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Dioxin, Furan and PCB Testing of Environmental and Food Samples using a GO-EHT Automated Clean-Up System

Compliance study for EPA method 1613B and EPA method 1668C – part 2: external tests

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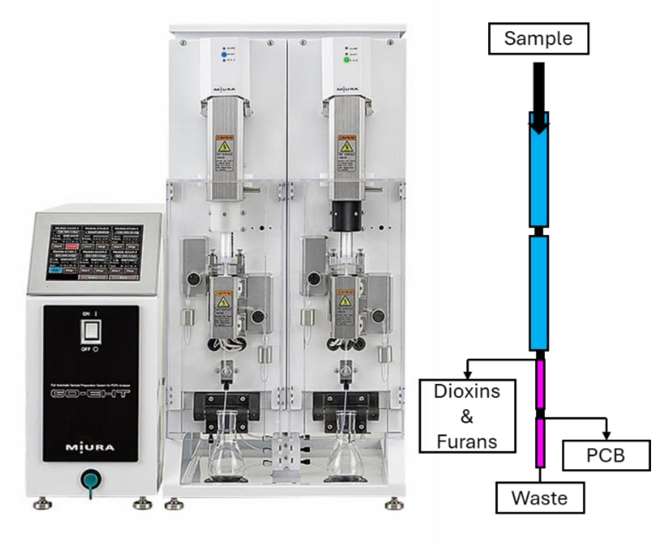


Figure 1. GO-2EHT automated clean-up system for dioxin, furan and PCB testing, and the sample/analyte schematic flow path (Miura, Japan).

Goal

The goal of this study is to establish the performance of the GO-EHT automated clean-up system for the testing of Dioxins, Furans and all 209 PCBs in environmental and food samples.

Introduction

The GO-EHT is an advanced, modular purification system designed to revolutionize sample clean-up. The GO-EHT features a sophisticated controller and up to three processing modules, each equipped with dual units for parallel and independent sample purification. Utilizing a consumable column set of 4 columns, dioxins and Furans, and PCB can be split over two fraction of each less than 1.5mL of toluene. Samples are loaded off-line to prevent cross-contamination and all analyte-contacting tubing and vials are disposable.

The application of GO-EHT automated clean-up for EPA method 1613B[1] (Dioxins and Furans) and EPA method 1668C[2] (PCBs) has been previously investigated in-house using both traditional GO-EHT column sets[3,4] and newly developed column sets tailored for these EPA methods[5]. These studies yielded satisfactory results, prompting the initiation of field experiments in external laboratories.

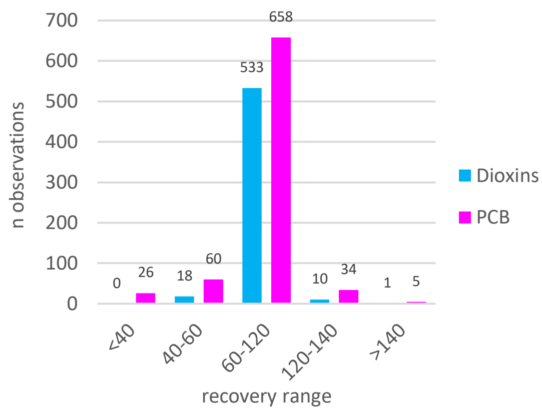
Experimental

For external testing of the new column sets 8 laboratories participated of which 5 returned results. Results were obtained using the newly optimized method program[5] as well as the traditional method program[3,4]. Difference between the two method is the temperature at which the silica columns are eluted and should only affect column capacity.

The experiment was performed on 18mm column sets on which a divers range of samples were applied. The total number of datasets for samples received was 33 including, solvent, water, air, emission, ash, sludge, carbon waste, top soil, ash, solids, canola oil, fish oil, and tissue. Certain labs also performed comparison measurements versus manual clean-up as well as compliance testing through certified reference material, and proficiency testing, and PBDE testing.

Figure 2 Column set of a 5g dried sewage sludge sample after GO-EHT clean-up from in-house experiments.

Figure 3 Histogram of recoveries of Dioxins and PCBs in 46 real samples obtained from external testing laboratories.



