

表4 高速加熱流下抽出と従来法におけるダイオキシン類異性体定量値の比較

Dioxins	スズキ (n=3)														
	プリ (n=3)					アルカリ分解・溶媒抽出 (A)					アルカリ分解・溶媒抽出 (B)				
	定量下限値 pg/g	高速加熱流下抽出 Mean±SD, pg/g	RSD, %	アルカリ分解・溶媒抽出 (B) Mean±SD, pg/g	RSD, %	比率 (A/B)	高速加熱流下抽出 (A) Mean±SD, pg/g	RSD, %	アルカリ分解・溶媒抽出 (B) Mean±SD, pg/g	RSD, %	比率 (A/B)				
2378-TCDD	0.014	0.13 ± 0.010	7.7	0.13 ± 0.010	7.7	1.0	0.11 ± 0.012	10.5	0.12 ± 0.020	16.7	0.9				
12378-PeCDD	0.022	0.27 ± 0.010	3.7	0.27 ± 0.020	7.4	1.0	0.19 ± 0.021	11.0	0.19 ± 0.025	13.2	1.0				
123478-HxCDD	0.038	tr <sup>1)</sup>	-	tr	-	-	nd	-	nd	-	-				
123678-HxCDD	0.035	0.11 ± 0.0058	5.2	0.12 ± 0.010	8.3	0.9	0.14 ± 0.021	14.9	0.13 ± 0.015	11.8	1.1				
123789-HxCDD	0.034	tr	-	tr	-	-	nd	-	nd	-	-				
1234678-HpCDD	0.030	0.079 ± 0.0031	3.9	0.077 ± 0.0066	8.5	1.0	0.046 ± 0.0081	17.6	0.049 ± 0.013	26.2	0.9				
OCDD	0.11	0.15 ± 0.023	15.4	0.14 ± 0.0	0.0	1.1	tr	-	tr	-	-				
2378-TCDF	0.0059	2.1 ± 0.12	5.5	1.9 ± 0.0	0.0	1.1	0.6 ± 0.057	10.2	0.6 ± 0.030	5.2	1.0				
12378-PeCDF	0.010	0.28 ± 0.010	3.6	0.27 ± 0.012	4.3	1.0	0.11 ± 0.017	15.7	0.11 ± 0.0	0.0	1.0				
23478-PeCDF	0.0069	0.91 ± 0.035	3.9	0.96 ± 0.010	1.0	0.9	0.48 ± 0.035	7.3	0.49 ± 0.020	4.1	1.0				
123478-HxCDF	0.014	0.052 ± 0.0091	17.4	0.050 ± 0.012	24.2	1.0	0.034 ± 0.0055	16.2	0.032 ± 0.0021	6.5	1.1				
123678-HxCDF	0.017	0.058 ± 0.0035	6.0	0.057 ± 0.0081	14.2	1.0	0.034 ± 0.0058	17.0	0.034 ± 0.0030	8.8	1.0				
123789-HxCDF	0.025	nd <sup>2)</sup>	-	nd	-	-	nd	-	nd	-	-				
234678-HxCDF	0.019	0.060 ± 0.0012	1.9	0.055 ± 0.0070	12.7	1.1	0.044 ± 0.0060	13.6	0.044 ± 0.0070	15.9	1.0				
1234678-HpCDF	0.040	tr	-	tr	-	-	tr	-	tr	-	-				
1234789-HpCDF	0.031	nd	-	nd	-	-	nd	-	nd	-	-				
OCDF	0.044	nd	-	nd	-	-	nd	-	nd	-	-				
33'44'-TCB (#77)	0.18	84 ± 2.1	2.5	83 ± 2.1	2.5	1.0	120 ± 10	8.3	130 ± 5.8	4.4	0.9				
344'5'-TCB (#81)	0.045	4.5 ± 0.058	1.3	4.4 ± 0.20	4.5	1.0	4.8 ± 0.46	9.5	4.8 ± 0.40	8.4	1.0				
33'44'5'-PeCB (#126)	0.018	22 ± 0.58	2.6	21 ± 0.58	2.7	1.0	19 ± 1.2	6.0	21 ± 1.5	7.3	0.9				
33'44'5'5'-HxCB (#169)	0.033	3.0 ± 0.058	1.9	3.0 ± 0.058	1.9	1.0	1.9 ± 0.15	8.2	1.9 ± 0.20	10.5	1.0				
233'44'-PeCB (#105)	1.4	910 ± 25	2.8	920 ± 12	1.3	1.0	3200 ± 210	6.5	3000 ± 170	5.8	1.1				
2344'5'-PeCB (#114)	0.51	62 ± 4.7	7.6	61 ± 2.6	4.3	1.0	230 ± 21	9.1	230 ± 10	4.3	1.0				
23'44'5'-PeCB (#118)	2.9	2800 ± 0	0.0	2800 ± 58	2.1	1.0	11000 ± 580	5.2	11000 ± 580	5.2	1.0				
2'344'5'-PeCB (#123)	0.52	45 ± 0.58	1.3	44 ± 2.1	4.7	1.0	190 ± 12	6.1	180 ± 25	14.0	1.1				
233'44'5'-HxCB (#156)	0.85	290 ± 5.8	2.0	290 ± 5.8	2.0	1.0	320 ± 64	7.8	310 ± 64	7.8	1.0				
233'44'5'-HxCB (#157)	0.76	84 ± 1.7	2.1	84 ± 2.0	2.4	1.0	200 ± 15	7.6	190 ± 15	8.0	1.1				
23'44'5'5'-HxCB (#167)	0.70	190 ± 0	0.0	180 ± 5.8	3.2	1.1	410 ± 50	12.2	400 ± 25	6.3	1.0				
233'44'5'5'-HpCB (#189)	2.2	31 ± 1.2	3.7	29 ± 1.5	5.3	1.1	45 ± 5.6	12.4	47 ± 4.0	8.6	1.0				

1) tr: trace (抽出下限 ≤ tr < 定量下限)

2) nd: not detected

表5 ASEと従来法による乾海苔試料中ダイオキシン類の定量値比較結果 (pg/g)

化合物	ASE (n=4)				振とう抽出 (n=4)				a/b
	範囲	平均 <sup>a</sup>	RSD(%)	範囲	平均 <sup>b</sup>	RSD(%)			
2,3,7,8-TeCDD	0.010 - 0.021	0.016	37	0.013 - 0.017	0.015	12	1.1		
1,2,3,7,8-PeCDD	0.011 - 0.017	0.014	19	(0.009) - 0.013	0.011	17	1.3		
1,2,3,7,8,9-HxCDD	0.026 - 0.031	0.028	8	0.013 - 0.015	0.013	7	2.1		
1,2,3,4,6,7,8-HpCDD	0.40 - 0.47	0.44	8	0.18 - 0.19	0.19	1	2.4		
OCDD	3.1 - 3.5	3.2	6	0.95 - 1.1	1.0	7	3.2		
2,3,7,8-TeCDF	0.029 - 0.038	0.033	11	0.020 - 0.026	0.023	12	1.4		
1,2,3,7,8-PeCDF	0.023 - 0.029	0.027	9	0.017 - 0.023	0.019	15	1.4		
2,3,4,7,8-PeCDF	0.016 - 0.018	0.017	7	(0.009) - 0.012	0.011	13	1.6		
1,2,3,4,7,8-HxCDF	0.023 - 0.033	0.026	20	(0.011) - 0.015	0.014	13	1.9		
1,2,3,4,6,7,8-HpCDF	0.075 - 0.076	0.075	1	0.033 - 0.041	0.037	10	2.1		
OCDF	0.047 - 0.057	0.051	10	0.021 - 0.026	0.023	11	2.2		
3,3',4,4'-TeCB(#77)	0.99 - 1.0	1.0	5	0.87 - 0.90	0.88	5	1.1		
3,4,4',5'-TeCB(#81)	0.15 - 0.17	0.16	2	0.12 - 0.14	0.13	1	1.2		
2,3,3',4,4'-PeCB(#105)	1.7 - 1.9	1.8	3	1.5 - 1.61	1.6	4	1.2		
2,3,4,4',5'-PeCB(#114)	0.36 - 0.43	0.38	9	0.28 - 0.32	0.30	6	1.2		
2,3',4,4',5'-PeCB(#118)	4.2 - 4.5	4.4	3	3.6 - 3.9	3.8	3	1.2		
2',3,4,4',5'-PeCB(#123)	0.14 - 0.17	0.15	9	(0.10) - 0.18	0.13	26	1.1		
2,3,3',4,4',5'-HxCB(#156)	0.26 - 0.35	0.30	14	0.23 - 0.29	0.25	11	1.2		
2,3',4,4',5,5'-HxCB(#167)	0.089 - 0.13	0.11	16	(0.057) - 0.10	0.084	23	1.3		

