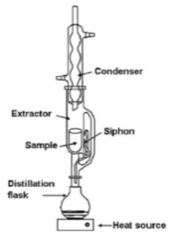
Rapid and reliable determination of PCDD/F and PCB with automatic clean up and GC-MS/MS (7010)

Dr. Thorsten Bernsmann
Chemical and Veterinary Analytical Institute
Münsterland-Emscher-Lippe
Joseph-König-Str. 40, 48147 Münster/Germany
(thorsten.bernsmann@cvua-mel.de)

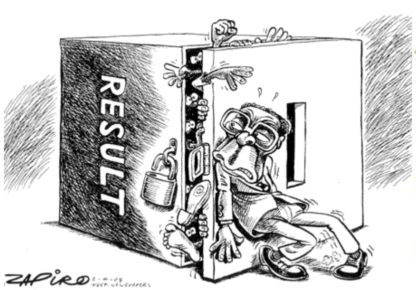
Outline

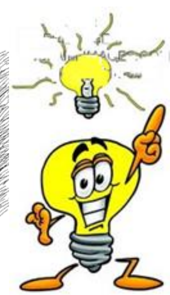
- Extraction

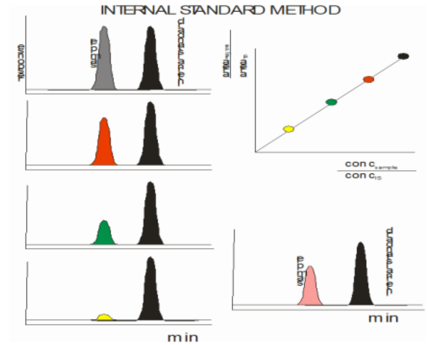


- Sample clean up

- Results







- Internal standard

- GC and MS settings

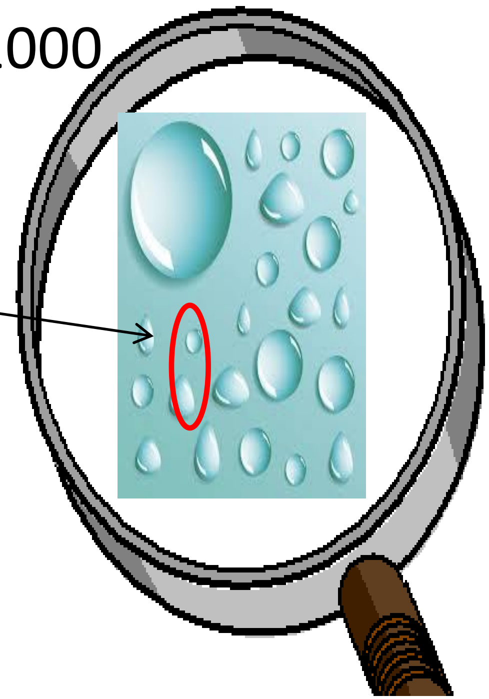
Target

- Concentration during processing

20 g feeding stuff

20 µl equal 0,02 ml

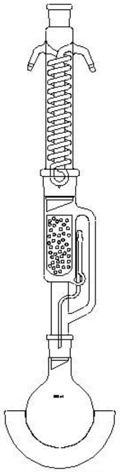
by a factor of 1000



Extraction

- Sample preparation/ homogenization/ particle size
- Solvent choice

- Extraction way
- Extraction with specific instruments:
  - Microwave oven
  - Supercritical fluid extraction
  - Pressurized fluid extraction
  - Automatic Soxhlet-type extraction
  - Ultrasound-assisted extraction
  - Robot automated extraction



Example of sample preparation

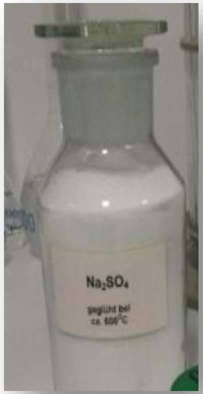
Egg: Homogenization

- Knock opens the eggs.

- Homogenization of the whole egg.

Additional Materials

- Take 70 g of sodium sulphate, baked at 600 °C.



- Take 25 g of glass granulate.

Homogenization

- Mix it and put it into a mortar (cleaned with acetone and dried).

- Make a hole and put up to 25 g egg homogenate into the hole.

- Pestle it until you get a fine powder.

Extraction

- Prepare a glass column.
- Put glass wool and a layer of sodium sulphate in the bottom.

- Put the egg-powder into the glass column.
- Extract the fat with 450 mL Cyclohexane/Dichloromethane 1:1.
- Collecting in round bottom flask.

Extraction of Fat

- Evaporate the solvent with a rotary evaporator .

- Dry in a gentle stream of nitrogen until all solvent is removed.

Determination of Fat

- The result of the fat extraction is approximately 2.5 g egg fat.
- The fat content lays between 9 and 11 %.
- The amount of this fat determination is comparable with the national and international regulations and fully meets the required analytical standards.

Internal Standard

- Add the 13C labeled internal standards.
- Re-dissolve the fat in 2 mL toluene and fill up with hexane to a maximum of 10 mL.
- Inject the whole mixture into the loop of the DEXTech™.
- Regulation (EU) no. 2017/664:
  For foodstuffs of animal origin containing less than 10 % fat, the addition of the internal standards is mandatory prior to extraction. For foodstuffs of animal origin containing more than 10 % fat, the internal standards may be added either before or after fat extraction.

An appropriate validation of the extraction efficiency shall be carried out, depending on the stage at which internal standards are introduced and on whether results are reported on product or fat basis.

Internal Standard: Regulation (EU) no 2017/664

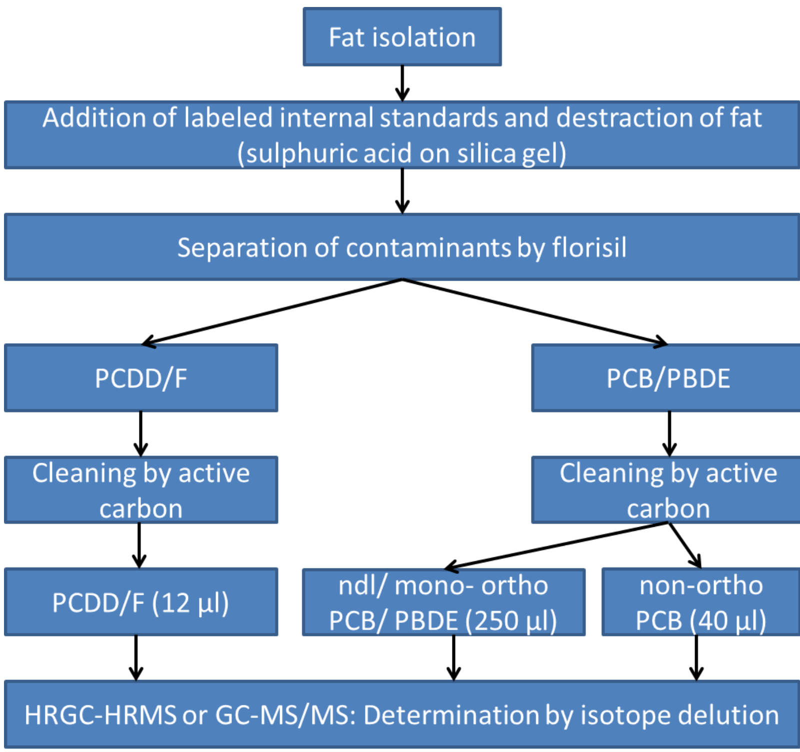
6.2

- For confirmatory methods, all seventeen 13C-labelled 2,3,7,8-substituted internal PCDD/F standards and all twelve 13C-labelled internal dioxin-like PCB standards shall be used.
- Prior to GC-MS analysis, one or two recovery (surrogate) standard(s) must be added.
- For confirmatory methods, the recoveries of the individual internal standards shall be in the range of 60 to 120 %.

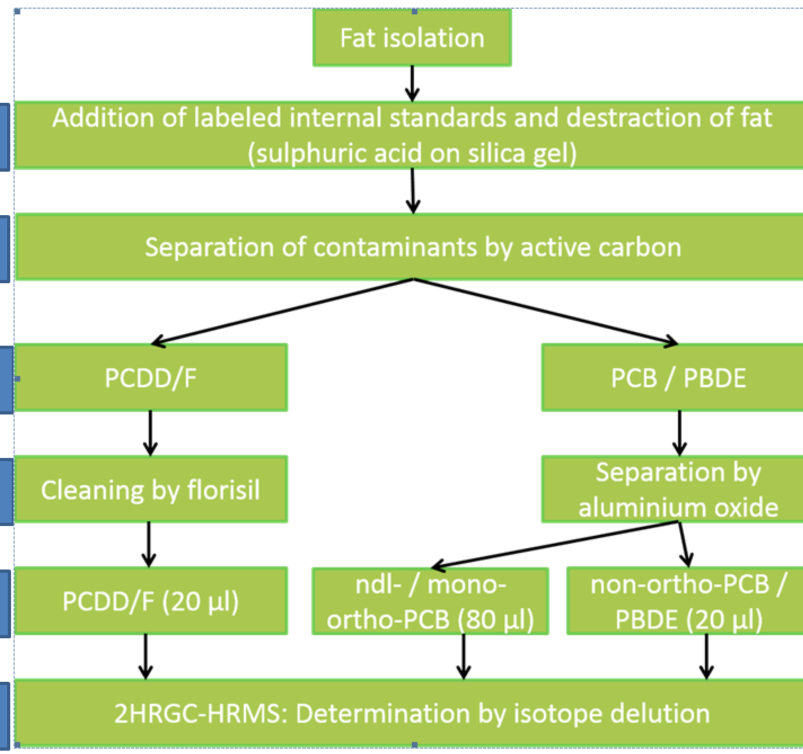
Manual sample preparation

Manual method of two dioxin laboratories

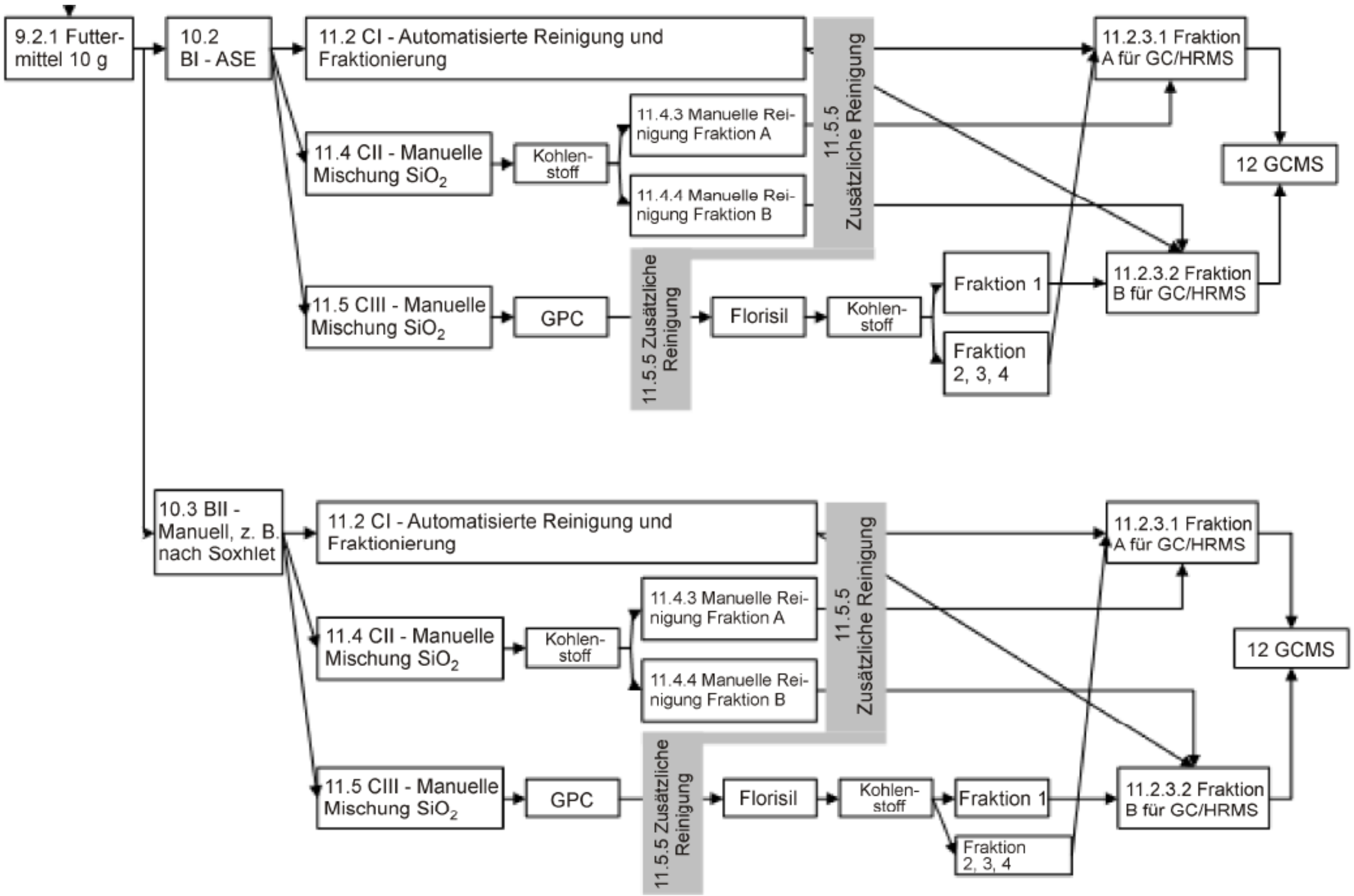
Chemical and Veterinary Analytical Institute Münsterland-Emscher-Lippe



