

SIMULTANEOUS ANALYSIS FOR DIOXINS, PCBS AND PBDES WITH A FULLY AUTOMATED SAMPLE PREPARATION SYSTEM

Hiroyuki FUJITA^{1*}, Takanori MAKINO¹,
Kenji INABA¹, Kazuki YAMAMOTO²

1: MIURA CO., LTD., 864-1, Hojotsuji, Matsuyama,
Ehime, 799-2430, JAPAN;

2: Ehime University, 3-5-7, Tarumi, Matsuyama,
Ehime, 790-8566, JAPAN;

Contact person; ➡



INTRODUCTION

We suggest a new simultaneous analysis for PCDDs / PCDFs / PCBs & PBDEs in food samples. In this presentation, we report a validated simultaneous analysis combined of the system and GC-HRMS for the monitoring of PCDDs / PCDFs / PCBs & PBDEs in food oil. This report mainly shows applications of the PBDEs measurement method with use of the system. Based on the results of quality control (QC) samples, real samples (unknown), procedure blanks, and certified reference material (CRM) samples, this report is discussed RSD, LOQ, trueness and recovery of PBDEs in PCB fractions obtained from the system.

CONCLUSIONS

The GO-HT system may perform simultaneous analysis of PBDEs together with dioxins and PCBs in food fat. Trueness obtained by use of CRM is within $\pm 20\%$. 209-decaBDE's blank is very low. The minimum recovery is 54% of 209-decaBDE. However, 209-decaBDE's recoveries in some of unknown samples are below 40%. We guess one reason why the low recovery is caused by purification shortage on purification columns. There is a necessary to keep studying ruggedness and stability of this simultaneous analysis.

SAMPLES AND STANDARD SOLUTIONS

Sample	ID Code	from	What for?
Cod Liver Oil	EDF-5462	CIL Inc.,	<i>Trueness, Repeatability, Recovery</i>
QC sample Fish Oil (Menhaden)	F8020-1L	SIGMA	
PFAD		an EU laboratory	
Pork fat	Freeze-dried & Soxhlet extracted (7:3/Tol:Ace) (in our laboratory)		<i>Ruggedness(minor changes), Recovery</i>
Egg fat			
Internal STD		Recovery STD	
Wellington Laboratories Inc., : BDE-CVS-G/MBDE-MXG-STK/MBDE-ISS-G-STK/BDE-MXE			
3L / 4-Br(¹³ C ₁₂)diphenyl ether	20 ppb	79L / 3,3',4,5'-Tetra-Br(¹³ C ₁₂)diphenyl ether	20 ppb
15L / 4,4'-DiBr(¹³ C ₁₂)diphenyl ether			
28L / 2,4,4'-TriBr(¹³ C ₁₂)diphenyl ether			
47L / 2,2',4,4'-TetraBr(¹³ C ₁₂)diphenyl ether			
99L / 2,2',4,4',5-PentaBr(¹³ C ₁₂)diphenyl ether			
100L / 2,2',4,4',6-PentaBr(¹³ C ₁₂)diphenyl ether	40 ppb	138L / 2,2',3,4,4',5'-Hexa-Br(¹³ C ₁₂)diphenyl ether	40 ppb
126L / 3,3',4,4',5-PentaBr(¹³ C ₁₂)diphenyl ether			
153L / 2,2',4,4',5,5'-HexaBr(¹³ C ₁₂)diphenyl ether			
154L / 2,2',4,4',5,6'-HexaBr(¹³ C ₁₂)diphenyl ether			
183L / 2,2',3,4,4',5',6-HeptaBr(¹³ C ₁₂)diphenyl ether			
197L / 2,2',3,3',4,4',6,6'-OctaBr(¹³ C ₁₂)diphenyl ether	100 ppb	206L / 2,2',3,3',4,4',5,5',6-Nona-Br(¹³ C ₁₂)diphenyl ether	100 ppb
207L / 2,2',3,3',4,4',5,6,6'-NonaBr(¹³ C ₁₂)diphenyl ether			
209L / DecaBr(¹³ C ₁₂)diphenyl ether			
Added amount 40 µL in Decane			