カッコ内の数値は検出下限未満の濃度を暫定値として示した。

表6 ASEと従来法によるマグロ試料中ダイオキシン類の定量値比較結果 (pg/g)

化合物	ASE (n=4)				アルカリ分解・溶媒抽出 (n=4)				a / b
	範囲	平均 <sup>a</sup>	RSD(%)	範囲	平均 <sup>b</sup>	RSD(%)			
2,3,7,8-TeCDD	0.61 - 0.67	0.64	4	0.60 - 0.72	0.67	7	0.96		
1,2,3,7,8-PeCDD	0.75 - 0.83	0.80	5	0.76 - 0.80	0.77	3	1.0		
1,2,3,4,7,8-HxCDD	0.023 - 0.035	0.028	19	0.020 - 0.030	0.024	16	1.2		
1,2,3,6,7,8-HxCDD	0.20 - 0.22	0.21	5	0.20 - 0.22	0.21	4	0.99		
1,2,3,7,8,9-HxCDD	0.026 - 0.037	0.032	17	0.022 - 0.028	0.025	12	1.2		
1,2,3,4,6,7,8-HpCDD	0.058 - 0.067	0.065	7	0.055 - 0.058	0.057	2	1.1		
OCDD	0.15 - 0.17	0.16	6	0.070 - 0.094	0.081	13	2.0		
2,3,7,8-TeCDF	4.4 - 5.5	5.0	9	4.8 - 5.3	5.1	5	0.98		
1,2,3,7,8-PeCDF	0.92 - 1.1	0.99	6	0.94 - 1.0	0.96	3	1.0		
2,3,4,7,8-PeCDF	2.7 - 3.1	2.9	5	2.7 - 2.8	2.7	2	1.1		
1,2,3,4,7,8-HxCDF	0.15 - 0.21	0.19	14	0.15 - 0.25	0.18	26	1.1		
1,2,3,6,7,8-HxCDF	0.14 - 0.21	0.18	19	0.17 - 0.21	0.18	11	1.0		
1,2,3,7,8,9-HxCDF	0.11 - 0.15	0.13	14	0.12 - 0.14	0.13	7	1.0		
2,3,4,6,7,8-HxCDF	ND	ND	-	ND	ND	-	-		
1,2,3,4,6,7,8-HpCDF	0.067 - 0.079	0.072	7	0.050 - 0.063	0.055	11	1.3		
1,2,3,4,7,8,9-HpCDF	ND	ND	-	ND	ND	-	-		
OCDF	ND	ND	-	ND	ND	-	-		
3,3',4,4'-TeCB(#77)	218 - 271	244	9	259 - 278	267	3	0.91		
3,3',4,5'-TeCB(#81)	17 - 21	19	9	20 - 21	20	1	0.94		
3,3',4,4',5'-PenCB(#126)	214 - 247	230	6	229 - 237	233	1	0.99		
3,3',4,4',5,5'-HxCB(#169)	26 - 29	27	5	28 - 28	28	1	0.97		
2,3,3',4,4'-PeCB(#105)	60000 - 72000	64000	9	50000 - 68000	61000	14	1.1		
2,3,4,4',5'-PeCB(#114)	2700 - 3400	3100	10	2700 - 2900	2800	4	1.1		
2,3',4,4',5'-PeCB(#118)	100000 - 12000	110000	6	110000 - 130000	120000	8	0.96		
2',3,4,4',5'-PeCB(#123)	2600 - 4100	3600	19	1900 - 3700	2700	27	1.4		
2,3,3',4,4',5'-HxCB(#156)	31000 - 37000	36000	9	32000 - 42000	39000	12	0.92		
2,3,3',4,4',5'-HxCB(#157)	8500 - 10000	9400	8	8000 - 11000	9700	13	0.97		
2,3',4,4',5,5'-HxCB(#167)	20000 - 23000	22000	7	20000 - 25000	23000	11	0.96		
2,3,3',4,4',5,5'-HpCB(#189)	4900 - 5900	5600	8	4400 - 5300	5000	9	1.1		

表7 魚油を使用した健康食品中の臭素化ダイオキシン類及びその関連化合物並びに塩素化ダイオキシン類の汚染濃度<sup>1)</sup>

測定対象物	製品 No.1 (A)	製品 No.1 (B)	製品 No.3	製品 No.5	製品 No.6
	測定値	測定値	測定値	測定値	測定値
臭素化・臭素系ダイオキシン類 (pgTEQ/g) <sup>2)</sup>	0 (1.3) <sup>3)</sup>	0 (1.3)	0.13 (0.48)	0 (1.3)	0.12 (0.47)
臭素化ジフェニルエーテル (pg/g)	210000	150000	1800	550	5700
ポリ塩化ビフェニル (ng/g)	18000	10000	140	52	110
塩素化ダイオキシン類 (pgTEQ/g) <sup>4)</sup>	510	250	9.9	3.3	7.0

- 1) 製品No.1(A)と(B)は購入時期が異なるため、賞味期限が異なる製品  
2) 対応する塩素化ダイオキシン類のTEFを使用し毒性等量濃度を算出  
3) 括弧内はND=1/2LOD, Tr=1/2LOQとして計算した値  
4) 別途調査した結果より引用

表 8 5 地域における臭素系ダイオキシン類及び臭化ジフェニルエーテルの一日摂取量総括表

	異柱体													合計
	1 群	2 群	3 群	4 群	5 群	6 群	7 群	8 群	9 群	10 群	11 群	12 群	13 群	
群別一日食事量 (g)	376.1	151.3	27.7	9.0	64.2	151.6	103.4	201.5	581.8	108.5	109.9	151.7	111.6	2148.3
PBDD/DFs, MeBrPCDD/DFs Total TEQ (ND=0) pgTEQ/day	0	0	0	0.013	0	0	0	0	0	0	0	0	0	0.013
PBDD/DFs, MeBrPCDD/DFs Total TEQ (ND=1/2LOD) pgTEQ/day	19.3	9.8	1.3	0.3	2.3	5.3	4.2	8.4	20.4	5.3	5.1	6.0	8.2	95.9
Total PBDEs (ND=0) ng/day	1.4	4.0	0.7	10.7	0.9	1.1	1.3	0.7	1.2	60.0	9.5	0.6	15.6	107.8
Total PBDEs (ND=1/2) ng/day	2.2	4.2	0.7	10.7	1.0	1.3	1.4	1.0	1.8	60.1	9.5	0.9	15.7	110.7
<b>(1) 中国四国地区</b>														
<b>(2) 関東地区</b>														
群別一日食事量 (g)	333.1	183.3	36.3	12.5	58.1	138.5	111.9	215.3	586.5	93.3	166.4	165.5	89.4	2190.1
PBDD/DFs, MeBrPCDD/DFs Total TEQ (ND=0) pgTEQ/day	0	0	0	0.021	0	0	0	0	0	0	0	0	0	0.021
PBDD/DFs, MeBrPCDD/DFs Total TEQ (ND=1/2LOD) pgTEQ/day	13.7	8.3	1.3	0.5	2.0	4.8	4.0	7.5	20.5	3.1	3.7	5.8	3.1	78.3
Total PBDEs (ND=0) ng/day	6.4	4.2	2.0	33.1	1.5	1.2	0.9	0.5	2.6	75.4	9.0	1.3	1.6	139.7
Total PBDEs (ND=1/2) ng/day	6.8	4.3	2.1	33.1	1.5	1.4	1.0	0.9	3.2	75.4	9.1	1.5	1.7	142.0