Bavarian Health and Food Safety Authority



Manual sample preparation

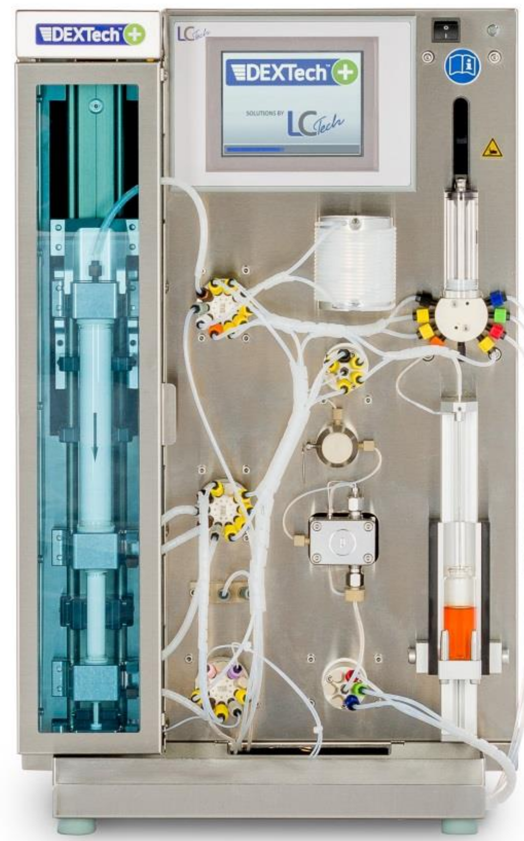


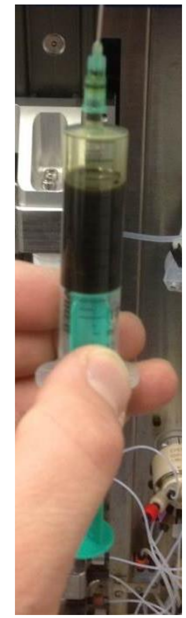
The European standard *EN 16215:2012* for determination of dioxins and dioxin-like PCBs by GC/HRMS and of indicator PCBs by GC/HRMS in animal feeding

Dioxin/PCB sample clean up

Manual clean up

Automatic systems





Injection without pre clean up

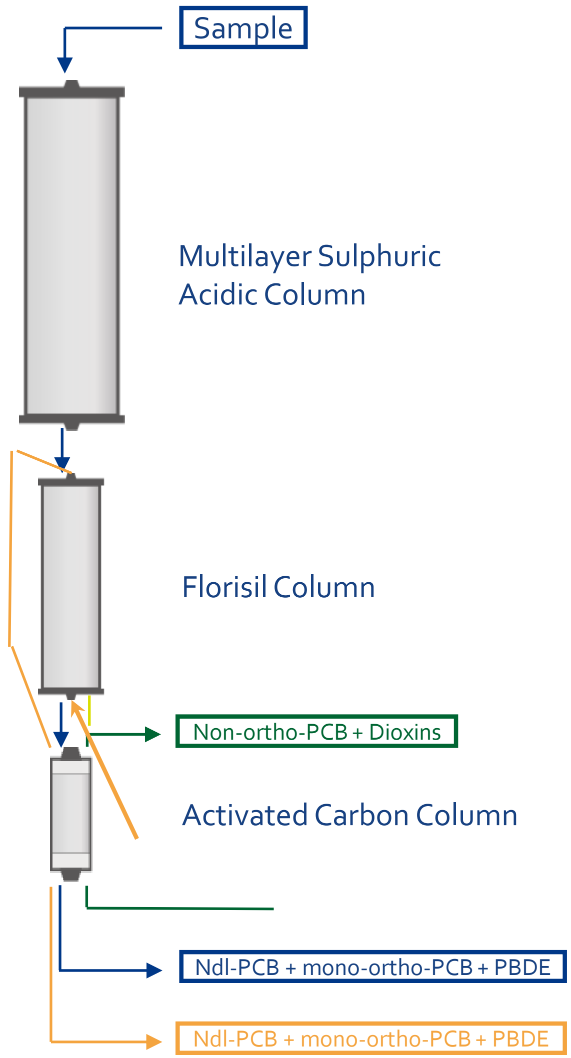
Different clean ups
- Florisil Column-

DEXTech™ Plus - 3 Column Setup

1. n-Hexane
   ndl-PCB + mono-ortho-PCB
   Fraction 1/2

2. Dichlormethane / n-Hexane
   ndl-PCB + Mono-ortho-PCB
   Fraction 1/2

3. Toluene
   Non-ortho-PCB + Dioxins
   Fraction 3



solvent	volumn
n-hexane	91
DCM/n-hexane	24
toluene	10
sum	125
time: 31 min	

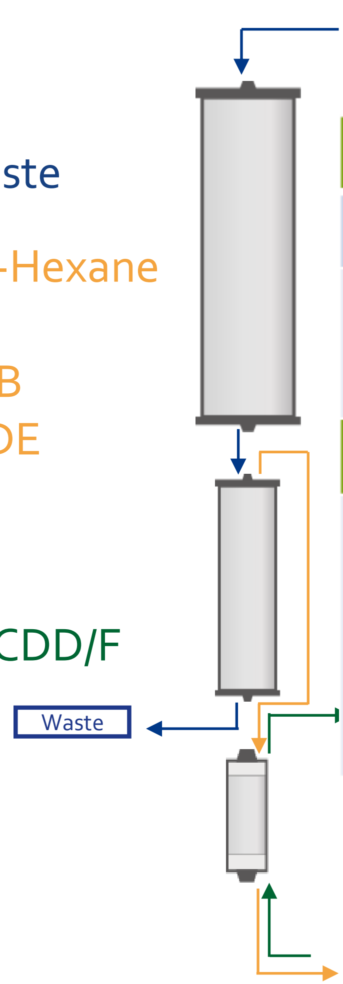
Total solvent consumption
Universal column ~ 195 mL
SMART column ~ 125 mL

Run time
Universal column: ~ 41 min.
SMART column: ~ 31 min.

Different clean ups
- Alumina Column-

DEXTech™ Plus - 3 Column Setup

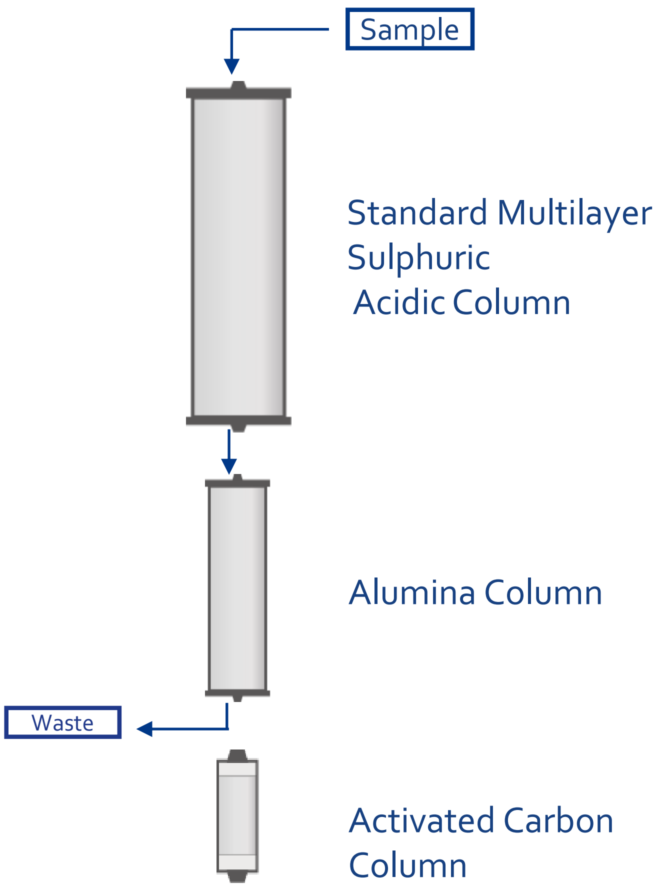
1. n-Hexane
   Sample loading / Waste
2. Dichlormethane / n-Hexane
   Fraction 1
   Mono-ortho-PCB
   + ndl-PCB + PBDE
3. Toluene
   Fraction 2
   Non-ortho-PCB + PCDD/F



	Universal	SMART
Process Time	51 min	35 min
Total Solvent Consumption (incl. conditioning and fractions)	265 mL	153 mL
	Fraction 1	**Fraction 2**
Fraction Volume	24 mL	10 mL
	ndl PCB mono-ortho PCB PBDE	non-ortho PCB PCDD/F

1. Sample loading / Waste

DEXTech™ Plus - 3 Column Setup



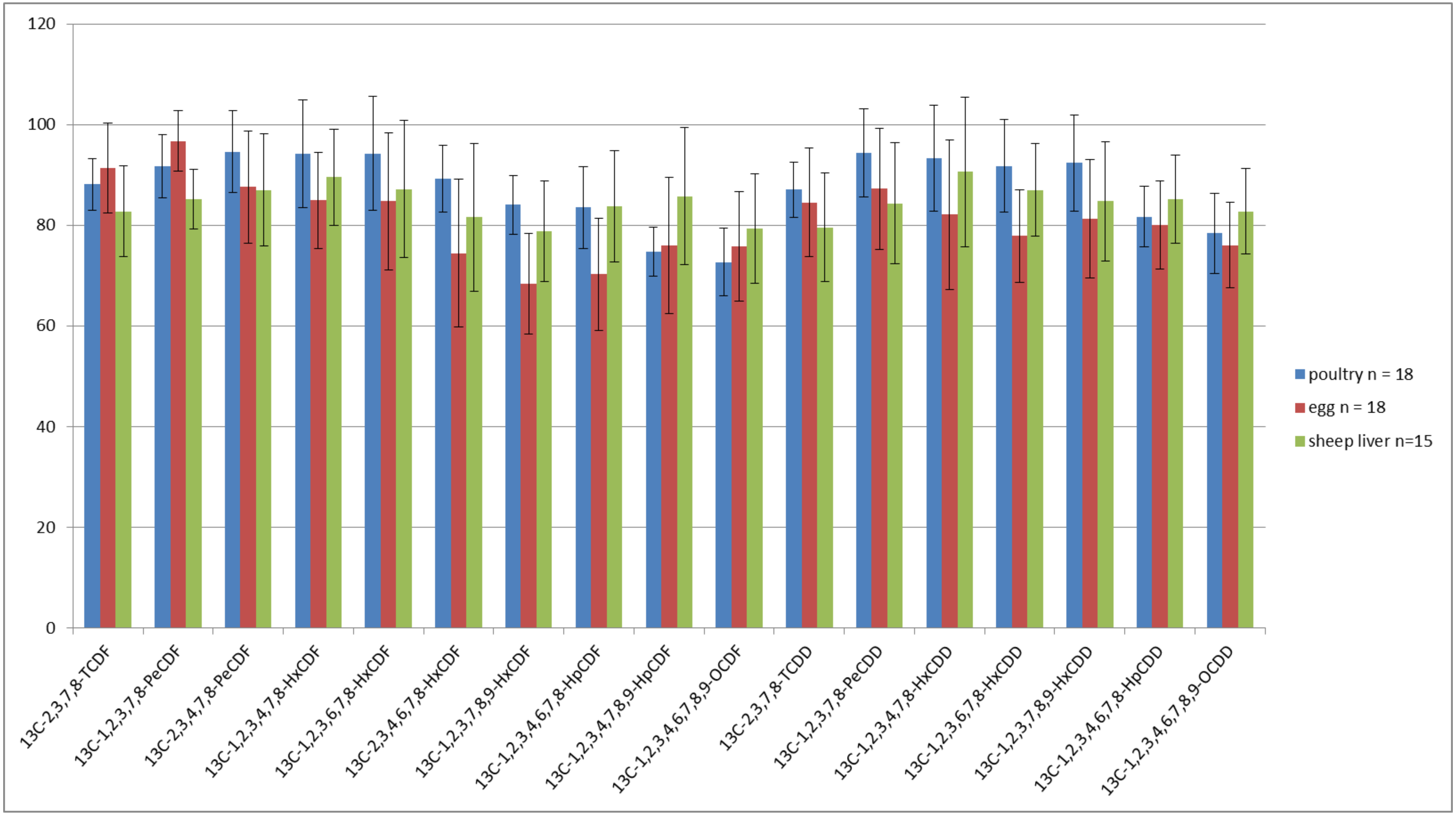
→ dead volumn S1: 5 min- 7 ml/min ~ 35 ml

→ all compounds like PCDD/F, PBDD/F, PCB and PBDE are eluted from S1 after 15 min ~ 105 ml