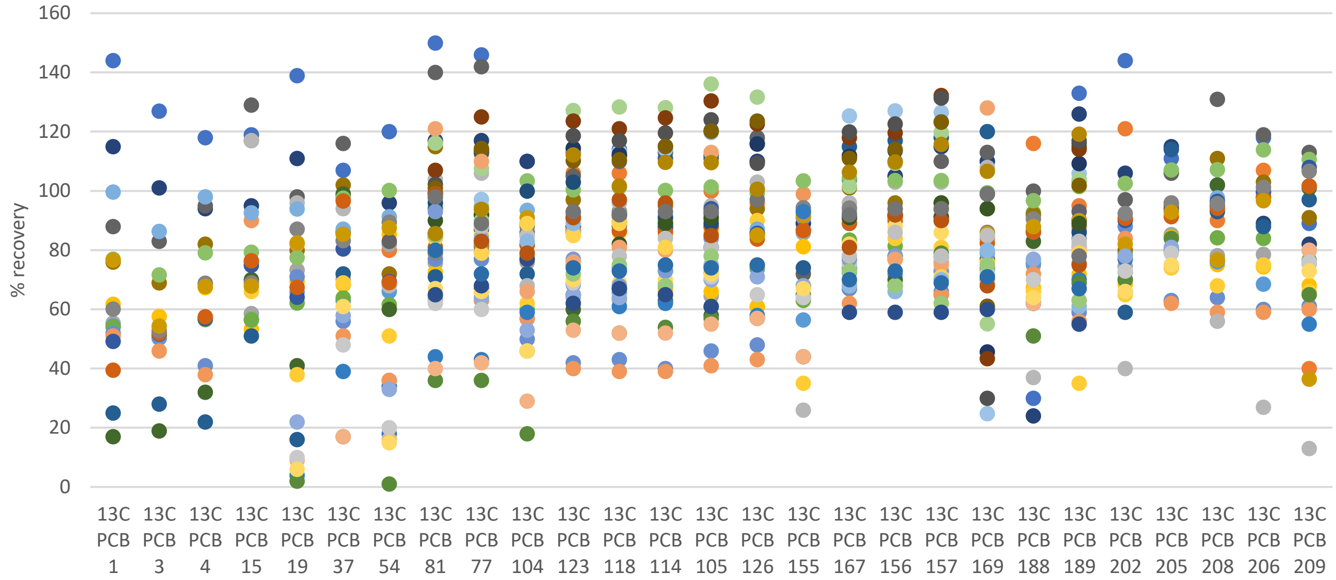


Figure 4 Individual recoveries for labelled PCBs in 46 externally tested samples.

Results and discussion

Recoveries of all internal standards were calculated and used for calculating initial precision and recovery (IPR). In total, recovery's of internal standards were obtained from 33 samples depending the congener (fig. 3,4 and 5). Average recoveries for Dioxins, Furans and PCBs were well within 60 to 100% (table 1). Standard deviations (relative) were between 5% and 61% with Dioxins averaging 14% and PCBs 30% complying (table 1). Both IPR for Dioxins and Furans, and for PCBs complied with IPR criteria of EPA method 1613B and EPA method 1668C.

On individual sample and congener base, recoveries below 60% were reported, mostly within specific groups of data. In isolated conditions lower recoveries are expected for ^{13}C PCB3 and ^{13}C PCB209 as these are critical parameters as first and last eluter. Since recoveries were lower for several other congeners as well within the same sample, external factors such as evaporation effects and extraction efficiencies may have influenced the results.

GO-EHT technology was developed based on an ideal philosophy. Two of the pillars are proficient recoveries