(3) 北海道地区

異性体	1 群 2 群 3 群 4 群 5 群 6 群 7 群 8 群 9 群 10 群 11 群 12 群 13 群 合計													
	1 群	2 群	3 群	4 群	5 群	6 群	7 群	8 群	9 群	10 群	11 群	12 群	13 群	合計
群別一日食事量 (g)	340.1	190.4	30.4	11.1	43.9	135.4	85.4	211.2	412.8	120.2	105.6	193.8	90.3	1970.6
PBDD/DFs, MoBrPCDD/DFs Total TEQ (ND=0) pgTEQ/day	0	0	0	0.028	0	0	0	0	0	0	0	0	0	0.028
PBDD/DFs, MoBrPCDD/DFs Total TEQ (ND=1/2LOD) pgTEQ/day	11.9	14.2	1.5	0.4	1.6	4.7	2.7	7.1	14.4	5.3	4.8	6.8	3.2	78.6
Total PBDEs (ND=0) ng/day	3.7	3.4	2.8	13.2	0.5	0.05	0.06	0.06	0.2	50.4	13.5	4.1	4.2	96.0
Total PBDEs (ND=1/2) ng/day	4.1	4.0	2.8	13.2	0.5	0.3	0.2	0.5	1.0	50.6	13.5	4.2	4.3	99.1

(4) 東北地区

異性体	1 群 2 群 3 群 4 群 5 群 6 群 7 群 8 群 9 群 10 群 11 群 12 群 13 群 合計													
	1 群	2 群	3 群	4 群	5 群	6 群	7 群	8 群	9 群	10 群	11 群	12 群	13 群	合計
群別一日食事量 (g)	382.0	164.8	30.9	10.6	58.9	128.2	95.7	213.7	389.5	92.8	104.7	162.9	78.0	1912.7
PBDD/DFs, MoBrPCDD/DFs Total TEQ (ND=0) pgTEQ/day	0	0	0	0.033	0	0	0	0	0	0	0	0	0	0.033
PBDD/DFs, MoBrPCDD/DFs Total TEQ (ND=1/2LOD) pgTEQ/day	13.4	5.9	1.1	0.4	3.4	4.5	3.1	6.9	13.6	2.9	3.1	5.7	2.7	66.7
Total PBDEs (ND=0) ng/day	8.4	2.6	2.1	15.8	1.6	0.4	0.7	1.4	1.3	30.4	5.8	4.9	4.7	80.2
Total PBDEs (ND=1/2) ng/day	8.8	2.8	2.1	15.8	1.8	0.6	0.8	1.7	1.9	30.5	5.9	5.1	4.8	82.5

(5) 中部地区

異性体	1 群 2 群 3 群 4 群 5 群 6 群 7 群 8 群 9 群 10 群 11 群 12 群 13 群 合計													
	1 群	2 群	3 群	4 群	5 群	6 群	7 群	8 群	9 群	10 群	11 群	12 群	13 群	合計
群別一日食事量 (g)	346.4	171.1	35.6	10.3	59.7	130.2	92.3	196.2	499.2	89.0	110.3	177.5	81.5	1999.3
PBDD/DFs, MoBrPCDD/DFs Total TEQ (ND=0) pgTEQ/day	0	0	0	0.045	0	0	0	0	0	0	0	0	0	0.045
PBDD/DFs, MoBrPCDD/DFs Total TEQ (ND=1/2LOD) pgTEQ/day	18.4	9.1	1.7	0.4	2.2	4.6	2.8	6.6	17.5	3.9	4.4	6.2	2.8	80.6
Total PBDEs (ND=0) ng/day	1.2	2.3	3.8	31.8	3.0	0.2	0.3	0.4	0.9	26.7	7.6	3.0	16.5	97.7
Total PBDEs (ND=1/2) ng/day	2.0	2.6	3.9	31.8	3.1	0.4	0.4	0.7	1.7	26.8	7.7	3.1	16.5	100.8

\* 10 群、11 群、12 群は、A と B の平均値を示す。

表9 魚介類中臭素系ダイオキシン類、臭素化ジフェニルエーテル、  
四臭素化ビスフェノールAの総括表

購入場所	No.	魚名	天然・養殖の別	脂肪含量 (%)	臭素系ダイオキシン類	臭素化ジフェニルエーテル	四臭素化ビスフェノールA
					pgTEQ/g wb	ng/g wb	ng/g wb
九州	1	マアジ	天然	5.67	ND	0.28	0.02
	2	アナゴ	天然	7.52	ND	0.11	0.03
	3	アラカブ	天然	0.37	ND	0.05	0.03
	4	ヤリイカ	天然	0.38	ND	0.17	0.01
	5	ユバイワシ	天然	0.74	ND	0.13	0.11
	6	エビ足赤	天然	0.19	ND	0.01	0.02
	7	カマス	天然	9.88	ND	0.70	0.04
	8	キビナゴ	天然	1.82	ND	0.09	ND
	9	クツゾコ	天然	1.42	ND	0.08	0.01
	10	マサバ	天然	20.45	ND	0.30	0.01
	11	タイ	天然	1.01	ND	0.05	0.02
	12	タチウオ	天然	0.33	ND	0.11	ND
	13	ツケアミ	加工食品	1.02	ND	0.05	0.01
	14	ヒラメ	天然	0.30	ND	0.04	0.02
	15	モチ魚	天然	3.93	ND	0.06	0.01
			平均値		3.67	0.035*	0.15
中国・四国	1	地アジ	天然	2.28	ND	0.12	ND
	2	アナゴ	天然	12.65	0.007	0.31	0.10
	3	エビ	天然	0.49	ND	0.01	ND
	4	カキ	養殖	2.26	ND	0.05	ND
	5	カレイ	天然	0.35	0.004	0.03	0.03
	6	グタ	天然	0.35	0.001	0.02	0.02
	7	サゴシ	天然	1.91	0.002	0.41	ND
	8	サヨリ	天然	0.92	ND	0.11	ND
	9	マダイ	天然	1.10	0.017	0.05	0.02
	10	マダイ	養殖	7.11	0.003	0.30	0.01
	11	イイダコ	天然	0.26	ND	0.02	0.01
	12	ハモ	天然	3.40	0.256	0.31	ND
	13	マグロ	天然	0.51	ND	0.04	0.01
	14	ママカリ	天然	4.53	0.001	0.53	ND
	15	メバル	天然	0.50	ND	0.12	0.01
		平均値		2.58	0.054*	0.16	0.02*
中部	1	アジ	天然	4.72	ND	0.66	ND
	2	スルメイカ	天然	1.19	ND	0.06	ND
	3	カマス	天然	4.50	ND	0.53	0.01
	4	キス	天然	0.46	ND	0.03	ND
	5	サゴシ	天然	1.30	ND	0.41	0.01
	6	サバ	天然	13.65	ND	1.77	ND
	7	サワラ	天然	11.27	ND	2.88	0.04
	8	スズキ	天然	0.72	ND	0.33	ND
	9	セイゴ	天然	0.98	ND	0.18	0.04
	10	タイ	養殖	8.12	ND	0.68	0.01
	11	タイ	養殖	9.36	ND	0.42	0.03
	12	タイ	養殖	4.10	ND	0.19	0.01
	13	タコ	天然	0.35	ND	0.02	0.03
	14	ブリ	養殖	17.28	ND	2.81	ND
	15	ボラ	天然	1.69	ND	0.25	ND
		平均値		5.31	0.035*	0.75	0.01*
東北	1	スズキ1	天然	2.40	ND	0.40	NA
	2	スズキ2	天然	3.40	ND	0.38	
	3	スズキ3	天然	2.50	ND	0.37	
	4	スズキ4	天然	1.30	ND	0.20	
	5	スズキ5	天然	1.40	ND	0.21	
	6	サケ1	養殖	14.30	ND	1.23	
	7	サケ2	養殖	10.80	ND	1.32	
	8	サケ3	養殖	10.20	ND	1.16	
	9	サケ4	養殖	10.80	ND	1.62	
	10	サケ5	養殖	14.50	ND	1.37	
		平均値		7.16	0.035*	0.83	
		最大値		20.45	0.256	2.88	0.11
		最小値		0.19	ND	0.01	ND
		平均値		4.45	0.040*	0.44	0.02*