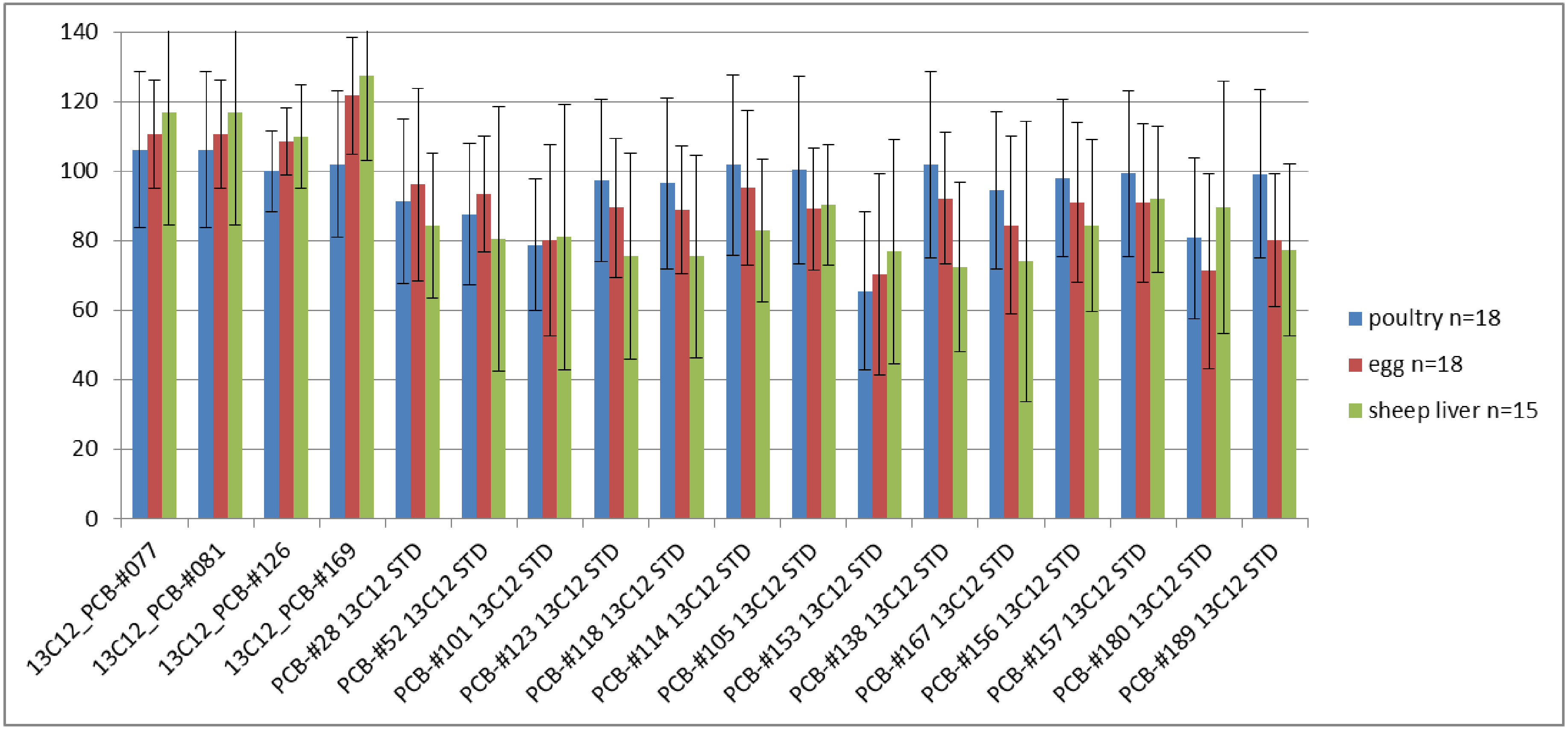
→ dead volumn of the Alox column: 1,5 min – 7 ml/min ~ 10.5 ml

