ANALYSING OF NON- AND MONO-ORTHO- PCBs, POLYCHLORINATED-P-DIOXIN AND POLYCHLORINATED FURANS FROM TURKEY AND SALMON MATRIXES.

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Introduction

The need for accurate determinations of polychlorinated-p-dioxin (PCDD), polychlorinated furans (PCDF) and non ortho- and mono-ortho-polychlorinated biphenyls (PCBs) are more important since the new EU legislation will soon include also the dioxin like PCBs. The legislation poses that the detection limit of determination must be for PCDD/PCDF 0.1 ng /kg fresh weight and for PCBs 1 ng /kg fresh weight. The samples used for determination of the PCDD, PCDF and non-ortho- and mono-ortho-PCBs were not fortified. The salmon and turkey samples were obtained from the food market and supplied by Norwegian Institute of Public Health. The capability of the in house method of VTT[1] for determination of PCDD/PCDF from food and feed samples using Accelerated Solvent Extraction (ASE) is demonstrated also for the PCBs.

Methods and Materials

Sample preparation included measuring the fat content of the two samples. The salmon sample and the turkey sample was each mixed with twice amount of sodium sulphate and then split into 12 equal specimens for ASE-extraction with hexane[2]. The internal standards were added by random to 4 of the extraction cells (10 µl ^{13}C-labelled PCDD/PCDF standard solution (16 out of 17 possible congeners) to each cell, total of 40 µl and 10 µl of ^{13}C-labelled PCB standard solution (12 compounds) to 1 cell). The twelve extracts were combined and evaporated to determine the fat content of the sample. The certified standards (CRM-614) used were: Solutions S 0-S 5 for calculation of response factors and testing the mass spectrometer linearity, internal standard solutions S 6, S 7 for quantitation and solution S 8 for recovery calculations of added ^{13}C-labeled standards. The ^{13}C-labelled PCB standard solution contained the reported 12 PCB compounds. The clean up consisted of basic silica/silica (fish column, AX-21 activated carbon on glass fibre[3] followed by basic alumina (ICN, Super grade I). The non-ortho-PCB samples were analysed after additional basic alumina clean up (dichloromethane PCB-fraction from AX-21 column).
Gas chromatographic-high resolution mass spectrometry-selected ion monitoring (GC-HRMS-SIM) analyses were performed on a JEOL SX-102 double focusing mass spectrometer equipped with a HP-5890 GC Series II. The ionization current was 600 µA, ionization voltage 40 eV. The resolution used was 9000-10000. The capillary column used was a Supelco EQUITY 5 (60 m, 0.25 mm id, 0.25 µm phase thickness). The gas chromatographic conditions used were, injection temperature 290 ° C, split less injection 1.0 minute, transfer line temperature 290 ° C and source temperature 250 ° C. Helium (purity grade ≥ 4.6) and an injection pressure about 30 psi (at 180 °C oven temperature) was used. The oven temperature program used was, 180 °C (2 min)-4 ° C/min-220 °C(12 min)-5 °C/min-235 ° C(7 min)- 5 ° C/min-330 ° C(2 min). Total runtime was 55.0 minutes.

Results and Discussion

The turkey and salmon samples were analysed and the fore coming limits of determination were reached. The results were calculated both on fresh weight and on lipid bases. The need to take part in these kind of interlaboratory studies increase as we go down in detection limits. It is necessary to prove that the results of each laboratory correlate with the results of other accredited laboratories. The results are presented in tables 1 and 2.

Table 1. The content of WHO-toxicity equivalents in turkey, ng / kg fresh weight.