\* : ND=1/2LODとして計算した。  
NAは未分析を示す。

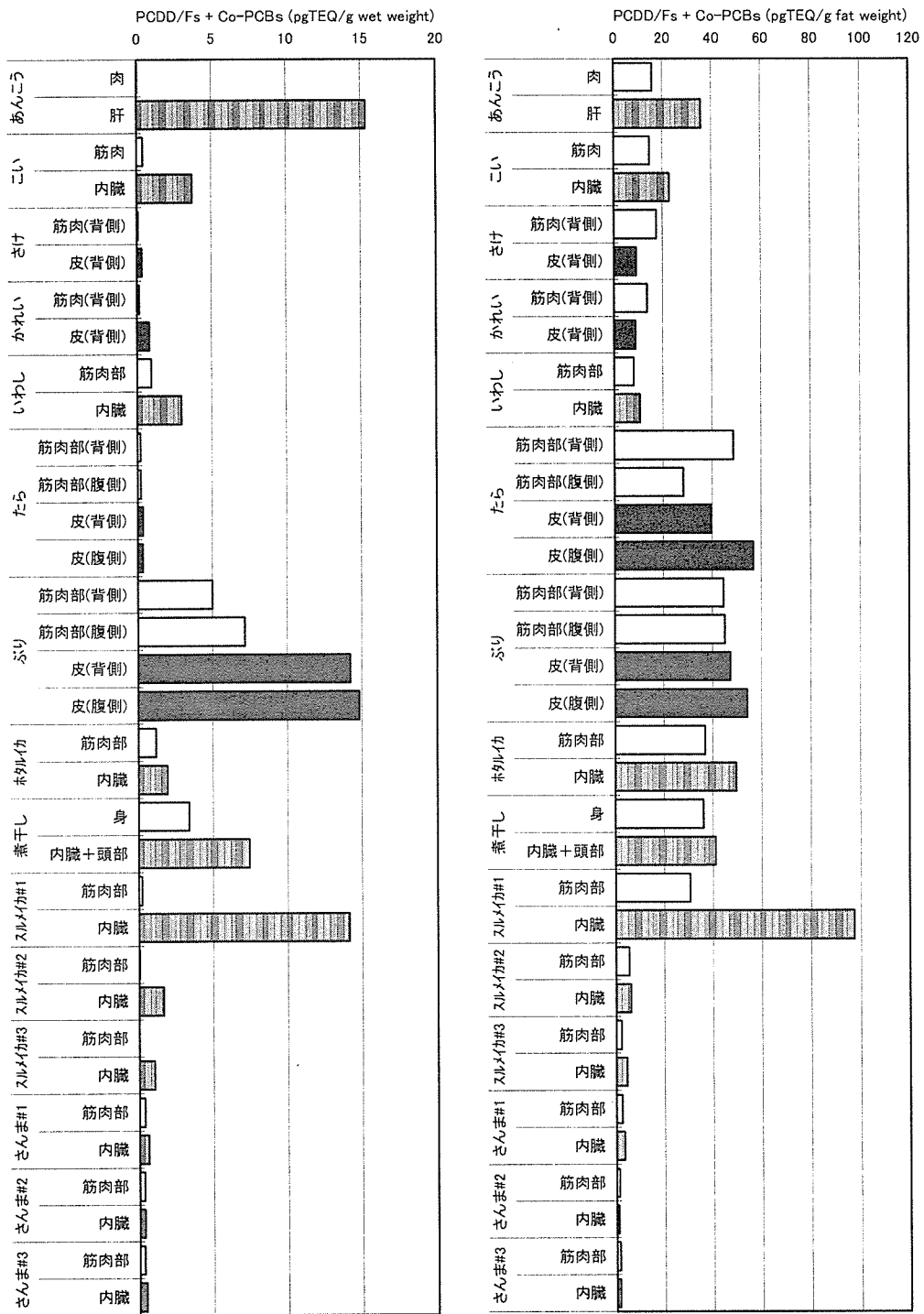


図1. 魚介類中のダイオキシン類の部位別分析結果

□ : 筋肉部, 身    ▨ : 内臓    ■ : 皮

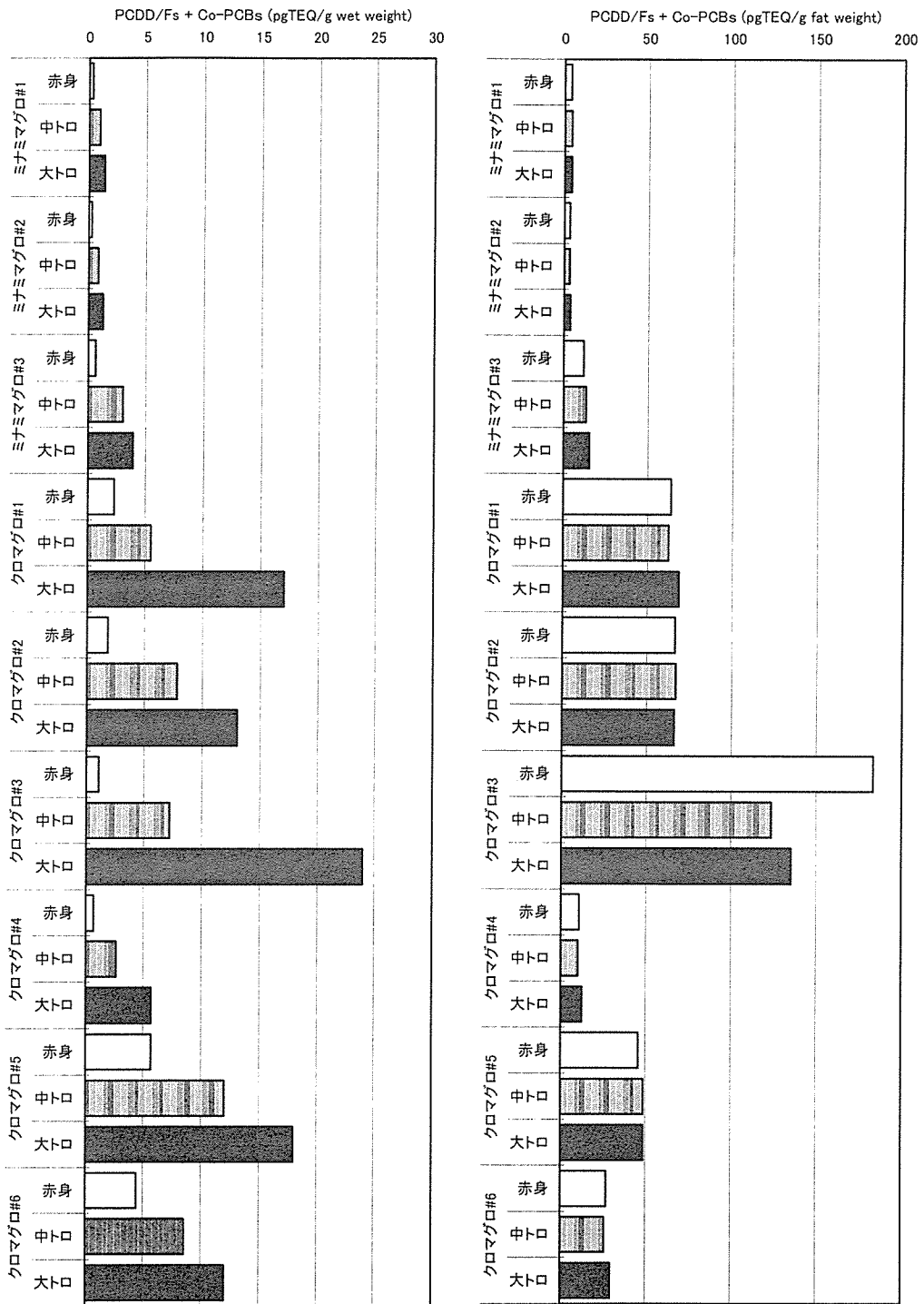


図2. マグロ筋肉部におけるダイオキシン類の部位別分析結果

□ : 赤身      ▨ : 中トロ      ■ : 大トロ