→ why additional cleaning for 7 min – 7 ml/min ~ 49 ml

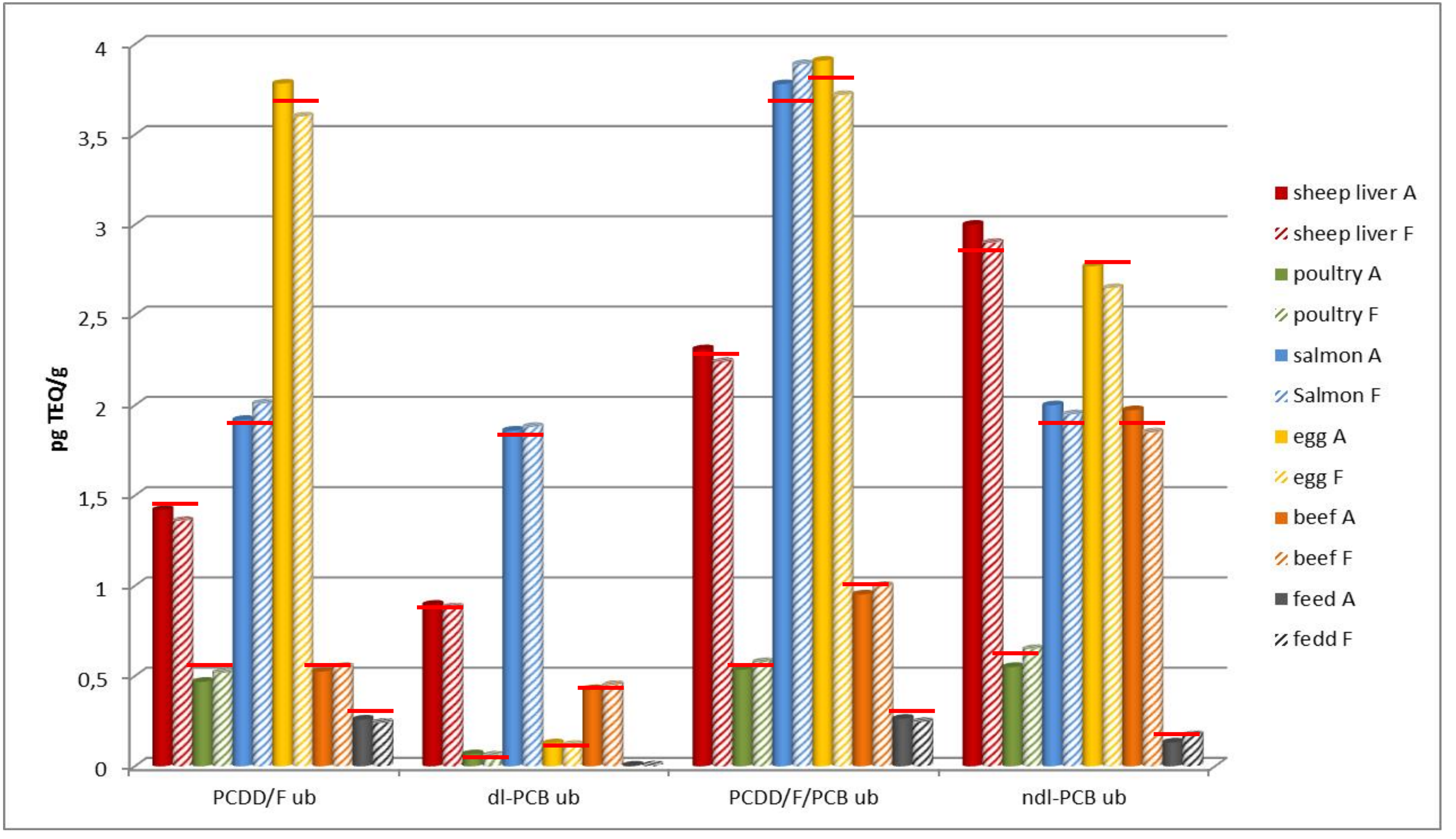
Results Dioxine



Results PCBs

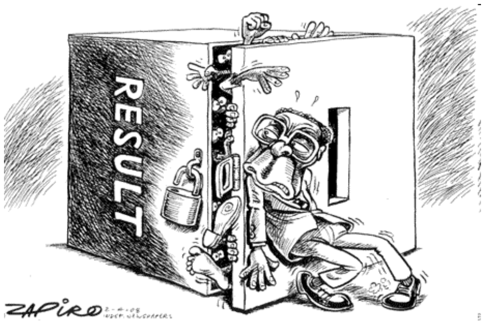


Comparision Alumina/Florisil

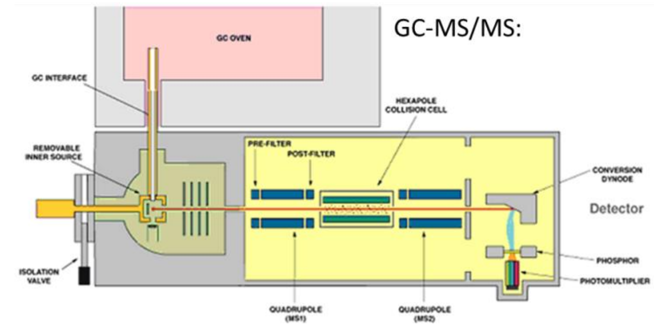


Sheep liver/salmon: fresh weight; poultry/egg/beef: fat; feed: 88 % dry weight

Determination of PCDD/F and PCB by GC-MS/MS

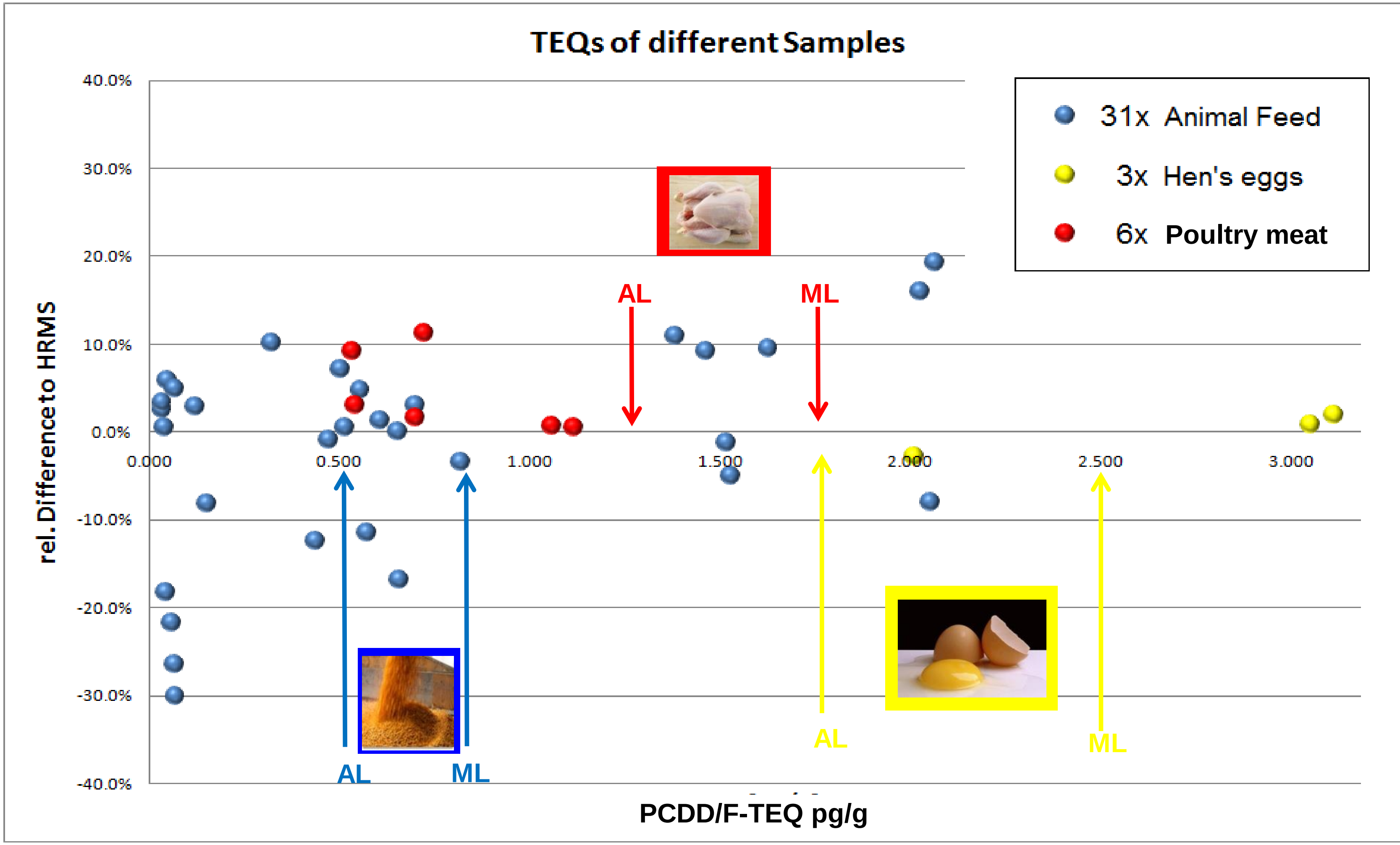


- Why?
- objectives 2010



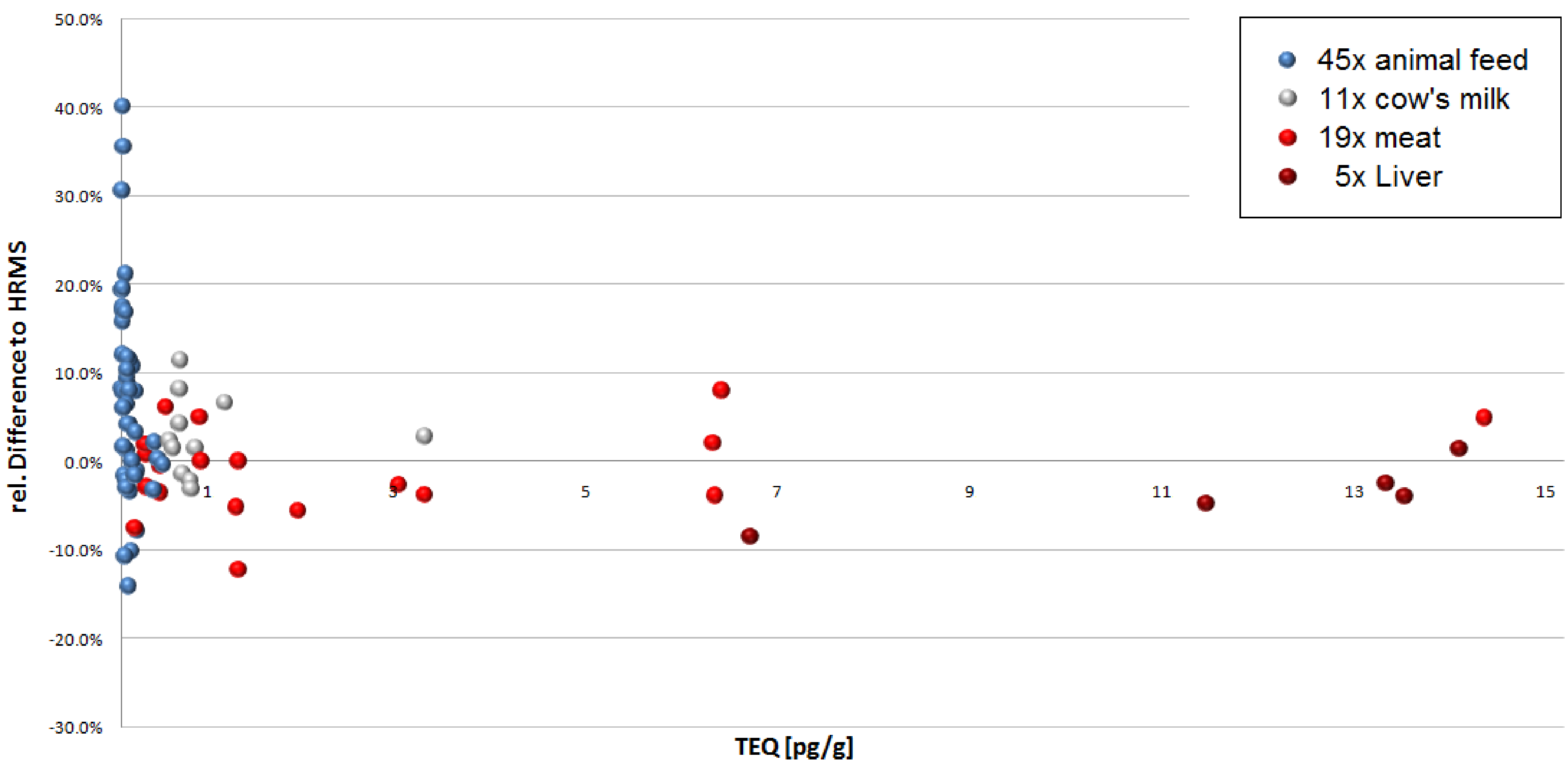
- To assess the performance of GC-MS/MS for the analysis of Dioxins and PCB in food and feed
- To check whether GC-MS/MS can be used as a sensitive screening method and eventually as a reliable and cost-effective alternative for GC-HRMS for confirmatory purposes in official food and feed control
- To investigate whether GC-MS/MS is capable to determine dl-PCBs and especially ndl-PCBs at the level of interest; dicussed in the framework of setting harmonized MRL-values for PCBs

GC-HRMS vs. GC-MS/MS results (upperbound TEQ)

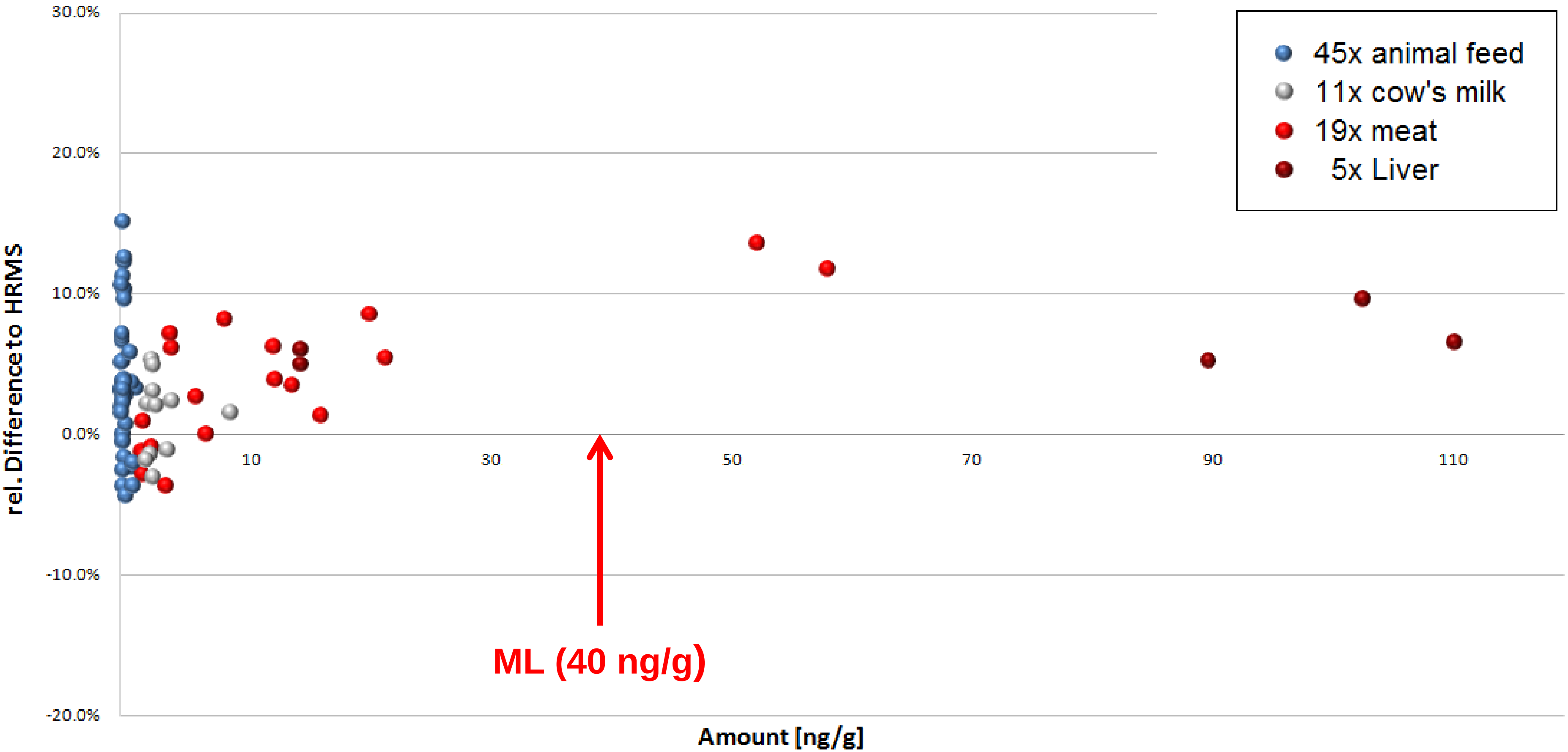


LOD feeding stuff: GC-HRMS: 0.01 - 0.06 pg/g; GC-MS/MS: 0.02 - 0.08 pg/g

GC-HRMS vs. GC-MS/MS results (upperbound dl-PCB-TEQ)



GC-HRMS vs. GC-MS/MS results (Sum of the 6 ndl PCB)



Results exceeding 30 ng/g are above the calibration curve and thus indicative.

Outcome
Criteria for the analysis of food and feed

- Change of the regulation after 4 years
- Regulation (EU) no. 709/2014 for feeding stuff
- Regulation (EU) no. 589/2014 for food
- **The confirmation of positive results had to be carried out with the GC-HRMS or GC-MS/MS!**

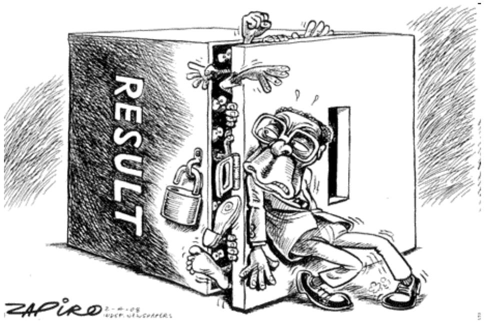
Food:
Regulation (EU) no. 2017/664

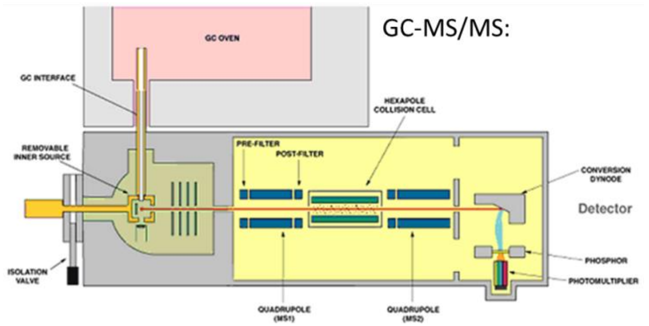
Feed:
Regulation (EU) no 2017/771 (amending Regulation (EC) no 152/2009)

Additional **Requirements** are laid down in the Guidance Documents:

1. Guidance Document on Measurement Uncertainty for Laboratories performing PCDD/F and PCB Analysis using Isotope Dilution Mass Spectrometry
2. The principles as described in the "Guidance Document on the Estimation of LOD and LOQ for Measurements in the Field of Contaminants in Feed and Food"

GC-MS/MS

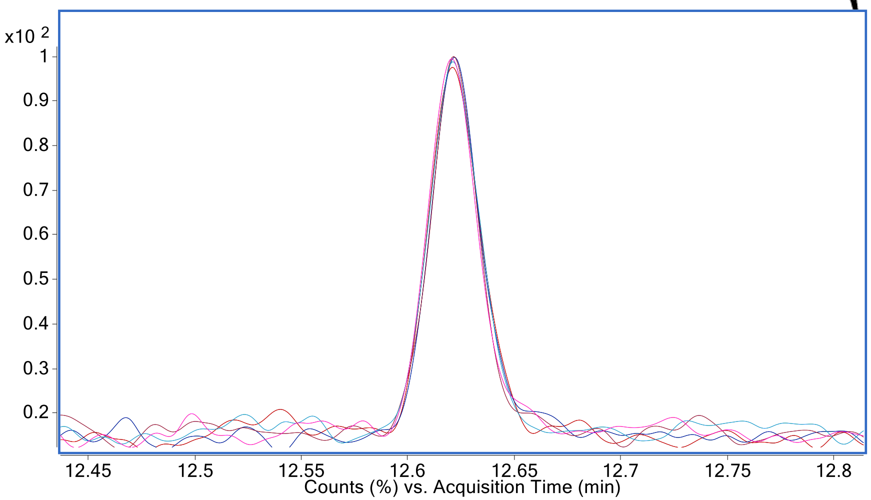




The question today is not whether GC-MS / MS can be used as a confirmation method for the dioxin determination, but when GC-MS / MS achieves the same or better performance as the high-resolution sector field mass spectrometer!

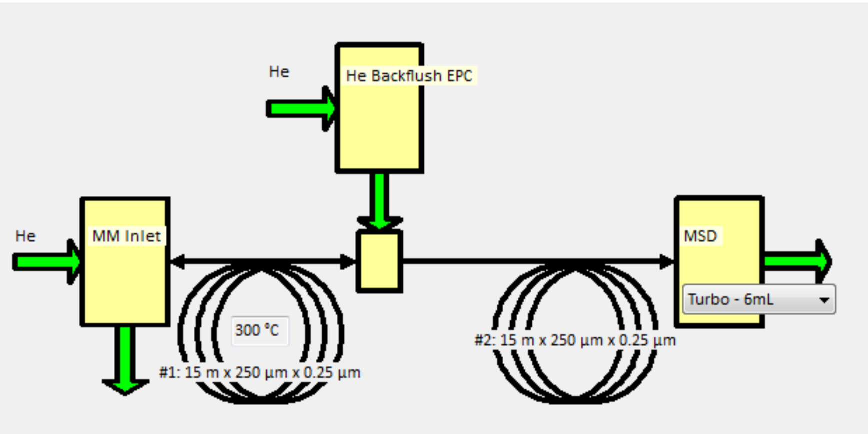
Agilent 7010
High Sensitive GC Triple Quad

2.3.7.8.-TCDD
(5 fg/µl; 2 µl injiziert)



GC settings

- Injector: MMI -> solvent vent;
- 5-10 µl



	Rate °C/min	Value °C	Hold Time min	Run Time min
(Initial)		40	0.5	0.5
Ramp 1	40	150	0	3.25
Ramp 2	2.5	250	0	43.25
Ramp 3	10	300	6	54.25
*				

Attention: These settings do not fulfill the legal requirements of Regulation (EU) No. 2017/664!

MS-settings

Dynamic MRM

Tune File

atunes.eihs — Browse...