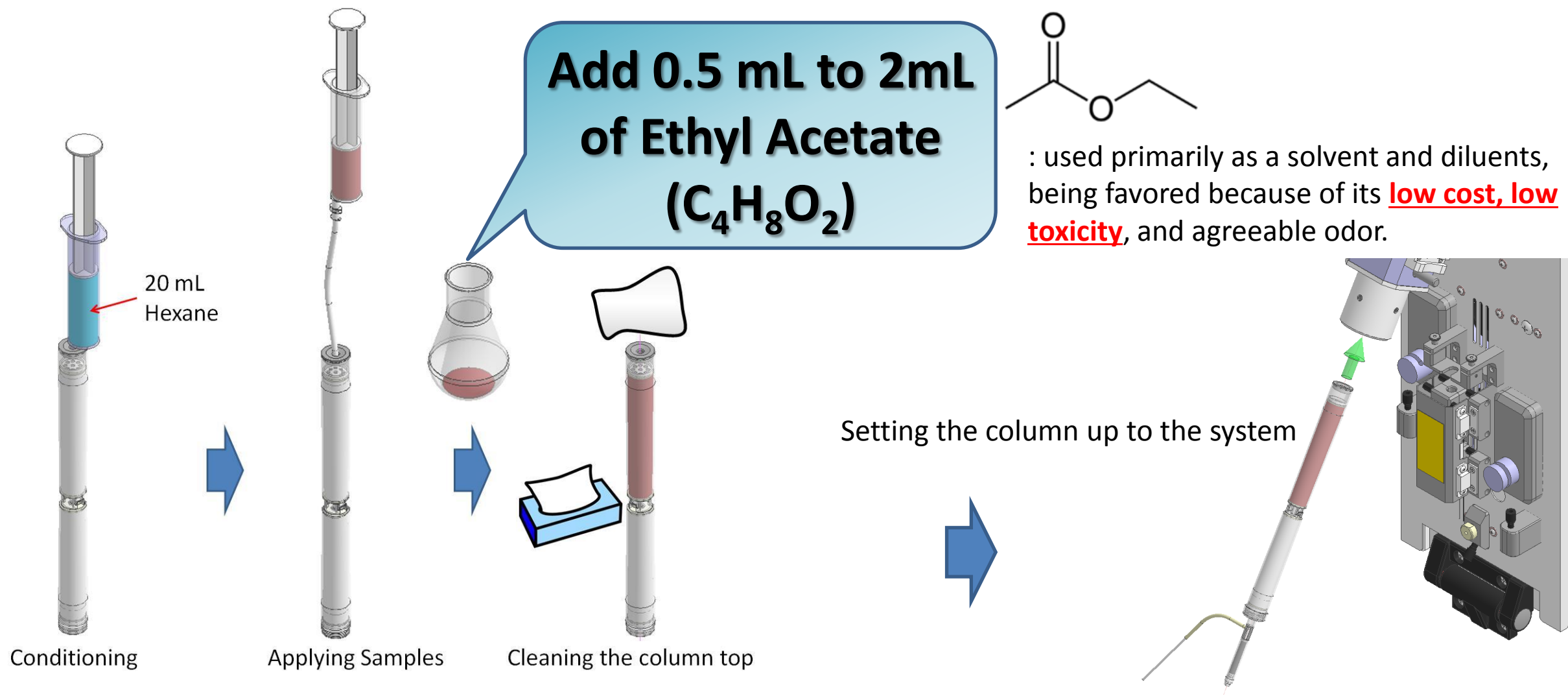
GC-MS CONDITIONS

Gas Chromatography Agilent 6890N GC	
Column	Non-polar fused silica capillary column 1.5m + DB-5HT (15m, 0.25mmID x 0.1µmFilmThickness)
GC temp. program	135°C(3min)→10°C/min → 215°C (0min) →5°C/min → 280°C (0min) →20°C/min → 325°C (3.75min)
Total Time	30 min
Inlet	Injection Vol.:2µL, 260°C, Splitless
Carrier Gas	He, Constant Flow1.2 mL/min
Transfer Line	Non-polar fused silica capillary column 1m, 280°C

Mass Spectrometer JMS-800 (JEOL Co., Ltd.)