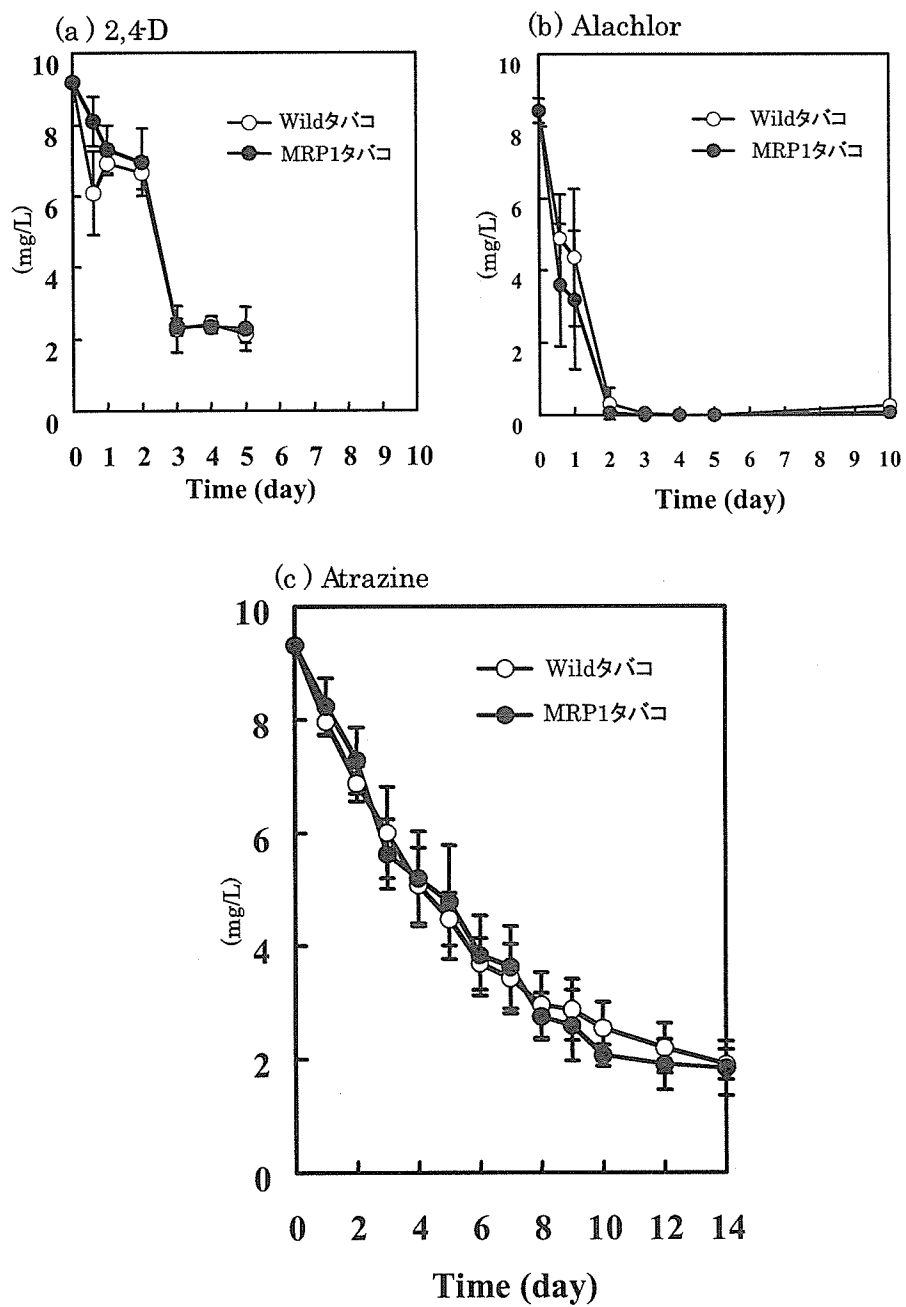


図3. タバコ (Wild, MRP1) の各有機塩素系農薬の吸収除去能 ( $n = 3$ )  
 (a) 2,4-D, (b) Alachlor, (c) Atrazine

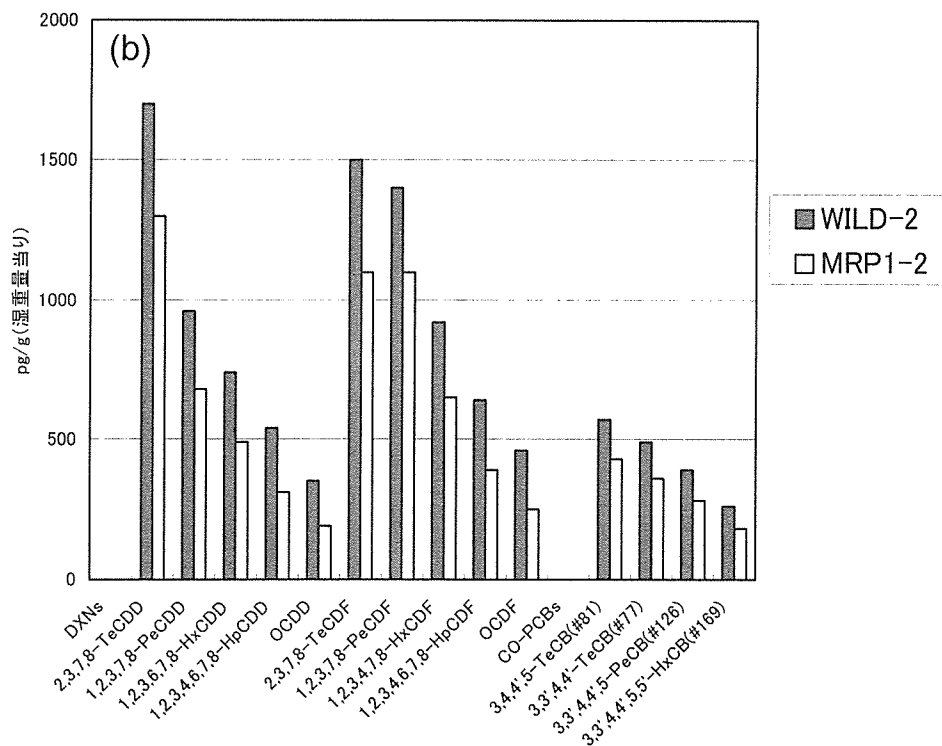
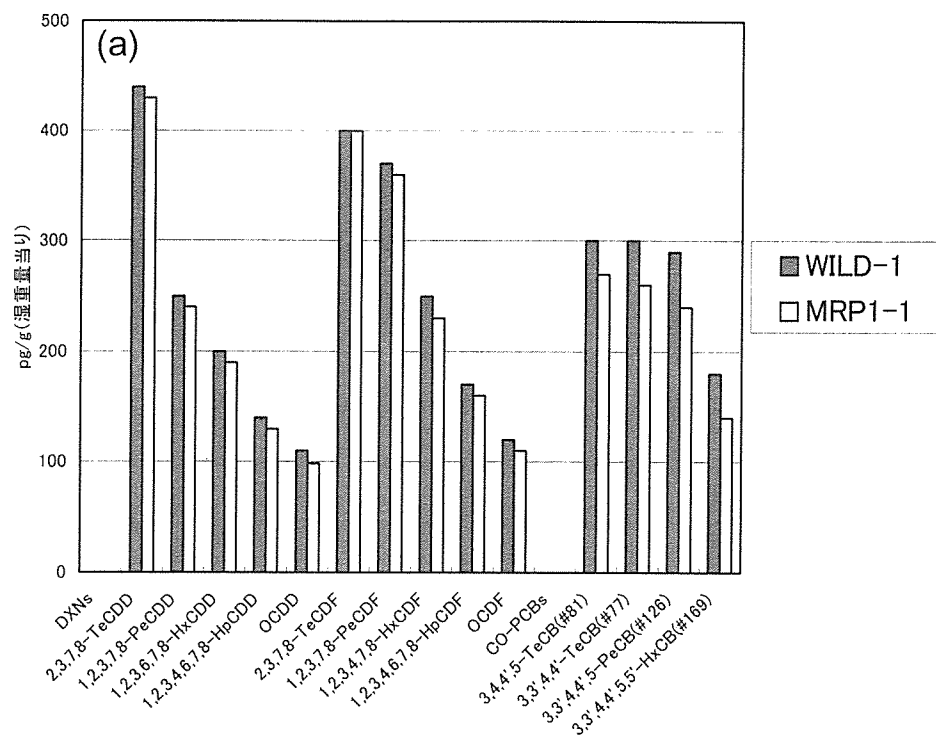