Source Parameters

- Ion Source: EI
- Source Temperature (°C): 280
- Electron Energy Mode: Use Tune Setting
- Electron Energy (eV): 70

Detector Setting

- ◉ Use Gain Factor: 10
- ○ Use Delta EMV:
- Calculated EMV: 1590.8
- ☑ EM Saver — Limit: 1E+08
- ☑ Data Saved

Run Time

- ☐ Run time (min): 1
- Solvent Delay (min): 5.4

Filtering

- ☐ Automatically Subtract Baseline
- * ☐ Advanced MRM/SIM filtering

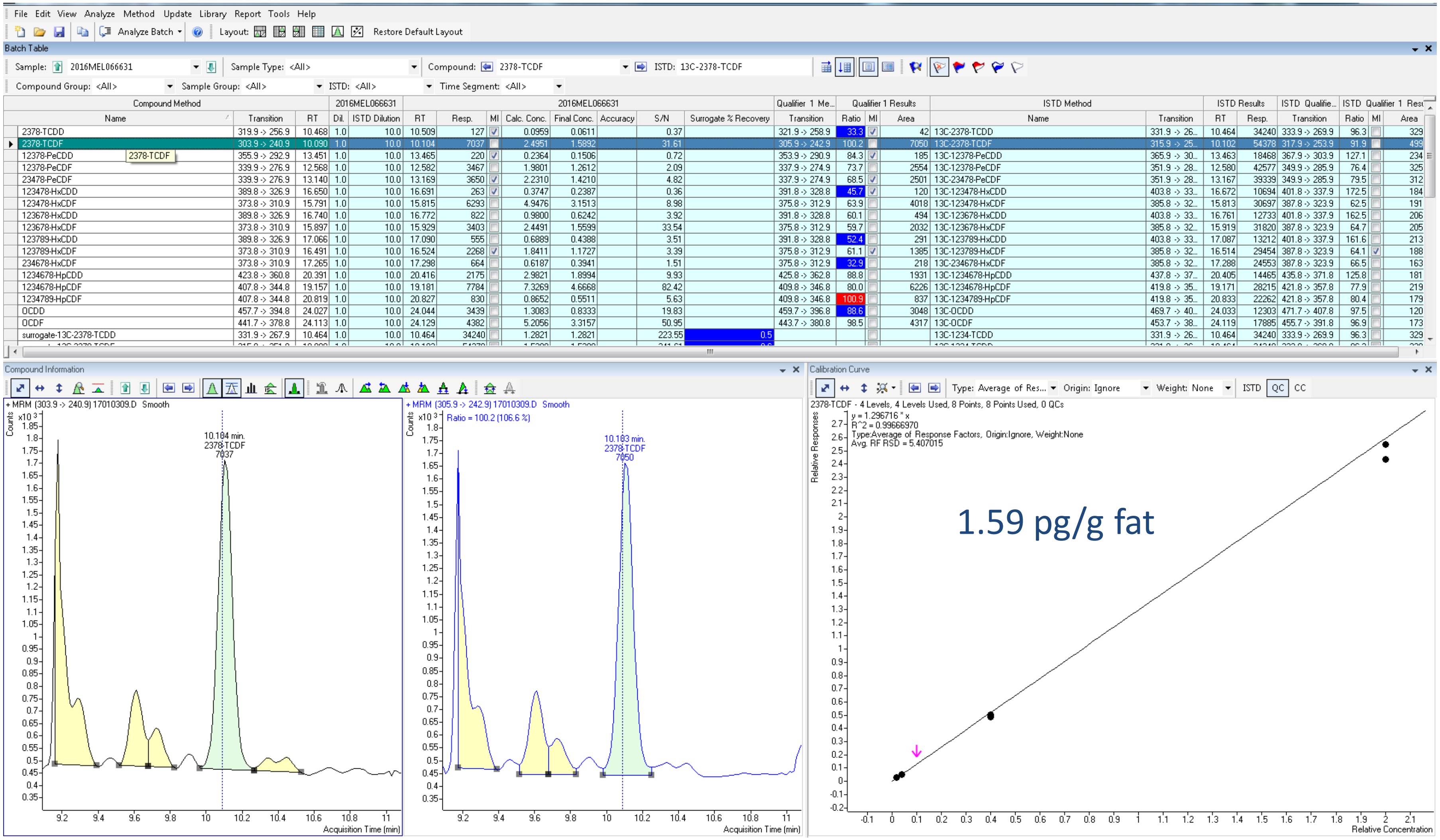
* The feature is instrument dependent

Scan Type dMRM
(use this to revert to non-dMRM method)

Compound Table

	Enable	Compound Name	CAS#	ISTD	Precursor Ion	MS1 Resolution	Product Ion	MS2 Resolution	RT (min)	Left RT Delta (min)	Right RT Delta (min)	Average Dwell (ms)	CE (eV)
1	☑	13C PCB 126		☐	337.9	Unit	267.9	Unit	10	2	10	26	30
2	☑	13C PCB 126		☐	335.9	Unit	265.9	Unit	10	2	10	26	28
3	☑	PCB 77 + 81		☐	291.9	Unit	222	Unit	10	2	5	28.3	28
4	☑	PCB 77 + 81		☐	289.9	Unit	220	Unit	10	2	5	28.3	28
5	☑	13C PCB 77 + 81		☐	303.9	Unit	234	Unit	10	2	5	28.3	28
6	☑	13C PCB 77 + 81		☐	301.9	Unit	232	Unit	10	2	5	28.3	28
7	☑	13C-HpCDD		☐	437.8	Unit	373.8	Unit	20	2	2	26	26
8	☑	13C-HpCDD		☐	435.8	Unit	371.8	Unit	20	2	2	26	26
9	☑	13C-HpCDF		☐	421.8	Unit	357.8	Unit	20	2	2	28.3	40
10	☑	13C-HpCDF		☐	419.8	Unit	355.8	Unit	20	2	2	28.3	40
11	☑	13C-HxCDD		☐	403.8	Unit	339.8	Unit	16.6	2	2	28.3	35
12	☑	13C-HxCDD		☐	401.8	Unit	337.8	Unit	16.6	2	2	28.3	35
13	☑	13C-HxCDF		☐	387.8	Unit	323.9	Unit	16.5	3	3	28.3	35
14	☑	13C-HxCDF		☐	385.8	Unit	321.9	Unit	16.5	3	3	28.3	35
15	☑	13C-OCDD		☐	471.7	Unit	407.7	Unit	24	1	2	28.3	26
16	☑	13C-OCDD		☐	469.7	Unit	405.7	Unit	24	1	2	28.3	26
17	☑	13C-OCDF		☐	455.7	Unit	391.8	Unit	24	1	2	23.3	40
18	☑	13C-OCDF		☐	453.7	Unit	389.8	Unit	24	1	2	23.3	40
19	☑	13C-PeCDD		☐	367.9	Unit	303.9	Unit	13.5	1	1	23.3	35
20	☑	13C-PeCDD		☐	365.9	Unit	301.9	Unit	13.5	1	1	23.3	35
21	☑	13C-PeCDF		☐	351.9	Unit	287.9	Unit	12.5	1	2.5	21.6	35
22	☑	13C-PeCDF		☐	349.9	Unit	285.9	Unit	12.5	1	2.5	21.6	35
23	☑	13C-TCDD		☐	333.9	Unit	269.9	Unit	10.5	1	1	21.6	24
24	☑	13C-TCDD		☐	331.9	Unit	267.9	Unit	10.5	1	1	21.6	24
25	☑	13C-TCDF		☐	317.9	Unit	253.9	Unit	10.1	1	1	20.6	35
26	☑	13C-TCDF		☐	315.9	Unit	251.9	Unit	10.1	1	1	20.6	35
27	☑	2378TCDD		☐	321.9	Unit	258.9	Unit	10.5	1	1	22.2	24
28	☑	2378TCDD		☐	319.9	Unit	256.9	Unit	10.5	1	1	22.2	24
29	☑	2378-TCDF		☑	305.9	Unit	242.9	Unit	10.1	1	1	20.6	35
30	☑	2378-TCDF		☐	303.9	Unit	240.9	Unit	10.1	1	1	20.6	35
31	☑	HpCDD		☐	425.8	Unit	362.8	Unit	20	2	2	21.2	26
32	☑	HpCDD		☐	423.8	Unit	360.8	Unit	20	2	2	21.2	26
33	☑	HpCDF		☐	409.8	Unit	346.8	Unit	20	2	2	21.8	40
34	☑	HpCDF		☐	407.8	Unit	344.8	Unit	20	2	2	21.8	40
35	☑	HxCDD		☐	391.8	Unit	328.8	Unit	16.5	2	2	21.8	35
36	☑	HxCDD		☐	389.8	Unit	326.9	Unit	16.5	2	2	21.8	35
37	☑	HxCDF		☐	375.8	Unit	312.9	Unit	16.5	3	3	21.8	35
38	☑	HxCDF		☐	373.8	Unit	310.9	Unit	16.5	3	3	21.8	35

2.3.7.8.-TCDF in a egg sample sample weight 1.6 g fat



1.2.3.7.8.-PeCDD in a egg sample

File Edit View Analyze Method Update Library Report Tools Help

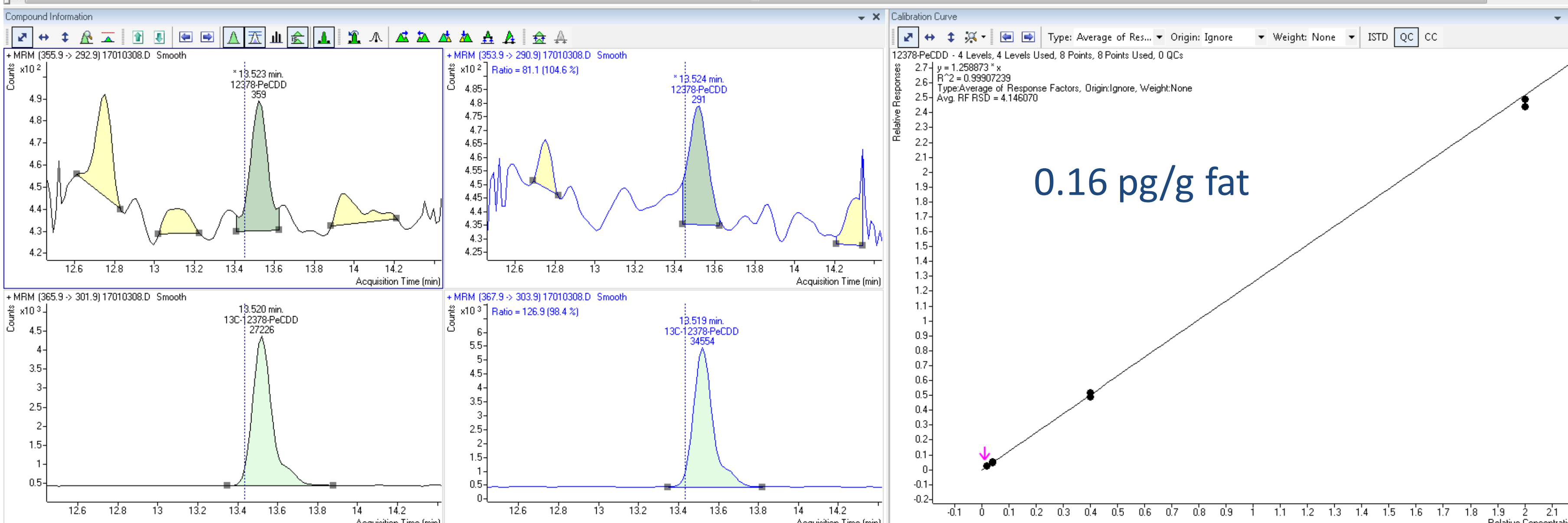
Analyze Batch Layout: Restore Default Layout

Batch Table

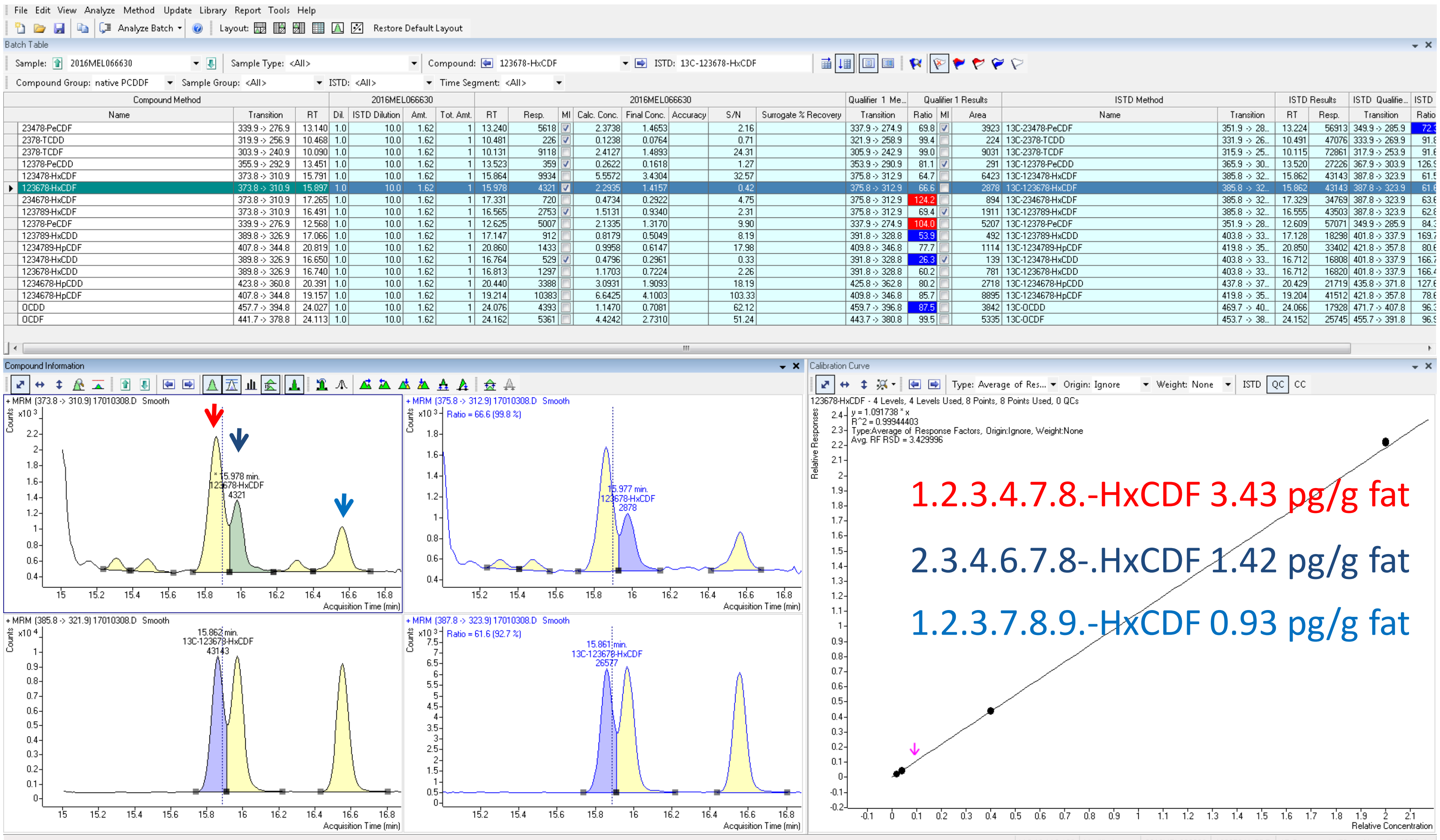
Sample: 2016MEL066630 Sample Type: <All> Compound: 12378-PeCDD ISTD: 13C-12378-PeCDD