Ionization		EI, Chamber Temperature 280°C, Voltage38eV, Emission Current 500µA, Maximum Acceleration Voltage 10kV				
	Gruop1 :	Gruop2 :	Gruop3 :	Gruop4 :	Gruop5 :	Gruop6 :
Start time [min]	3.0	5.2	8.8	13.6	22.1	27.0
MoBDEs	247.9837/249.9816					
¹³ C ₁₂ -MoBDEs	260.0239/262.0219					
DiBDEs		325.8942/327.8921				
¹³ C ₁₂ -DiBDEs		337.9344/339.9324				
TrBDEs			405.8027/407.8006			
¹³ C ₁₂ -TrBDEs			417.8429/419.8409			
TeBDEs			483.7132/485.7111			
¹³ C ₁₂ -TeBDEs			495.7534/497.7514			
PeBDEs				563.6216/565.6196		
¹³ C ₁₂ -PeBDEs				575.6619/577.6599		
HxBDEs				481.6976/483.6957		
¹³ C ₁₂ -HxBDEs				493.7379/495.7390		
HpBDEs				561.6060/563.6040		
¹³ C ₁₂ -HpBDEs				573.6462/575.6442		
OcBDEs					799.3510/801.3490	
¹³ C ₁₂ -OcBDEs					811.3912/813.3892	
NoBDEs					719.4250/721.4230	
¹³ C ₁₂ -NoBDEs					731.4652/733.4632	
DeBDE						797.3355/799.3335
¹³ C ₁₂ -DeBDE						809.3758/811.3737
Lock Mass	254.9856	342.9792	480.9697	554.9665	730.9537	780.9505

