.261	0.273	0.051	0.337	0.024	0.216

Interlaboratory Validation （EU-China）

	ST-14011203		PL-10000528		PL-10000704		PM-09026096	
	RAFA	CFSA	**RAFA**	CFSA	**RAFA**	CFSA	**RAFA**	CFSA
PCDD/F	**1.980**	**1.709**	**31.977**	**29.665**	**5.326**	**5.085**	**1.219**	**1.046**
Sum WHO-TEQ(PCDD/Fs + PCBs)	**3.461**	**3.126**	**32.001**	**29.822**	**5.354**	**5.098**	**1.239**	**1.068**
2,3,7,8-TCDD	0.200	0.163	0.010	0.008	0.014	0.008	0.028	0.008
1,2,3,7,8-PeCDD	0.759	0.712	0.036	0.016	0.027	0.016	0.036	0.017
1,2,3,4,7,8-HxCDD	0.166	0.095	0.301	0.223	0.163	0.116	0.028	0.032
1,2,3,6,7,8-HxCDD	0.521	0.475	0.642	0.568	0.295	0.280	0.028	0.032
1,2,3,7,8,9-HxCDD	0.245	0.099	0.195	0.090	0.060	0.032	0.028	0.032
1,2,3,4,6,7,8-HpCDD	0.573	0.469	28.676	28.637	7.188	7.694	0.077	0.032
OCDD	1.249	1.580	154.922	180.208	75.390	84.211	0.531	0.177
2,3,7,8-TCDF	3.284	2.873	0.104	0.008	0.040	0.008	0.049	0.011
1,2,3,7,8-PeCDF	0.662	0.588	0.053	0.016	0.014	0.016	0.018	0.034
2,3,4,7,8-PeCDF	1.684	1.330	87.322	80.137	13.838	13.089	3.224	2.815
1,2,3,4,7,8-HxCDF	0.238	0.189	34.597	34.288	6.030	6.130	0.937	0.943
1,2,3,6,7,8-HxCDF	0.207	0.193	10.583	9.808	1.840	1.675	0.375	0.355
1,2,3,7,8,9-HxCDF	0.007	0.016	0.028	0.060	0.011	0.016	0.028	0.020
2,3,4,6,7,8-HxCDF	0.217	0.158	4.054	3.989	0.742	0.774	0.352	0.294
1,2,3,4,6,7,8-HpCDF	0.141	0.219	31.681	32.160	11.434	12.134	0.334	0.248
1,2,3,4,7,8,9-HpCDF	0.007	0.021	2.540	2.669	0.542	0.569	0.046	0.026
OCDF	0.076	0.030	21.564	24.515	4.388	5.326	0.142	0.062

Interlaboratory Validation （EU-China）

e

$y = 0.932x - 0.1199$
$R^2 = 0.9984$

EU-China

EU-China Data share