図4. タバコ(Wild, MRP1)のダイオキシンの吸収除去能

(a) PCDD/PCDF類, Co-PCB類 各30 ng暴露

(b) PCDD/PCDF類 各60 ng, Co-PCB類 各100 ng暴露

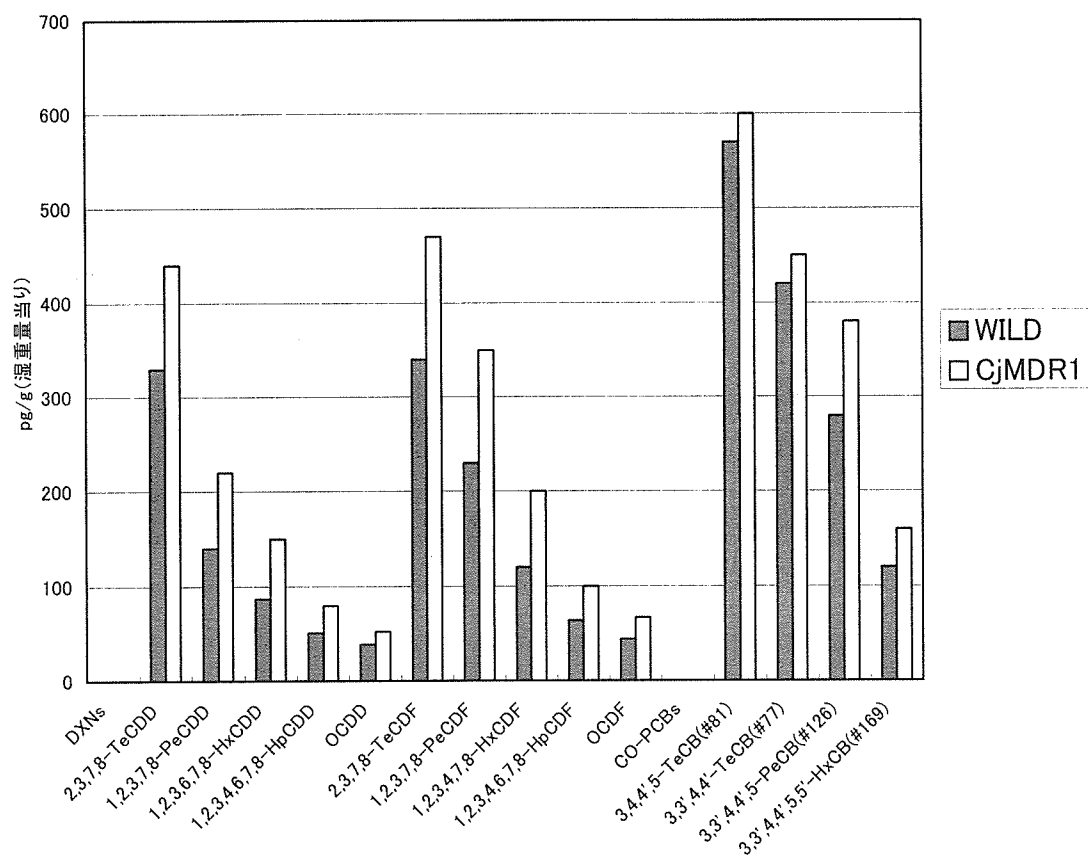


図5. シロイヌナズナ(Wild, CjMDR1)のダイオキシンの吸収除去能 (PCDD/PCDF類, Co-PCB類 各10 ng暴露)

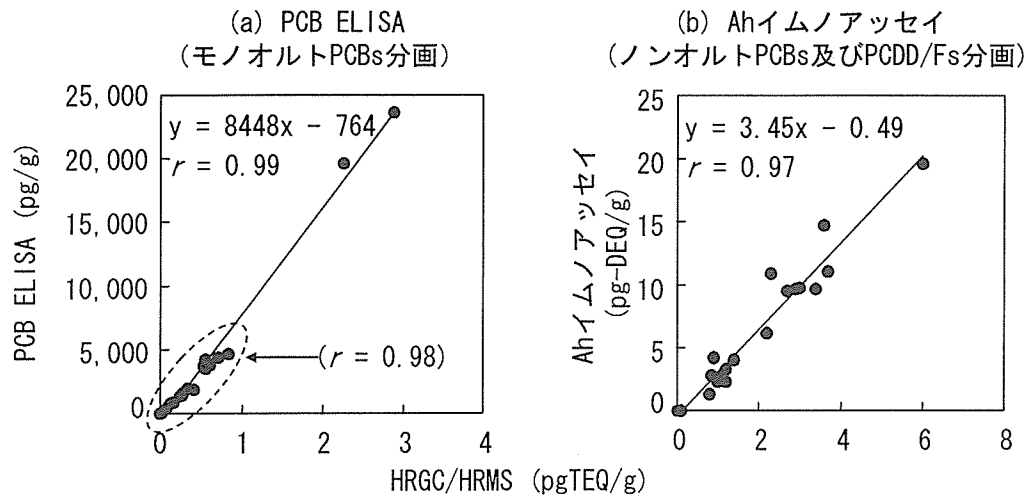


図6. HRGC/HRMSによる毒性等量濃度との比較 ( $n = 20$ )  
 市販魚(カジキ, サケ, サバ, スズキ, ブリ, マグロなど)を比較検体として測定した.

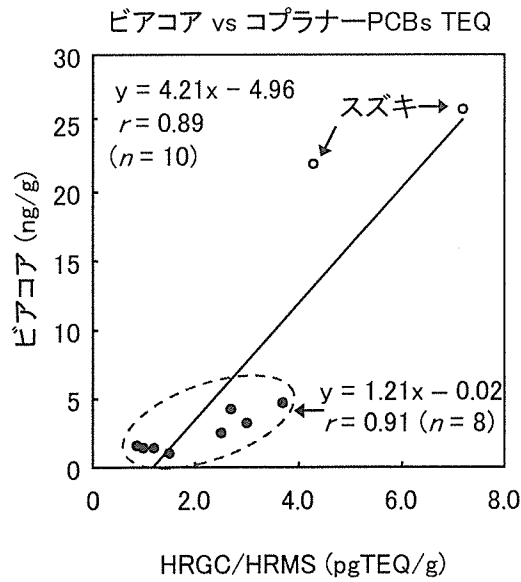


図7. HRGC/HRMSによる毒性等量濃度との比較

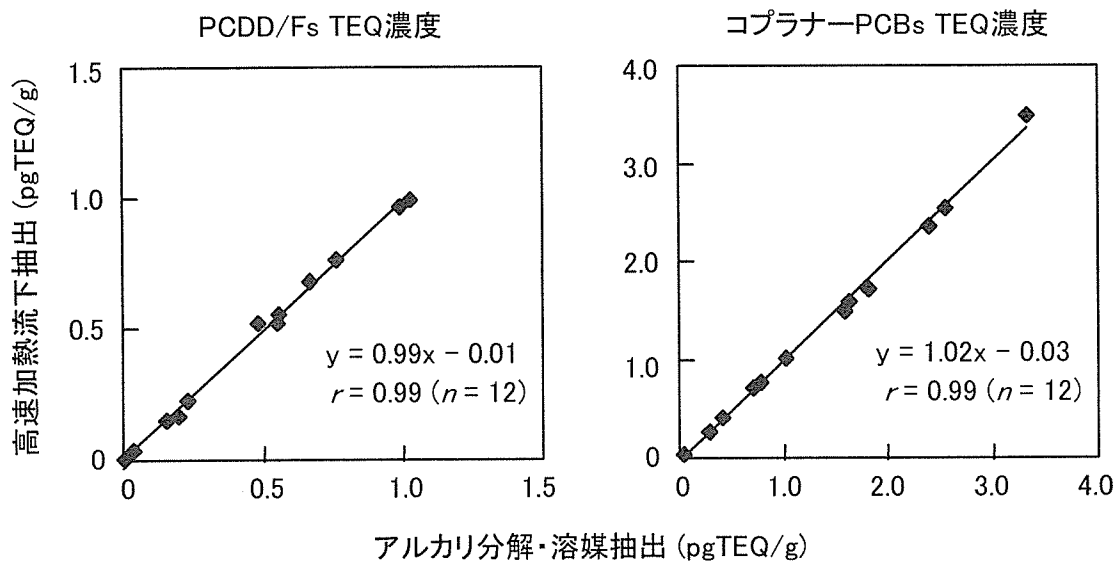


図8. 種々の魚試料における毒性等量濃度の比較

12試料(アジ1試料, アナゴ1試料, イワシ1試料, カジキ1試料, カツオ1試料, サケ2試料, ブリ4試料, マグロ1試料)に両抽出法を適用した.