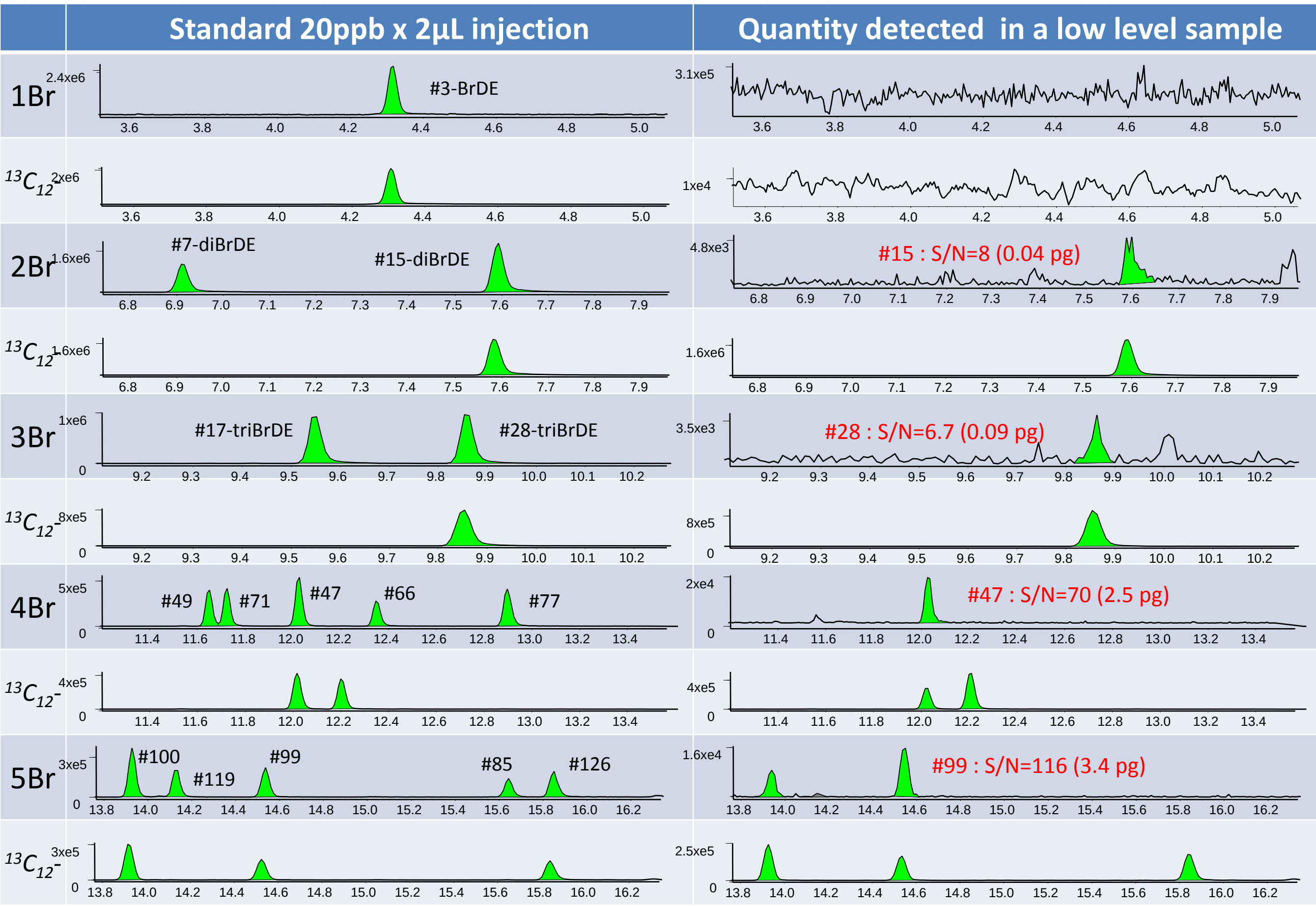
SAMPLE PREPARATION WITH THE SYSTEM



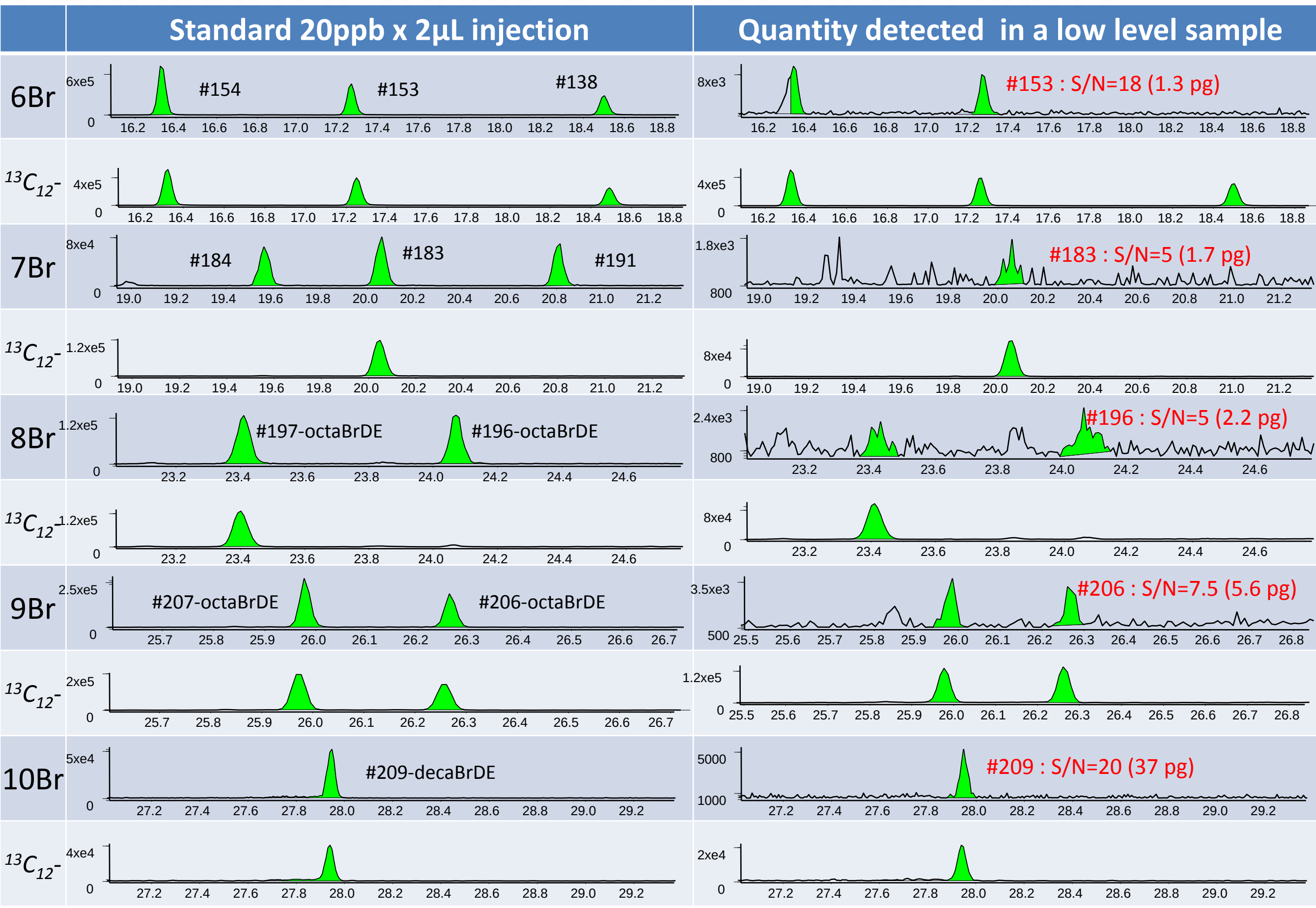
Because adsorption activity of the silica gel in the purification column is too strong for PBDEs, when applying sample, it is necessary to add a polar-solvent in the sample solutions, for example, Ethyl Acetate, Dichloromethane or Diethyl ether. Also, it is necessary to pay attention that additive amount of the polar solvents will vary depending on the sample volume as follows.