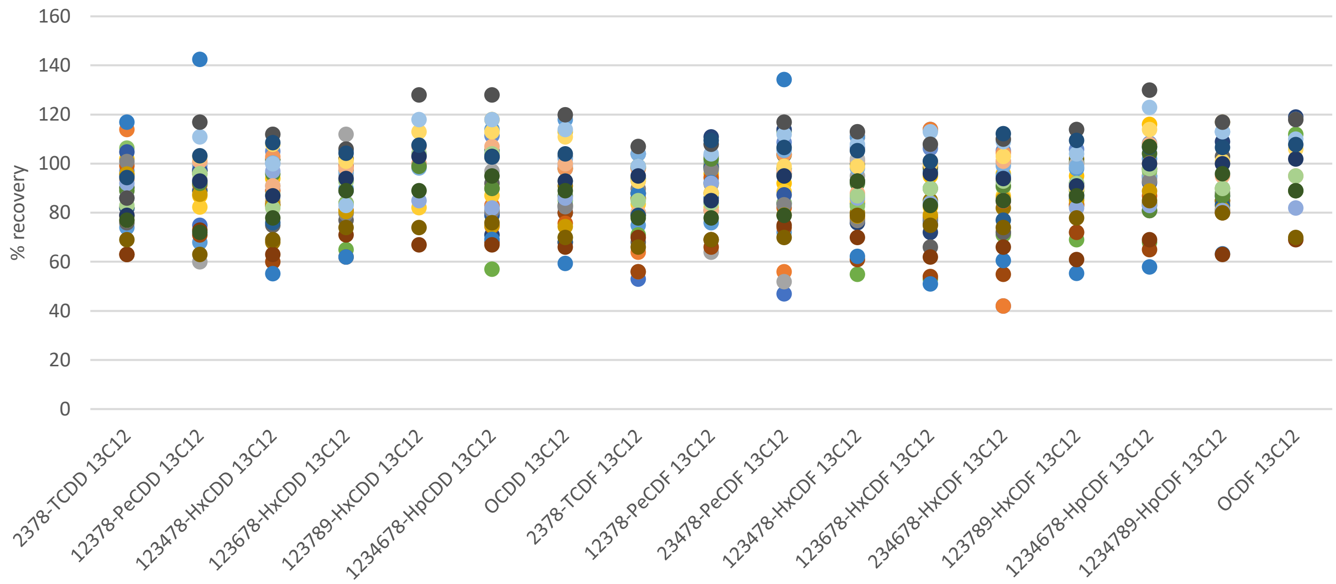


Figure 5 Individual recoveries for labelled Dioxins and Furans in 36 externally tested samples.

and great purity of the final extract. One lab repeated two complex solid samples yielding low recoveries in manual clean-up using the GO-EHT technology. Recoveries for these samples rose to proficient levels while it was feasible to inject a concentrated extract without compromising recoveries (table 2).

In terms of accuracy, another lab analysed a PT sample ash for a selection of PCBs and total PCB content. Back calculated z-scores for the sample were between -1.5 and 0.7 demonstrating the competence for accurate testing.

A third laboratory tested the system for PBDEs as they elute within the PCB fraction as well. Recoveries were mostly around 100% with SDs below 10%. Three congeners recoveries deviated over 40% from the designated value.

Conclusion

The results of the study demonstrate the suitability of GO-EHT technology for purification of various environmental and food sample extracts in routine environment for EPA method 1613B[1] and EPA method 1668C[2].

Aside from Dioxins, Furans and all 209 PCBs GO-EHT technology performed well for PBDE testing.

Acknowledgements

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References

1) EPA; U.S. Environmental Protection Agency (1994) Method 1613: Tetra- through Octa-Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS. Revision B

2) US Environmental Protection Agency, Method 1668C, chlorinated biphenyl congeners in water, soil, sediment, biosolids and tissue by HRGC/HRMS, revision C, (2010)

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Table 1 Average recovery internal standards and standard deviation of 33 tested samples in 5 external laboratories.