Compound Group: native PCDDF Sample Group: <All> ISTD: <All> Time Segment: <All>

Compound Method			2016MEL066630												Qualifier 1 Me...	Qualifier 1 Results			ISTD Method		ISTD Results		ISTD Qualifie...	ISTD
Name	Transition	RT	Dil.	ISTD Dilution	Amt.	Tot. Amt.	RT	Resp.	MI	Calc. Conc.	Final Conc.	Accuracy	S/N	Surrogate % Recovery	Transition	Ratio	MI	Area	Name	Transition	RT	Resp.	Transition	Ratio
23478-PeCDF	339.9 -> 276.9	13.140	1.0	10.0	1.62	1	13.240	5618	✓	2.3738	1.4653		2.16		337.9 -> 274.9	69.8	✓	3923	13C-23478-PeCDF	351.9 -> 28...	13.224	56913	349.9 -> 285.9	72.3
2378-TCDD	319.9 -> 256.9	10.468	1.0	10.0	1.62	1	10.481	226	✓	0.1238	0.0764		0.71		321.9 -> 258.9	99.4		224	13C-2378-TCDD	331.9 -> 26...	10.491	47076	333.9 -> 269.9	91.8
2378-TCDF	303.9 -> 240.9	10.090	1.0	10.0	1.62	1	10.131	9118		2.4127	1.4893		24.31		305.9 -> 242.9	99.0		9031	13C-2378-TCDF	315.9 -> 25...	10.115	72861	317.9 -> 253.9	91.6
12378-PeCDD	355.9 -> 292.9	13.451	1.0	10.0	1.62	1	13.523	359	✓	0.2622	0.1618		1.27		353.9 -> 290.9	81.1	✓	291	13C-12378-PeCDD	365.9 -> 30...	13.520	27226	367.9 -> 303.9	126.9
123478-HxCDF	373.8 -> 310.9	15.791	1.0	10.0	1.62	1	15.864	9934		5.5572	3.4304		32.57		375.8 -> 312.9	64.7		6423	13C-123478-HxCDF	385.8 -> 32...	15.862	43143	387.8 -> 323.9	61.5
123678-HxCDF	373.8 -> 310.9	15.897	1.0	10.0	1.62	1	15.978	4321	✓	2.2935	1.4157		0.42		375.8 -> 312.9	66.6		2878	13C-123678-HxCDF	385.8 -> 32...	15.862	43143	387.8 -> 323.9	61.6
234678-HxCDF	373.8 -> 310.9	17.265	1.0	10.0	1.62	1	17.331	720		0.4734	0.2922		4.75		375.8 -> 312.9	124.2		894	13C-234678-HxCDF	385.8 -> 32...	17.329	34769	387.8 -> 323.9	63.6
123789-HxCDF	373.8 -> 310.9	16.491	1.0	10.0	1.62	1	16.565	2753	✓	1.5131	0.9340		2.31		375.8 -> 312.9	69.4	✓	1911	13C-123789-HxCDF	385.8 -> 32...	16.555	43503	387.8 -> 323.9	62.8
12378-PeCDF	339.9 -> 276.9	12.568	1.0	10.0	1.62	1	12.625	5007		2.1335	1.3170		9.90		337.9 -> 274.9	104.0		5207	13C-12378-PeCDF	351.9 -> 28...	12.609	57071	349.9 -> 285.9	84.3
123789-HxCDD	389.8 -> 326.9	17.066	1.0	10.0	1.62	1	17.147	912		0.8179	0.5049		8.19		391.8 -> 328.8	53.9		492	13C-123789-HxCDD	403.8 -> 33...	17.128	18298	401.8 -> 337.9	169.7
1234789-HpCDF	407.8 -> 344.8	20.819	1.0	10.0	1.62	1	20.860	1433		0.9958	0.6147		17.98		409.8 -> 346.8	77.7		1114	13C-1234789-HpCDF	419.8 -> 35...	20.850	33402	421.8 -> 357.8	80.6
123478-HxCDD	389.8 -> 326.9	16.650	1.0	10.0	1.62	1	16.764	529	✓	0.4796	0.2961		0.33		391.8 -> 328.8	26.3	✓	139	13C-123478-HxCDD	403.8 -> 33...	16.712	16808	401.8 -> 337.9	166.7
123678-HxCDD	389.8 -> 326.9	16.740	1.0	10.0	1.62	1	16.813	1297		1.1703	0.7224		2.26		391.8 -> 328.8	60.2		781	13C-123678-HxCDD	403.8 -> 33...	16.712	16820	401.8 -> 337.9	166.4
1234678-HpCDD	423.8 -> 360.8	20.391	1.0	10.0	1.62	1	20.440	3388		3.0931	1.9093		18.19		425.8 -> 362.8	80.2		2718	13C-1234678-HpCDD	437.8 -> 37...	20.429	21719	435.8 -> 371.8	127.6
1234678-HpCDF	407.8 -> 344.8	19.157	1.0	10.0	1.62	1	19.214	10383		6.6425	4.1003		103.33		409.8 -> 346.8	85.7		8895	13C-1234678-HpCDF	419.8 -> 35...	19.204	41512	421.8 -> 357.8	78.6
OCDD	457.7 -> 394.8	24.027	1.0	10.0	1.62	1	24.076	4393		1.1470	0.7081		62.12		459.7 -> 396.8	87.5		3842	13C-OCDD	469.7 -> 40...	24.066	17928	471.7 -> 407.8	96.3
OCDF	441.7 -> 378.8	24.113	1.0	10.0	1.62	1	24.162	5361		4.4242	2.7310		51.24		443.7 -> 380.8	99.5		5335	13C-OCDF	453.7 -> 38...	24.152	25745	455.7 -> 391.8	96.9



HxCDF in a egg sample



Name	Transition	RT	Dil.	ISTD Dilution	Amt.	Tot. Amt.	RT	Resp.	MI	Calc. Conc.	Final Conc.	Accuracy	S/N	Surrogate % Recovery	Transition	Ratio	MI	Area	Name	Transition	RT	Resp.	Transition	Ratio
23478-PeCDF	339.9 -> 276.9	13.140	1.0	10.0	1.62	1	13.240	5618	✓	2.3738	1.4653		2.16		337.9 -> 274.9	69.8	✓	3923	13C-23478-PeCDF	351.9 -> 28...	13.224	56913	349.9 -> 285.9	72.3
2378-TCDD	319.9 -> 256.9	10.468	1.0	10.0	1.62	1	10.481	226	✓	0.1238	0.0764		0.71		321.9 -> 258.9	99.4		224	13C-2378-TCDD	331.9 -> 26...	10.491	47076	333.9 -> 269.9	91.8
2378-TCDF	303.9 -> 240.9	10.090	1.0	10.0	1.62	1	10.131	9118		2.4127	1.4893		24.31		305.9 -> 242.9	99.0		9031	13C-2378-TCDF	315.9 -> 25...	10.115	72861	317.9 -> 253.9	91.6
12378-PeCDD	355.9 -> 292.9	13.451	1.0	10.0	1.62	1	13.523	359	✓	0.2622	0.1618		1.27		353.9 -> 290.9	81.1	✓	291	13C-12378-PeCDD	365.9 -> 30...	13.520	27226	367.9 -> 303.9	126.9
123478-HxCDF	373.8 -> 310.9	15.791	1.0	10.0	1.62	1	15.864	9934		5.5572	3.4304		32.57		375.8 -> 312.9	64.7		6423	13C-123478-HxCDF	385.8 -> 32...	15.862	43143	387.8 -> 323.9	61.5
123678-HxCDF	373.8 -> 310.9	15.897	1.0	10.0	1.62	1	15.978	4321	✓	2.2935	1.4157		0.42		375.8 -> 312.9	66.6		2878	13C-123678-HxCDF	385.8 -> 32...	15.862	43143	387.8 -> 323.9	61.6
234678-HxCDF	373.8 -> 310.9	17.265	1.0	10.0	1.62	1	17.331	720		0.4734	0.2922		4.75		375.8 -> 312.9	124.2		894	13C-234678-HxCDF	385.8 -> 32...	17.329	34769	387.8 -> 323.9	63.6
123789-HxCDF	373.8 -> 310.9	16.491	1.0	10.0	1.62	1	16.565	2753	✓	1.5131	0.9340		2.31		375.8 -> 312.9	69.4	✓	1911	13C-123789-HxCDF	385.8 -> 32...	16.555	43503	387.8 -> 323.9	62.8
12378-PeCDF	339.9 -> 276.9	12.568	1.0	10.0	1.62	1	12.625	5007		2.1335	1.3170		9.90		337.9 -> 274.9	104.0		5207	13C-12378-PeCDF	351.9 -> 28...	12.609	57071	349.9 -> 285.9	84.3
123789-HxCDD	389.8 -> 326.9	17.066	1.0	10.0	1.62	1	17.147	912		0.8179	0.5049		8.19		391.8 -> 328.8	53.9		492	13C-123789-HxCDD	403.8 -> 33...	17.128	18298	401.8 -> 337.9	169.7
1234789-HpCDF	407.8 -> 344.8	20.819	1.0	10.0	1.62	1	20.860	1433		0.9958	0.6147		17.98		409.8 -> 346.8	77.7		1114	13C-1234789-HpCDF	419.8 -> 35...	20.850	33402	421.8 -> 357.8	80.6
123478-HxCDD	389.8 -> 326.9	16.650	1.0	10.0	1.62	1	16.764	529	✓	0.4796	0.2961		0.33		391.8 -> 328.8	26.3	✓	139	13C-123478-HxCDD	403.8 -> 33...	16.712	16808	401.8 -> 337.9	166.7
123678-HxCDD	389.8 -> 326.9	16.740	1.0	10.0	1.62	1	16.813	1297		1.1703	0.7224		2.26		391.8 -> 328.8	60.2		781	13C-123678-HxCDD	403.8 -> 33...	16.712	16820	401.8 -> 337.9	166.4
1234678-HpCDD	423.8 -> 360.8	20.391	1.0	10.0	1.62	1	20.440	3388		3.0931	1.9093		18.19		425.8 -> 362.8	80.2		2718	13C-1234678-HpCDD	437.8 -> 37...	20.429	21719	435.8 -> 371.8	127.6
1234678-HpCDF	407.8 -> 344.8	19.157	1.0	10.0	1.62	1	19.214	10383		6.6425	4.1003		103.33		409.8 -> 346.8	85.7		8895	13C-1234678-HpCDF	419.8 -> 35...	19.204	41512	421.8 -> 357.8	78.6
OCDD	457.7 -> 394.8	24.027	1.0	10.0	1.62	1	24.076	4393		1.1470	0.7081		62.12		459.7 -> 396.8	87.5		3842	13C-OCDD	469.7 -> 40...	24.066	17928	471.7 -> 407.8	96.3
OCDF	441.7 -> 378.8	24.113	1.0	10.0	1.62	1	24.162	5361		4.4242	2.7310		51.24		443.7 -> 380.8	99.5		5335	13C-OCDF	453.7 -> 38...	24.152	25745	455.7 -> 391.8	96.9

OCDD in a egg sample

File Edit View Analyze Method Update Library Report Tools Help

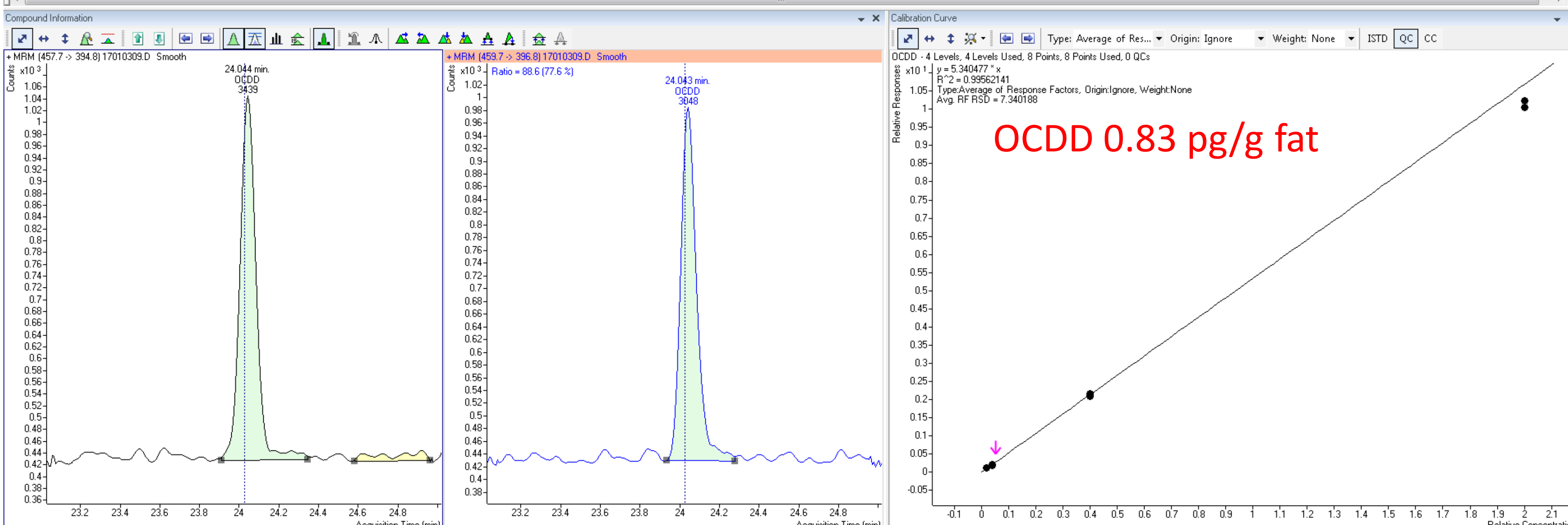
Analyze Batch | Layout: | Restore Default Layout