Congener	pg/g fresh weight		pg/g lipid			WHO-	T-175	T-175
	Level	LOD	Level	LOD	Com.	TEF	pg/g fresh	pg/g lipid
2,3,7,8-TCDD	0.12	0.02	2.8	1.0		1	0.12	2.8
1,2,3,7,8-PeCDD	0.095	0.02	2.2	1.0		1	0.095	2.2
1,2,3,4,7,8-HxCDD	0.046	0.02	1.1	1.0		0.1	0.0046	0.11
1,2,3,6,7,8-HxCDD	0.046	0.02	1.1	1.0		0.1	0.0046	0.11
1,2,3,7,8,9-HxCDD	0.02	0.02	1.0	1.0	N.D.	0.1	0.002	0.1
1,2,3,4,6,7,8-HpCDD	0.27	0.1	6.1	2.0		0.01	0.0027	0.061
1,2,3,4,6,7,8,9-OCDD	1.2	0.1	28	2.0		0.0001	0.00012	0.0028
2,3,7,8-TCDF	0.02	0.02	1.0	1.0	N.D.	0.1	0.002	0.1
1,2,3,7,8-PeCDF	0.02	0.02	1.0	1.0	N.D.	0.05	0.001	0.05
2,3,4,7,8-PeCDF	0.02	0.02	1.0	1.0	N.D.	0.05	0.001	0.05
1,2,3,4,7,8-HxCDF	0.02	0.02	1.0	1.0	N.D.	0.1	0.002	0.1
1,2,3,6,7,8-HxCDF	0.02	0.02	1.0	1.0	N.D.	0.1	0.002	0.1
2,3,4,6,7,8-HxCDF	0.02	0.02	1.0	1.0	N.D.	0.1	0.002	0.1
1,2,3,7,8,9-HxCDF	0.02	0.02	1.0	1.0	N.D.	0.1	0.002	0.1
1,2,3,4,6,7,8-HpCDF	0.27	0.1	6.2	2.0		0.01	0.0027	0.062
1,2,3,4,7,8,9-HpCDF	0.1	0.1	2.0	2.0	N.D.	0.01	0.001	0.02
1,2,3,4,6,7,8,9-OCDF	0.26	0.1	5.9	2.0		0.0001	0.000026	0.0006
PCB 77	4.8	1.0	111	20		0.0001	0.00048	0.011
PCB 126	1.0	1.0	20	20	N.D.	0.1	0.1	2.0
PCB 169	1.0	1.0	20	20	N.D.	0.01	0.01	0.2
PCB 81	1.0	1.0	20	20	N.D.	0.0001	0.0001	0.002
PCB 105	24	1.0	547	20		0.0001	0.0024	0.055
PCB 114	1.0	1.0	20	20	N.D.	0.0005	0.0005	0.01
PCB 118	39	1.0	893	20		0.0001	0.0039	0.089
PCB 123	2.0	1.0	46	20		0.0001	0.00020	0.0046
PCB 156	11	1.0	247	20		0.0005	0.0054	0.12
PCB 157	1.5	1.0	34	20		0.0005	0.00074	0.017
PCB 167	5.0	1.0	116	20		0.00001	0.00005	0.0012
PCB 189	1.2	1.0	28	20		0.0001	0.00012	0.0028
					Sum	TEF	0.37	8.6
Sample intake (g)	110.1							
Lipid intake (g)	4.7727							
Measured lipid Content (%)	4.33							

Table 2. The content of WHO-toxicity equivalents in salmon, ng / kg fresh weight.