研究成果の刊行に関する一覧表

及び

研究成果の刊行物・別刷

## 研究成果の刊行に関する一覧表

雑誌

	発表者氏名	論文タイトル	発表誌名	巻号	ページ	出版年
1	Hori, T., Tobiishi, K., Ashizuka, Y., Nakagawa, R., Iida, T., Tsutsumi, T., Sasaki, K.	Comparison of accelerated solvent extraction and standard shaking extraction for determination of dioxins in foods	Organohalogen Compounds	66	537-541	2004
2	Ashizuka, Y., Nakagawa, R., Hori, T., Tobiishi, K., Iida, T.	Levels of polybrominated diphenyl-ethers and polybrominated dioxins in fish, total diet study food groups and Japanese meals	Organohalogen Compounds	66	2524- 2529	2004
3	Ashizuka, Y., Nakagawa, R., Hori, T., Tobiishi, K., Iida, T.	Determination of polybrominated diphenyl ethers(PBDEs) and polybrominated dibenzo- <i>p</i> - dioxins, dibenzofurans (PBDD/DFs) in marine products	J. Agri. Food Chem.	43	3807- 3813	2005
4	Tsutsumi, T., Amakura, Y., Ashieda, K., Okuyama, A., Tanioka, Y., Sakata, K., Kobayashi, Y., Sasaki, K., Maitani, T.	Screening for dioxins in retail fish using a combination of a PCB ELISA and an aryl hydrocarbon receptor immunoassay (Ah- immunoassay)	Organohalogen Compounds	67	42-45	2005
5	Nakagawa, R., Ashizuka, Y., Hori, T., Tobiishi, K., Yasutake, D., Sasaki, K.	Determination of brominated flame retardants in fish and market basket food samples of Japan	Organohalogen Compounds	67	498-501	2005
6	Tsutsumi, T., Amakura, Y., Matsumoto, T., Ito, Y., Kurihara, H., Sasaki, K., Maitani, T.	Removal of dioxins from retail fish by high-speed solvent extraction	Organohalogen Compounds	68	2473- 2476	2006
7	Nakagawa, R., Ashizuka, Y., Hori, T., Yasutake, D., Tobiishi, K., Sasaki, K.	Determination of brominated flame retardants and brominated dioxins in fish collected from three regions of Japan	Organohalogen Compounds	68	2166- 2169	2006
8	Tsutsumi, T., Amakura, Y., Okuyama, A., Tanioka, Y., Sakata, K., Sasaki, K., Maitani, T.	Application of an ELISA for PCB 118 to the screening of dioxin-like PCBs in retail fish	Chemosphere	65	467-473	2006
9	Tsutsumi, T., Amakura, Y., Sasaki, K., Maitani, T.	Dioxin concentrations in the edible parts of Japanese common squid and saury	J. Food Hyg. Soc. Japan	48	8-12	2007

## Comparison of Accelerated Solvent Extraction and Standard Shaking Extraction for Determination of Dioxins in Foods

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### Introduction

We previously developed a highly sensitive method for determining dioxin content in food using a solvent cut large volume (SCLV) injection system coupled to a cyanopropyl phase capillary column<sup>1</sup>. The SCLV injection system coupled to a 40m-length Rtx-2330 column showed sufficient separation of 2,3,7,8-chlorine substituted isomers, and had at least five-times higher sensitivity than the conventional injection technique<sup>2</sup>. In the current method, a large volume of sample (generally 100g) must be treated collectively in order to attain the desirable limit of detection (LODs) at low ppt levels, namely 0.01pg/g for tetra-CDD and -CDF. The present method allowed the reduction of sample volume from 100g to 20g when such usual LODs are demanded. The SCLV injection technique is expected to improve the efficiency of laboratory performance, especially when it is coupled to an automated extraction method, such as accelerated solvent extraction (ASE).

In order to examine the applicability of ASE for the determination of dioxins in food samples, it is important to verify its extraction efficacy against that of the conventional technique. In the present study we examine the applicability of an ASE for the determination of dioxins in food samples, and the method's performance was compared with that of standard conventional shaking extraction (separatory funnel extraction) regarding recovery rates and quantitative determination. It is considered that homogeneous tissue, such as dried seaweed powder or dried milk powder, is suitable for the method's quantitative validation.

### Methods and Materials

For the examination of recovery rate, extracts were prepared from homogenates of various fresh vegetables purchased at a market in Japan. The recovery rates for 17 kinds of <sup>13</sup>C-labeled 2,3,7,8-substituted PCDD/Fs and <sup>13</sup>C-labeled 12 kinds of dioxin-like PCBs were evaluated. For the comparison of quantitative determination, about 1 kg of domestic dried seaweed ('*Nori*') was purchased and ground in a mill, giving a homogeneous powder.



QUALITY OF POP ANALYSIS

The analytical procedures used in this study are summarized in Table 1. Automated extraction was performed using an ASE-300 (Dionex, USA) under the conditions of 1500psi, 150°C. Shaking extraction was twice carried out using a 1L separatory funnel for one hour each time. Four individual experiments and four simultaneous blank tests were performed for each extraction method. Dioxins were analysed using a model 6890 gas chromatograph (Agilent Technologies, USA) coupled to a model Autospec-Ultima mass spectrometer (Micromass, UK). We employed an Rtx-2330 (0.18mm x 40m) capillary column (Restek, USA) on an SCLV injection system (SGE, Australia) in order to determine tetra- and pentaCDD/Fs, and hexaCDFs. The details of the operating conditions for the SCLV injection system are described in another paper<sup>2</sup>. The LOD for each congener was determined according to the provisional guidelines for analysis of dioxins in foods issued by the Ministry of Health and Welfare of Japan in 1999 ('Guideline'): An absolute quantity corresponding to S/N = 3 is evaluated on HRGC/HRMS chromatograms using verification standards.

Table 1. Analytical procedures for determination of dioxins in food.

		Method 1	Method 2
Extraction		Shaking extraction* Sample size: 20g Time: 60min x 2 (120min) Solvent: acetone/n-hexane (1:1, v/v), 600mL (300mL x 2)	Accelerated solvent extraction (ASE) Sample size: 20g Time: 25min Solvent: acetone/n-hexane (1:1, v/v) 200mL
Cleanup		Sulfuric acid treatment □« Multi-layer silica gel column « Active carbon-dispersed silica gel column	
HRGC/ HRMS analysis	PCDD/DFs and non-ortho PCBs	SCLV injection Injection volume: 4 µL / 20µL Pre-column:BPX-5 (0.25mm x 5m) Analytical columns: a) Rtx-2330 (0.18mm x 40m) b) BPX-5 (0.15mm x 30m)	
	Mono-ortho PCBs	Splitless injection Injection volume: 1µL/20 µL Analytical column: HT-8 (0.22mm x 50m)	

\* Method recommended for plant food samples in 'Guideline'.

**Results and Discussion**

As shown in Table 2, our analysis of 20 g of various plant food items according to Method 2, including the ASE and SCLV injection technique, showed recovery rates for <sup>13</sup>C-labeled 29 kinds of isomers ranging from 40.4 to 117%, within the range recommended by the Guideline (40-120%). Data regarding the quantification of principal isomers in dried seaweed are shown in Table 3. Generally, it was found that concentrations from ASE were higher than those from shaking extraction. The greatest difference between the methods was observed regarding OCDD. The ratios of estimated concentrations from ASE to those from shaking extraction ranged from 1.1 for 2,3,7,8-

TCDD, PCB#77 and PCB#123 to 3.2 for OCDD. In contrast, the average concentration of PCB#118 on ASE, that was nearly the same as that of OCDD, showed only a slight difference against shaking extraction. The averaged recovery rates for <sup>13</sup>C-labeled OCDD were 85% for ASE, which was similar to that for shaking extraction (89%). On the other hand, the results of method blank showed that the contribution of contamination was negligible on the quantification data, and chromatograms of seaweed extract also showed little interference near the retention time of OCDD. The above results suggested that ASE exhibited a superior extraction efficacy, while the extractions were incomplete on shaking extraction. However, ASE's significant predominance against shaking extraction was not observed in another examination using fresh vegetable samples (data not shown). It could be said that higher chlorinated PCDD/F isomer in the seaweed was more strongly adsorbed on the plant's structure than in the other plant foods. Actually, the solid residue after the shaking extraction process was enclosed in an ASE vessel and then re-extracted, with the result that peaks representing OCDD and other dioxin-isomers were observed on their chromatograms (Fig. 1).