Batch Table

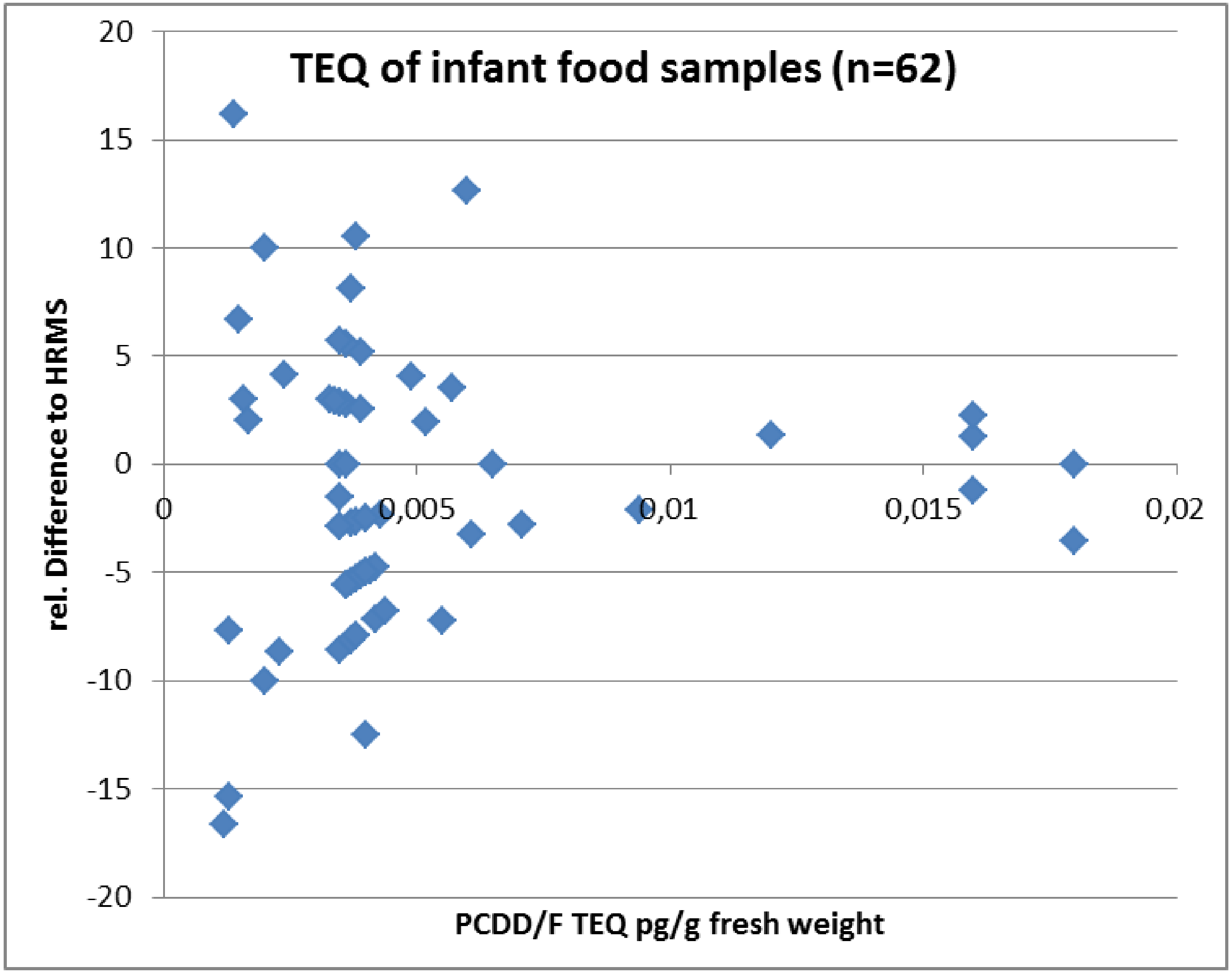
Sample: 2016MEL066631 | Sample Type: <All> | Compound: OCDD | ISTD: 13C-OCDD

Compound Group: <All> | Sample Group: <All> | ISTD: <All> | Time Segment: <All>

Compound Method			2016MEL066631		2016MEL066631								Qualifier 1 Me...	Qualifier 1 Results			ISTD Method		ISTD Results		ISTD Qualifie...	ISTD Qualifier 1 Resu...		
Name	Transition	RT	Dil.	ISTD Dilution	RT	Resp.	MI	Calc. Conc.	Final Conc.	Accuracy	S/N	Surrogate % Recovery	Transition	Ratio	MI	Area	Name	Transition	RT	Resp.	Transition	Ratio	MI	Area
2378-TCDD	319.9 -> 256.9	10.468	1.0	10.0	10.509	127	✓	0.0959	0.0611		0.37		321.9 -> 258.9	33.3	✓	42	13C-2378-TCDD	331.9 -> 26...	10.464	34240	333.9 -> 269.9	96.3		329
2378-TCDF	303.9 -> 240.9	10.090	1.0	10.0	10.104	7037		2.4951	1.5892		31.61		305.9 -> 242.9	100.2		7050	13C-2378-TCDF	315.9 -> 25...	10.102	54378	317.9 -> 253.9	91.9		499
12378-PeCDD	355.9 -> 292.9	13.451	1.0	10.0	13.465	220	✓	0.2364	0.1506		0.72		353.9 -> 290.9	84.3	✓	185	13C-12378-PeCDD	365.9 -> 30...	13.463	18468	367.9 -> 303.9	127.1		234
12378-PeCDF	339.9 -> 276.9	12.568	1.0	10.0	12.582	3467		1.9801	1.2612		2.09		337.9 -> 274.9	73.7		2554	13C-12378-PeCDF	351.9 -> 28...	12.580	42577	349.9 -> 285.9	76.4		325
23478-PeCDF	339.9 -> 276.9	13.140	1.0	10.0	13.169	3650	✓	2.2310	1.4210		4.82		337.9 -> 274.9	68.5	✓	2501	13C-23478-PeCDF	351.9 -> 28...	13.167	39339	349.9 -> 285.9	79.5		312
123478-HxCDD	389.8 -> 326.9	16.650	1.0	10.0	16.691	263	✓	0.3747	0.2387		0.36		391.8 -> 328.8	45.7	✓	120	13C-123478-HxCDD	403.8 -> 33...	16.672	10694	401.8 -> 337.9	172.5		184
123478-HxCDF	373.8 -> 310.9	15.791	1.0	10.0	15.815	6293		4.9476	3.1513		8.98		375.8 -> 312.9	63.9		4018	13C-123478-HxCDF	385.8 -> 32...	15.813	30697	387.8 -> 323.9	62.5		191
123678-HxCDD	389.8 -> 326.9	16.740	1.0	10.0	16.772	822		0.9800	0.6242		3.92		391.8 -> 328.8	60.1		494	13C-123678-HxCDD	403.8 -> 33...	16.761	12733	401.8 -> 337.9	162.5		206
123678-HxCDF	373.8 -> 310.9	15.897	1.0	10.0	15.929	3403		2.4491	1.5599		33.54		375.8 -> 312.9	59.7		2032	13C-123678-HxCDF	385.8 -> 32...	15.919	31820	387.8 -> 323.9	64.7		205
123789-HxCDD	389.8 -> 326.9	17.066	1.0	10.0	17.090	555		0.6889	0.4388		3.51		391.8 -> 328.8	52.4		291	13C-123789-HxCDD	403.8 -> 33...	17.087	13212	401.8 -> 337.9	161.6		213
123789-HxCDF	373.8 -> 310.9	16.491	1.0	10.0	16.524	2268	✓	1.8411	1.1727		3.39		375.8 -> 312.9	61.1	✓	1385	13C-123789-HxCDF	385.8 -> 32...	16.514	29454	387.8 -> 323.9	64.1	✓	188
234678-HxCDF	373.8 -> 310.9	17.265	1.0	10.0	17.298	664		0.6187	0.3941		1.51		375.8 -> 312.9	32.9		218	13C-234678-HxCDF	385.8 -> 32...	17.288	24553	387.8 -> 323.9	66.5		163
1234678-HpCDD	423.8 -> 360.8	20.391	1.0	10.0	20.416	2175		2.9821	1.8994		9.93		425.8 -> 362.8	88.8		1931	13C-1234678-HpCDD	437.8 -> 37...	20.405	14465	435.8 -> 371.8	125.8		181
1234678-HpCDF	407.8 -> 344.8	19.157	1.0	10.0	19.181	7784		7.3269	4.6668		82.42		409.8 -> 346.8	80.0		6226	13C-1234678-HpCDF	419.8 -> 35...	19.171	28215	421.8 -> 357.8	77.9		219
1234789-HpCDF	407.8 -> 344.8	20.819	1.0	10.0	20.827	830		0.8652	0.5511		5.63		409.8 -> 346.8	100.9		837	13C-1234789-HpCDF	419.8 -> 35...	20.833	22262	421.8 -> 357.8	80.4		179
OCDD	457.7 -> 394.8	24.027	1.0	10.0	24.044	3439		1.3083	0.8333		19.83		459.7 -> 396.8	88.6		3048	13C-OCDD	469.7 -> 40...	24.033	12303	471.7 -> 407.8	97.5		120
OCDF	441.7 -> 378.8	24.113	1.0	10.0	24.129	4382		5.2056	3.3157		50.95		443.7 -> 380.8	98.5		4317	13C-OCDF	453.7 -> 38...	24.119	17885	455.7 -> 391.8	96.9		173
surrogate-13C-2378-TCDD	331.9 -> 267.9	10.464	1.0	10.0	10.464	34240		1.2821	1.2821		223.55	0.5					13C-1234-TCDD	331.9 -> 26...	10.464	34240	333.9 -> 269.9	96.3		329

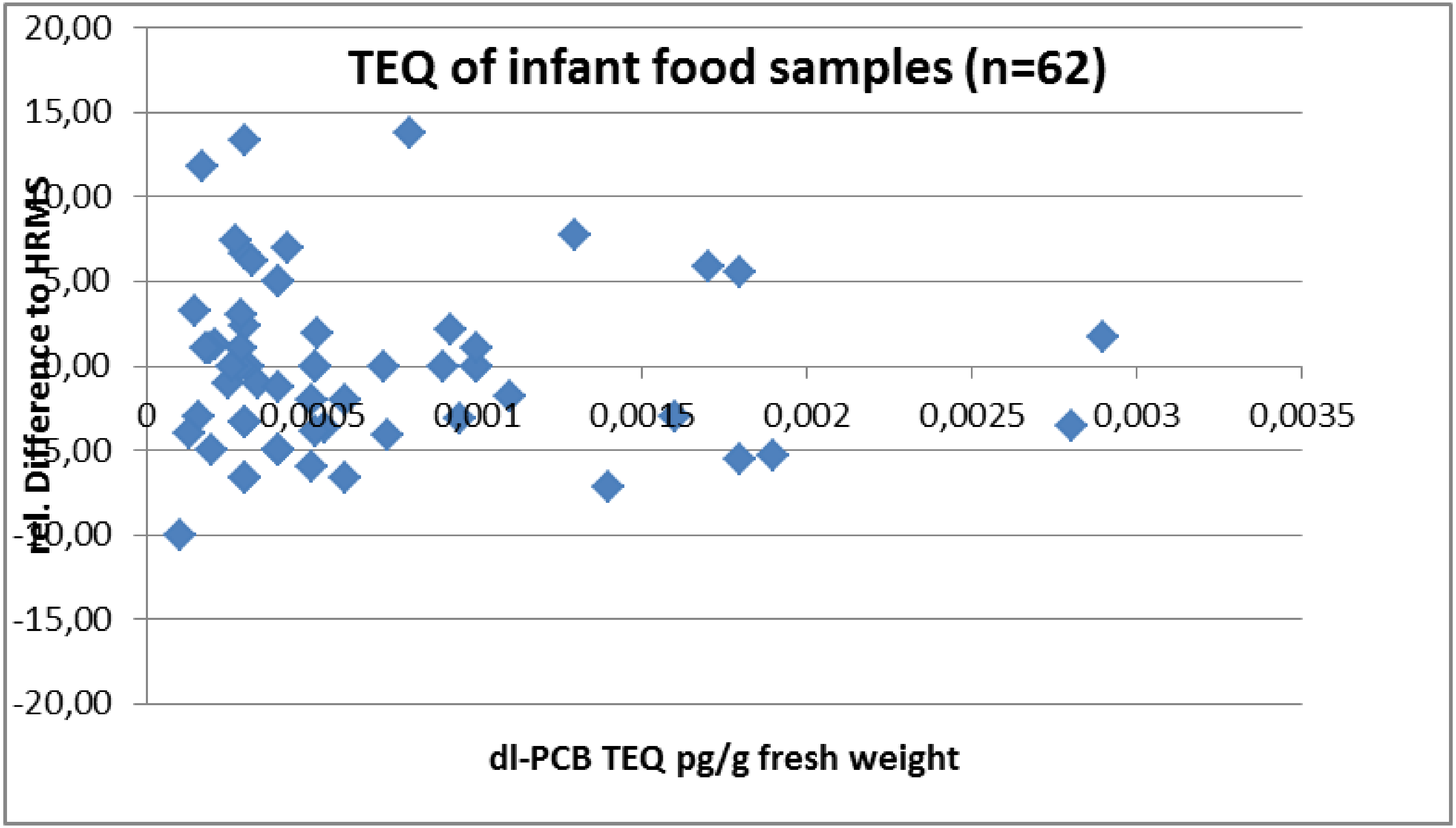


GC-HRMS vs. GC-MS/MS results PCDD/F (upperbound TEQ)