	average recovery %		Precision			n
Congener	Experimental	Criterium IPR	SD	RSD %	Criterium IPR	
2378-TCDD 13C12	88	28-134	13	-	37	34
12378-PeCDD 13C12	93	27-184	16	-	39	34
123478-HxCDD 13C12	88	29-147	15	-	41	34
123678-HxCDD 13C12	89	34-122	13	-	38	36
123789-HxCDD 13C12	100	-	16	-		19
1234678-HpCDD 13C12	93	34-129	18	-	35	36
OCDD 13C12	90	41-276	17	-	95	36
2378-TCDF 13C12	85	31-113	15	-	35	36
12378-PeCDF 13C12	91	27-156	13	-	34	36
23478-PeCDF 13C12	92	16-279	19	-	38	36
123478-HxCDF 13C12	90	27-152	16	-	43	36
123678-HxCDF 13C12	88	30-122	17	-	35	36
234678-HxCDF 13C12	87	29-136	18	-	37	36
123789-HxCDF 13C12	89	24-157	13	-	40	36
1234678-HpCDF 13C12	95	32-110	17	-	41	36
1234789-HpCDF 13C12	92	28-141	15	-	40	30
OCDF 13C12	99	-	16	-		15
13C PCB 1	66	20-135	-	47	70	18
13C PCB 3	61	20-135	-	42	70	18
13C PCB 4	67	20-135	-	38	70	18
13C PCB 15	81	20-135	-	30	70	20
13C PCB 19	60	20-135	-	61	70	26
13C PCB 37	74	20-135	-	35	70	27
13C PCB 54	61	20-135	-	51	70	27
13C PCB 81	89	45-135	-	26	50	46
13C PCB 77	87	45-135	-	27	50	46
13C PCB 104	73	45-135	-	29	50	37
13C PCB 123	85	45-135	-	25	50	46
13C PCB 118	85	45-135	-	25	50	46
13C PCB 114	85	45-135	-	25	50	46
13C PCB 105	87	45-135	-	26	50	46
13C PCB 126	88	45-135	-	26	50	36
13C PCB 155	75	45-135	-	27	50	27
13C PCB 167	88	45-135	-	20	50	46
13C PCB 156	89	45-135	-	20	50	46
13C PCB 157	90	45-135	-	23	50	46
13C PCB 169	80	45-135	-	27	50	46
13C PCB 188	73	45-135	-	29	50	27
13C PCB 189	87	45-135	-	24	50	46
13C PCB 202	82	45-135	-	25	50	27
13C PCB 205	89	45-135	-	16	50	27
13C PCB 208	88	45-135	-	21	50	21
13C PCB 206	88	45-135	-	25	50	21
13C PCB 209	77	45-135	-	32	50	27

Table 2 Results using GO-EHT (18mm column set) of 2 samples sludge yielding low recoveries with a manual method.

	Solids			Solids		
Internal standard	Manual	Manual repeat	GO-EHT 18mm	Manual	Manual repeat	GO-EHT 18mm
13C 2,3,7,8-TCDD	23	62	94	26	46	95
13C 1,2,3,7,8-PeCDD	63	77	98	65	65	100
13C 1,2,3,4,7,8-HxCDD	66	87	103	68	71	100
13C 1,2,3,6,7,8-HxCDD	76	85	98	73	74	96
13C 1,2,3,4,6,7,8-HpCDD	66	82	100	65	71	99
13C OCDD	60	77	104	52	68	103
13C 2,3,7,8-TCDF	12	57	98	13	42	100
13C 1,2,3,7,8-PeCDF	55	74	98	59	62	104
13C 2,3,4,7,8-PeCDF	54	77	99	56	63	103
13C 1,2,3,4,7,8-HxCDF	68	85	104	72	71	106
13C 1,2,3,6,7,8-HxCDF	66	82	101	68	69	102
13C 1,2,3,7,8,9-HxCDF	64	79	100	64	65	100
13C 2,3,4,6,7,8-HxCDF	67	80	104	68	71	101
13C 1,2,3,4,6,7,8-HpCDF	64	82	100	59	71	100
13C 1,2,3,4,7,8,9-HpCDF	69	82	100	69	72	95
37CL-2,3,7,8-TCDD	25	65	91	27	53	98
13C PCB1	1	14	49	1	4	40
13C PCB3	2	22	52	3	11	52
13C PCB4	3	25	57	3	13	58
13C PCB15	18	46	75	26	39	76
13C PCB19	7	36	64	11	27	67
13C PCB37	49	59	80	52	58	97
13C PCB54	14	43	69	19	35	69
13C PCB81	70	69	84	70	71	81
13C PCB77	72	70	82	72	72	79
13C PCB104	39	52	82	41	50	82
13C PCB123	73	68	87	69	73	87
13C PCB118	74	69	88	71	75	87
13C PCB114	74	69	87	70	74	86
13C PCB105	75	71	94	74	76	88
13C PCB126	81	73	86	79	80	84
13C PCB155	63	61	87	56	66	87
13C PCB167	83	70	89	74	80	89
13C PCB156/157	83	69	91	75	78	90
13C PCB156/157	83	69	91	75	78	90
13C PCB169	83	47	86	76	74	82
13C PCB188	86	196	86	83	94	86
13C PCB189	96	88	90	88	95	88
13C PCB202	92	192	90	88	99	91
13C PCB205	86	83	94	79	81	91
13C PCB208	91	62	96	85	91	94
13C PCB206	78	103	100	74	70	98
13C PCB209	78	124	108	68	72	102
13C PCB28	31	46	79	40	51	79
13C PCB111	71	69	86	67	77	86
13C PCB178	87	74	99	75	86	97