Table 2. Recoveries of added 29 kinds of <sup>13</sup>C-labeled compounds on various plant food samples using ASE.

No.	Sample	Range (%)
1	<i>Komatsuna</i>	42 - 81
2	<i>Komatsuna</i>	47 - 82
3	<i>Komatsuna</i>	46 - 77
4	<i>Komatsuna</i>	43 - 94
5	<i>Shungiku</i>	44 - 87
6	<i>Shungiku</i>	44 - 72
7	<i>Shungiku</i>	48 - 91
8	Celery	42 - 93
9	Celery	43 - 94
10	Celery	44 - 94
11	Seaweed (dry)	42 - 85
12	Seaweed (dry)	55 - 88
13	Pear	45 - 90
14	Pear	51 - 84
15	Japanese parsley	50 - 93
16	<i>Shimeji</i>	52 - 90
17	Broccoli	45 - 120
18	Lotus root	40 - 93
19	Tomato	48 - 98
20	Bamboo shoot	42 - 70

Table 3. Concentrations (pg/g) of dioxins in seaweed. Comparison of ASE versus Shaking extraction.

Congeners	ASE (n=4)		Shaking extraction (n=4)		a / b
	Mean <sup>a</sup>	Range	Mean <sup>b</sup>	Range	
2,3,7,8-TCDD	0.016	0.010 - 0.021	0.015	0.013 - 0.017	1.1
1,2,3,7,8-PeCDD	0.014	0.011 - 0.017	0.011	(0.009) - 0.013	1.3
1,2,3,7,8,9-HxCDD	0.028	0.026 - 0.031	0.013	0.013 - 0.015	2.1
1,2,3,4,6,7,8-HpCDD	0.441	0.398 - 0.474	0.185	0.183 - 0.189	2.4
OCDD	3.200	3.053 - 3.470	1.008	0.946 - 1.105	3.2
2,3,7,8-TCDF	0.033	0.029 - 0.038	0.023	0.020 - 0.026	1.4
1,2,3,7,8-PeCDF	0.027	0.023 - 0.029	0.019	0.017 - 0.023	1.4
2,3,4,7,8-PeCDF	0.017	0.016 - 0.018	0.011	(0.009) - 0.012	1.6
1,2,3,4,7,8-HxCDF	0.026	0.023 - 0.033	0.014	(0.011) - 0.015	1.9
1,2,3,4,6,7,8-HpCDF	0.075	0.075 - 0.076	0.037	0.033 - 0.041	2.1
OCDF	0.051	0.047 - 0.057	0.023	0.021 - 0.026	2.2
3,3',4,4'-TCB(#77)	1.003	0.987 - 1.036	0.881	0.871 - 0.896	1.1
3,4,4',5'-TCB(#81)	0.157	0.147 - 0.166	0.128	0.121 - 0.138	1.2
2,3,3',4,4'-PeCB(#105)	1.795	1.741 - 1.873	1.552	1.461 - 1.611	1.2
2,3,4,4',5'-PeCB(#114)	0.377	0.360 - 0.425	0.305	0.282 - 0.323	1.2
2,3',4,4',5'-PeCB(#118)	4.352	4.222 - 4.550	3.755	3.637 - 3.910	1.2
2',3,4,4',5'-PeCB(#123)	0.153	0.139 - 0.166	0.134	(0.100) - 0.179	1.1
2,3,3',4,4',5'-HxCB(#156)	0.299	0.256 - 0.352	0.252	0.232 - 0.291	1.2
2,3',4,4',5,5'-HxCB(#167)	0.108	0.089 - 0.126	0.084	(0.057) - 0.100	1.3

Trace data are shown in parentheses and counted in the mean value.

In conclusion, ASE could extract dioxins at high efficiency using a low-volume solvent and could provide a high level of performance for various plant matrices, especially regarding those from which dioxins are difficult to extract using conventional shaking extraction. The applicability of combined SCLV injection and ASE methodology is continuously verified for use regarding animal products.

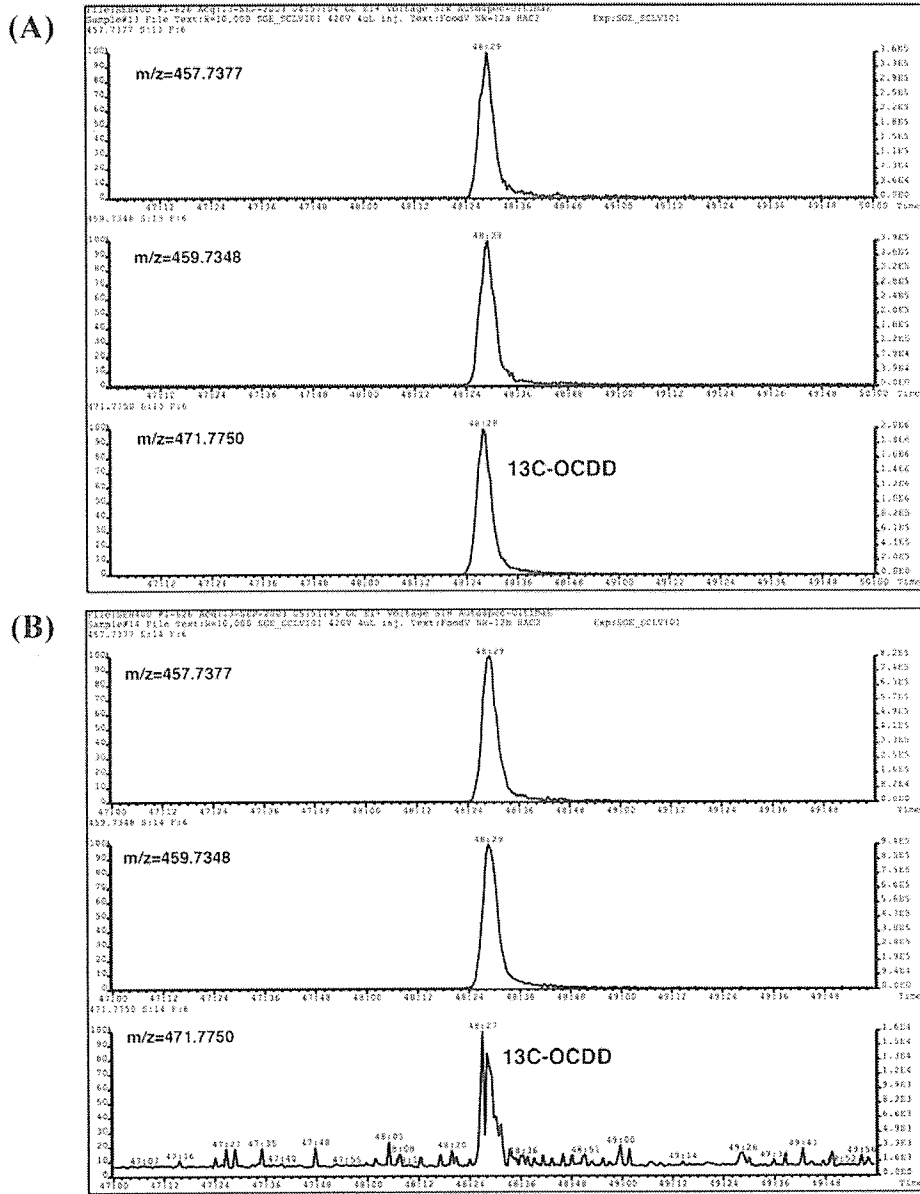


Fig. 1 HRGC/HRMS chromatograms of OCDD (A) obtained from seaweed sample using shaking extraction (B) obtained from the solid residue of shaking extraction process subsequently extracted by ASE.

**Acknowledgement**

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**References**

- 1 Hori, T., Tobiishi, K., Ashizuka, Y., Nakagawa, R., and Iida, T. *Organohalogen Compounds*, 55, 95-98 (2002)
- 2 Tobiishi, K., Hori, T., Kurokawa, Y., Ishiguro, Y., and Iida, T. *Organohalogen Compounds*, 55, 179-182 (2002)