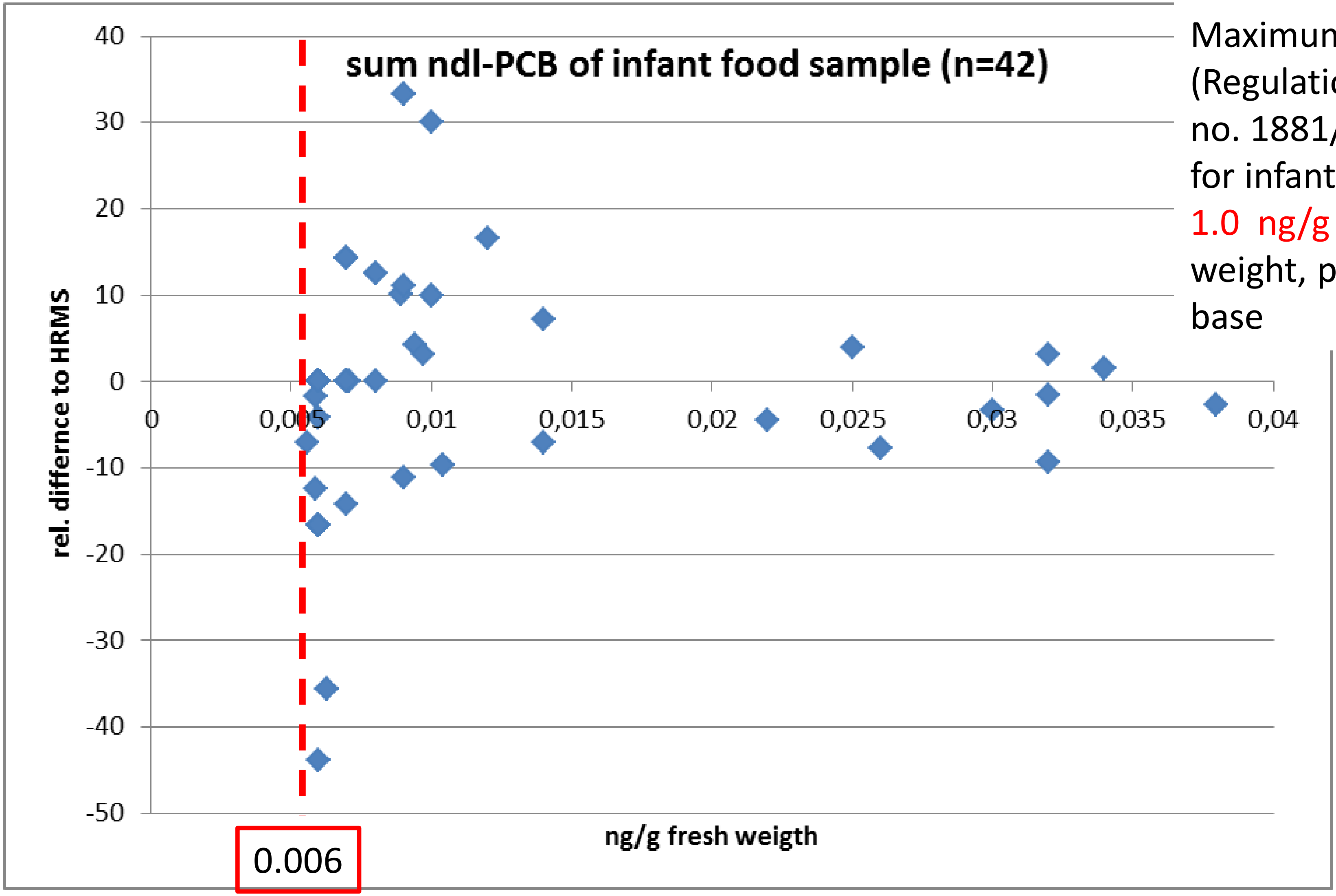
Maximum level (Regulation (EC) no. 1881/2006) for infant food: 0.1 pg TEQ/g fresh weight, product base

GC-HRMS vs. GC-MS/MS results (upperbound dl-PCB-TEQ)



GC-HRMS vs. GC-MS/MS results

(Sum of the 6 ndl PCB)



Maximum level (Regulation (EC) no. 1881/2006) for infant food: 1.0 ng/g fresh weight, product base

report

Batch Info

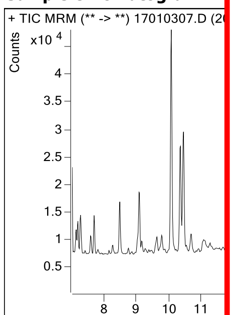
Batch Data Path D:\CVUA_MEL\Projekte\AG62_dioxine\2017\170103\QuantResults\170103.batch.bin

Analysis Time	8.15.2017 2:57 PM	**Analyst Name**	QQQ-7010B\Admin
Report Time	8.15.2017 2:59 PM	**Reporter Name**	QQQ-7010B\Admin
Last Calib Update	8.15.2017 2:57 PM	**Batch State**	Processed

Analysis Info

Acq Time	03.01.2017 15:28
Sample Type	Sample
Position	7
Level	

Sample Chromatogra



Quantitation Resu

Compound	ISTD	RT	Response	ISTD Resp	Weight (g)	ISTD (pg)	Gehalt (pg/g)	WDF (%)
2378-TCDF	13C-2378-TCDF	10,1	7118	59024	1,530	25,0	1,508	80
2378-TCDD	13C-2378-TCDD	10,5	135	36588	1,530	25,0	0,059	75
12378-PeCDF	13C-12378-PeCDF	12,6	3308	44897	1,530	25,0	1,156	105
23478-PeCDF	13C-23478-PeCDF	13,2	3279	43190	1,530	25,0	1,189	90
12378-PeCDD	13C-12378-PeCDD	13,5	405	18765	1,530	25,0	0,249	103
123478-HxCDF	13C-123478-HxCDF	15,8	6667	35539	1,530	25,0	3,003	102
123678-HxCDF	13C-123678-HxCDF	15,9	3336	38778	1,530	25,0	1,262	105
123789-HxCDF	13C-123789-HxCDF	16,5	2231	35630	1,530	25,0	0,978	101
123478-HxCDD	13C-123478-HxCDD	16,7	206	13848	1,530	25,0	0,146	102
123678-HxCDD	13C-123678-HxCDD	16,8	448	13860	1,530	25,0	0,325	105
123789-HxCDD	13C-123789-HxCDD	17,1	285	16082	1,530	25,0	0,190	108
234678-HxCDF	13C-234678-HxCDF	17,3	481	31127	1,530	25,0	0,229	103
1234678-HpCDF	13C-1234678-HpCDF	19,2	7133	33446	1,530	25,0	3,709	98
1234678-HpCDD	13C-1234678-HpCDD	20,4	2160	17238	1,530	25,0	1,607	95
1234789-HpCDF	13C-1234789-HpCDF	20,9	854	25776	1,530	25,0	0,494	97
OCDD	13C-OCDD	24,0	2767	13220	1,530	25,0	0,637	90
OCDF	13C-OCDF	24,1	3455	20369	1,530	25,0	2,439	89

Quantitation Resu
Compound

1234789-HpCDF	13C-1234789-HpCDF	20,9	854	25776	1,530	25,0	0,494	97
OCDD	13C-OCDD	24,0	2767	13220	1,530	25,0	0,637	90
OCDF	13C-OCDF	24,1	3455	20369	1,530	25,0	2,439	89

Report 2

Polychlorierte Dibenzodioxine, -furane (PCDD/F) und polychlorierte Biphenyle mit PCDD/F-ähnlicher Toxizität

Messung in: (•) Fett ( ) AGF / Frischsub. ( ) Trockenmasse

Matrix: (•) Lebensmittel ( ) Futtermittel

LIMS-Ausgabe: (•) Spalte B ( ) Spalte C

Probe:	**2017-0014609**
Datum:	26.1.2017
Einwaage in g	1,84
Fettgehalt in %	**9,10**
Trockenmasse in %	

geprüft und in LIMS übertragen:

erzeuge LIMS-Daten

☑ unauffällig ☐ auffällig ☐ beanstandet

dioxine und -furane (PCDD/F-TEQ)

	Werte in pg/g bezogen auf	Werte in pg/g bezogen auf
	Fett	Angebotsform
(WHO-TEF 2005) lower bound	5,5580	0,506
(WHO-TEF 2005) medium bound	5,5580	0,506
(WHO-TEF 2005) upper bound	**5,5580**	**0,506**
(WHO-TEF 1998) lower bound	6,7470	0,614
(WHO-TEF1998) medium bound	6,7470	0,614
(WHO-TEF 1998) upper bound	6,7470	0,614
(NATO 1988) lower bound	6,5350	0,595
(NATO 1988) medium bound	6,5350	0,595

Polychlorierte Biphenyle (WHO-non-ortho-PCB-TEQ)

	Werte in pg/g bezogen auf	Werte in pg/g bezogen auf
	Fett	Angebotsform
(WHO-TEF 2005) upper bound	1,6200	0,147
(WHO-TEF 1998) upper bound	1,5300	0,139

WHO-mono-ortho-PCB-TEQ

	Werte in pg/g bezogen auf	Werte in pg/g bezogen auf
	Fett	Angebotsform
(WHO-TEF 2005) upper bound	0,0550	0,005
(WHO-TEF 1998) upper bound	0,3000	0,027

Summe PCB-TEQ

	Werte in pg/g bezogen auf	Werte in pg/g bezogen auf
	Fett	Angebotsform
(WHO-TEF 2005) lower bound	1,6750	0,152
(WHO-TEF 2005) medium bound	1,6750	0,152
(WHO-TEF 2005) upper bound	**1,6750**	**0,152**
(WHO-TEF 1998) lower bound	1,8300	0,167
(WHO-TEF 1998) medium bound	1,8300	0,167
(WHO-TEF 1998) upper bound	1,8300	0,167

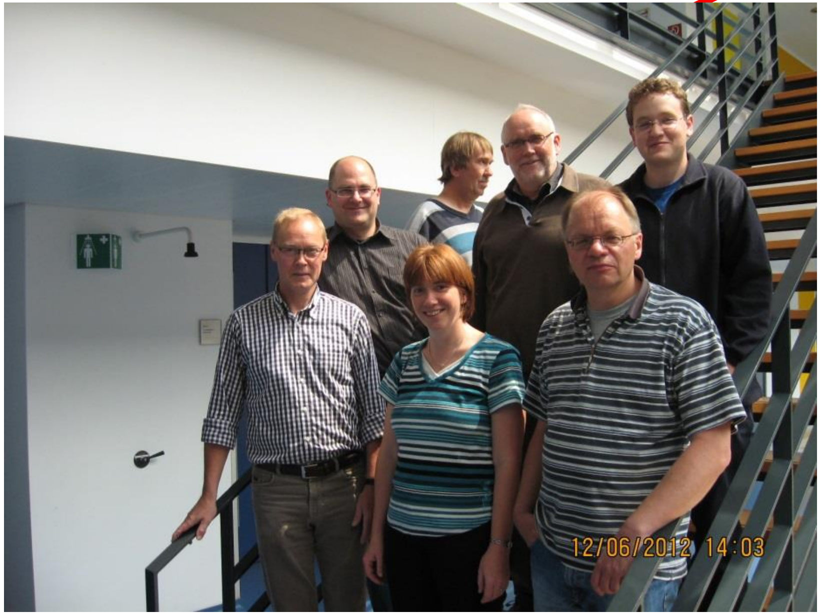
	Werte in pg/g bezogen auf	Werte in pg/g bezogen auf
	Fett	Angebotsform
(WHO-TEF 2005) lower bound	5,5580	0,506
(WHO-TEF 2005) medium bound	5,5580	0,506
(WHO-TEF 2005) upper bound	**5,5580**	**0,506**
(WHO-TEF 1998) lower bound	6,7470	0,614
(WHO-TEF1998) medium bound	6,7470	0,614
(WHO-TEF 1998) upper bound	6,7470	0,614
(NATO 1988) lower bound	6,5350	0,595
(NATO 1988) medium bound	6,5350	0,595

Summe PCB-TEQ

	Werte in pg/g bezogen auf	Werte in pg/g bezogen auf
	Fett	Angebotsform
(WHO-TEF 2005) lower bound	1,6750	0,152
(WHO-TEF 2005) medium bound	1,6750	0,152
(WHO-TEF 2005) upper bound	**1,6750**	**0,152**
(WHO-TEF 1998) lower bound	1,8300	0,167
(WHO-TEF 1998) medium bound	1,8300	0,167
(WHO-TEF 1998) upper bound	1,8300	0,167

Many thanks to the people „behind the work“

Dr. Michael Albrecht
Bavarian Health and Food Safety Authority



and
you for
your attention!

Dr. Thorsten Bernsmann
CVUA-MEL
Joseph-König-Straße 40
48147 Münster
Germany
+ 49 251-9821 217
thorsten.bernsmann@cvua-mel.de
www.cvua-mel.de