Congener	pg/g fresh weight		pg/g lipid			WHO-	S-013	S-013
	Level	LOD	Level	LOD	Com.	TEF	pg/g fresh	pg/g lipid
2,3,7,8-TCDD	0.43	0.02	4.2	1.0		1	0.43	4.2
1,2,3,7,8-PeCDD	0.82	0.02	8.0	1.0		1	0.82	8.0
1,2,3,4,7,8-HxCDD	0.02	0.02	1.0	1.0	N.D.	0.1	0.002	0.1
1,2,3,6,7,8-HxCDD	0.42	0.02	4.1	1.0		0.1	0.042	0.41
1,2,3,7,8,9-HxCDD	0.02	0.02	1.0	1.0	N.D.	0.1	0.002	0.1
1,2,3,4,6,7,8-HpCDD	0.30	0.1	2.9	2.0		0.01	0.0030	0.029
1,2,3,4,6,7,8,9-OCDD	1.5	0.1	15	2.0		0.0001	0.0002	0.0014
2,3,7,8-TCDF	7.6	0.02	74	1.0		0.1	0.76	7.4
1,2,3,7,8-PeCDF	1.3	0.02	12	1.0		0.05	0.063	0.61
2,3,4,7,8-PeCDF	6.4	0.02	63	1.0		0.05	0.32	3.1
1,2,3,4,7,8-HxCDF	0.13	0.02	1.3	1.0		0.1	0.013	0.13
1,2,3,6,7,8-HxCDF	0.21	0.02	2.0	1.0		0.1	0.021	0.20
2,3,4,6,7,8-HxCDF	0.12	0.02	1.1	1.0		0.1	0.012	0.11
1,2,3,7,8,9-HxCDF	0.02	0.02	1.0	1.0	N.D.	0.1	0.002	0.1
1,2,3,4,6,7,8-HpCDF	0.67	0.1	6.6	2.0		0.01	0.0067	0.065
1,2,3,4,7,8,9-HpCDF	0.1	0.1	2.0	2.0	N.D.	0.01	0.001	0.02
1,2,3,4,6,7,8,9-OCDF	0.46	0.1	4.4	2.0		0.0001	4.6e-5	0.0004
PCB 77	192	1.0	1872	20		0.0001	0.019	0.19
PCB 126	61	1.0	592	20		0.1	6.1	59
PCB 169	13	1.0	124	20		0.01	0.13	1.2
PCB 81	2.9	1.0	29	20		0.0001	0.0003	0.0029
PCB 105	3212	1.0	31332	20		0.0001	0.32	3.1
PCB 114	124	1.0	1213	20		0.0005	0.062	0.61
PCB 118	5384	1.0	52519	20		0.0001	0.54	5.3
PCB 123	230	1.0	2245	20		0.0001	0.023	0.22
PCB 156	1593	1.0	15540	20		0.0005	0.80	7.8
PCB 157	376	1.0	3668	20		0.0005	0.19	1.8
PCB 167	1675	1.0	16339	20		0.00001	0.017	0.16
PCB 189	158	1.0	1546	20		0.0001	0.016	0.15
					Sum of	TEF	10.7	104
Sample intake (g)	54.06							
Lipid intake (g)	5.5416							
Measured lipid Content (%)	10.25							

The limit of determination for the method for PCDD/PCDF was 0.02 (tetra-, penta- and hexa-PCDD/PCDF) ng/kg fresh weight, 0.1 (hepta- and octa-PCDD/PCDF) ng/kg fresh weight and for PCBs 1.0 ng/kg fresh weight.

The method performed well for all tested samples. The AX-21 activated carbon glass fibre column has the advantages of, very low background, repeated usability (tested for more than 30 samples) and good performance for samples containing high lipid levels (10 g).
The turkey and salmon samples analysed showed that the method work well with the two different food samples with significantly different fat contents. The extraction of fat using n-hexane is efficient and the added ^{13}C-labelled internal standards have recoveries of 80-110 %.

Tabel 3. The recoveries of some of the ^{13}C-labelled internal standard compounds added prior to the extraction. Matrix solution is shown only as a comparison. It shows typical recoveries of ^{13}C-labelled compounds in a standard solution.

Dioxins and furans	T-175 recovery %	S-013 recovery %	Matrix solution recovery %
13C12-2,3,7,8-TCDD	94	82	110
13C12-1,2,3,7,8-PeCDD	107	86	105
13C12-1,2,3,4,7,8-HxCDD	114	105	106
13C12-1,2,3,6,7,8-HxCDD	113	106	103
13C12-1,2,3,4,6,7,8-HpCDD	94	83	103
13C12-1,2,3,4,6,7,8,9-OCDD	90	85	108
13C12-2,3,7,8-TCDF	99	89	112
13C121,2,3,7,8-PeCDF	101	88	117
13C12-2,3,4,7,8-PeCDF	101	88	117
13C12-1,2,3,4,7,8-HxCDF	116	117	113
13C12-1,2,3,6,7,8-HxCDF	125	123	117
13C12-2,3,4,6,7,8-HxCDF	107	98	109
13C12-1,2,3,7,8,9-HxCDF	107	98	109
13C12-1,2,3,4,6,7,8-HpCDF	110	104	113
13C12-1,2,3,4,7,8,9-HpCDF	110	104	113

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