Conditioning of column	Fat Sample	Ethyl Acetate
15 to 20 mL of Hexane	$\leq 1\text{ g}$	2 mL
	$\geq 1\text{ g to }2.5\text{ g}$	1mL to 1.5 mL
	$\geq 2.5\text{ g to }3.5\text{ g}$	0.5 mL to less than 1 mL

CHROMATOGRAMS & DETECTION LIMITS



CHROMATOGRAMS & DETECTION LIMITS



VALIDATION RESULTS

pg/g fat

Sample	CIL EDF-5463 Cod liver oil 1 g										Blank		Egg fat
	Reference Value		Results by using GO-HT								AcEt 1mL	AcEt 2mL	Estimated LOQ
isomers	Assigned	± SD x 2	N=1	N=2	N=3	N=4	Average	SD	RSDr	Deviation	N=1	N=2	by S/N3 [pg]
#3-MoBDE	-	-	-	-	-	-	-	-	-	-	-	-	-
#15-DiBDE	-	-	2	2	2	2	2	0.2	10%	-	ND	ND	≤ 0.02 to 0.1
#17-TriBDE	8.83	± 5.76	6	7	8	8	7	0.7	10%	-19%	ND	ND	
#28-TriBDE	40.1	± 13.9	39	36	38	40	38	1.5	4%	-5%	ND	ND	
#47-TeBDE	1480	± 480	1511	1488	1436	1561	1499	51.8	3%	1%	ND	ND	
#66-TeBDE	48.4	± 29.4	44	45	58	53	50	6.7	13%	3%	ND	ND	≤ 0.1
#100-PeBDE	357	± 50.6	369	331	339	364	351	18.6	5%	-2%	ND	ND	
#99-PeBDE	193	± 70.4	157	166	156	163	161	4.9	3%	-17%	ND	ND	
#154-HxBDE	229	± 88.8	210	197	208	214	207	7.4	4%	-10%	ND	ND	
#153-HxBDE	33.9	± 6.64	32	34	29	33	32	2.1	7%	-5%	ND	ND	≤ 1-2
#183-HpBDE	-	-	13	10	11	11	11	0.8	7%	-	ND	ND	
#197-OcBDE	-	-	ND	ND	ND	ND	-	-	-	-	ND	ND	
#196-OcBDE	-	-	ND	ND	ND	ND	-	-	-	-	ND	ND	
#207-NoBDE	-	-	25.5	20.5	25.3	24.7	24	2.4	10%	-	ND	ND	
#206-NoBDE	-	-	30.0	29.5	27.3	35.6	31	3.5	12%	-	ND	ND	
#209-DeBDE	-	-	110	180	120	135	136	30.8	23%	-	ND	ND	≤ 5 to 10
Recovery													
#3-MoBDE	-	-	0.0	0.0	0.0	0.0					0.0	0.0	-
#15-DiBDE	-	-	80.1	77.3	79.9	82.0					76.4	84.1	-
#28-TriBDE	-	-	76.3	80.6	89.2	90.4					102.4	101.2	-
#47-TeBDE	-	-	57.5	55.4	100.5	98.9					93.8	95.2	-
#99-PeBDE	-	-	62.3	82.1	114.9	109.6					87.5	93.9	-
#154-HxBDE	-	-	65.0	68.7	94.9	98.6					89.2	84.4	-
#153-HxBDE	-	-	70.4	74.1	108.4	101.4					81.2	87.2	-
#183-HpBDE	-	-	84.8	89.8	107.7	100.9					85.7	96.4	-
#197-OcBDE	-	-	63.4	73.6	114.1	96.7					83.8	80.6	-
#207-NoBDE	-	-	69.0	66.9	92.0	90.3					84.4	91.9	-
#209-DeBDE	-	-	92.5	54.7	61.9	63.6					69.4	82.9	-