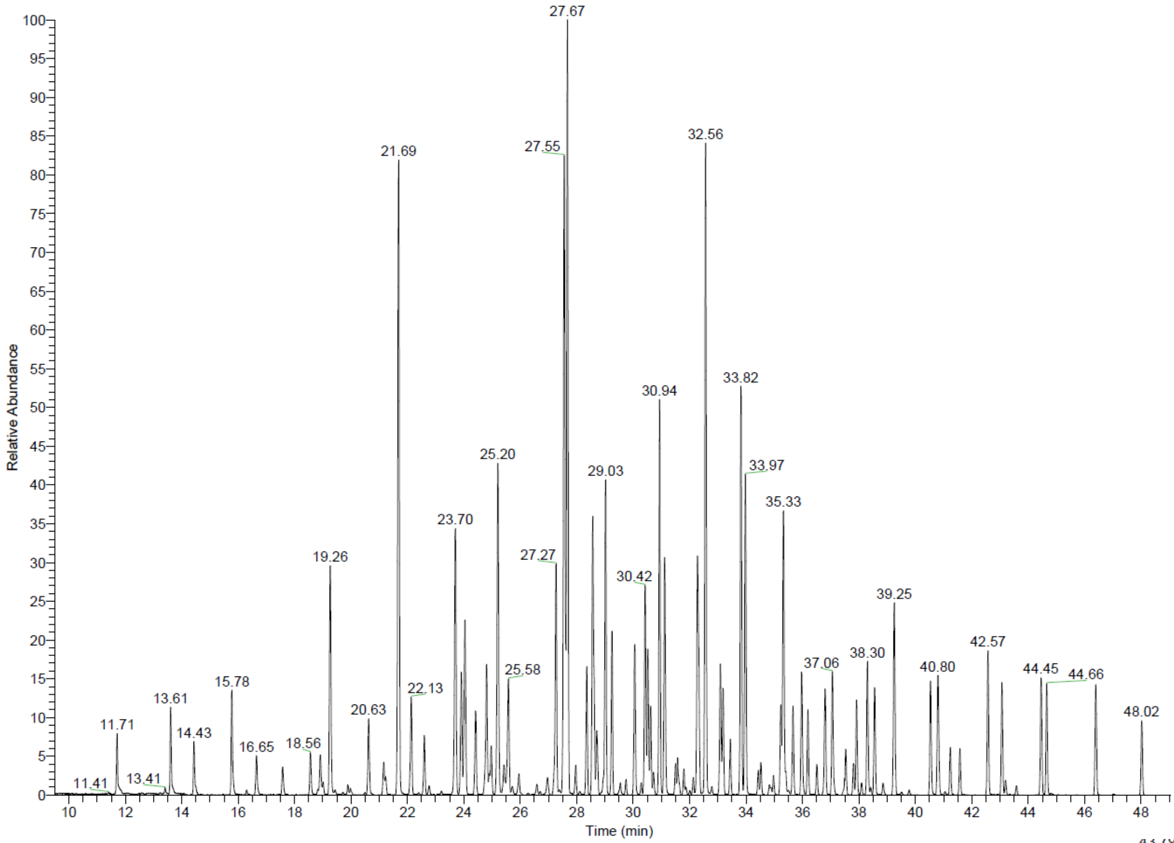
Table 3 Results using GO-EHT (18mm column set) of a proficiency test sample Ash.

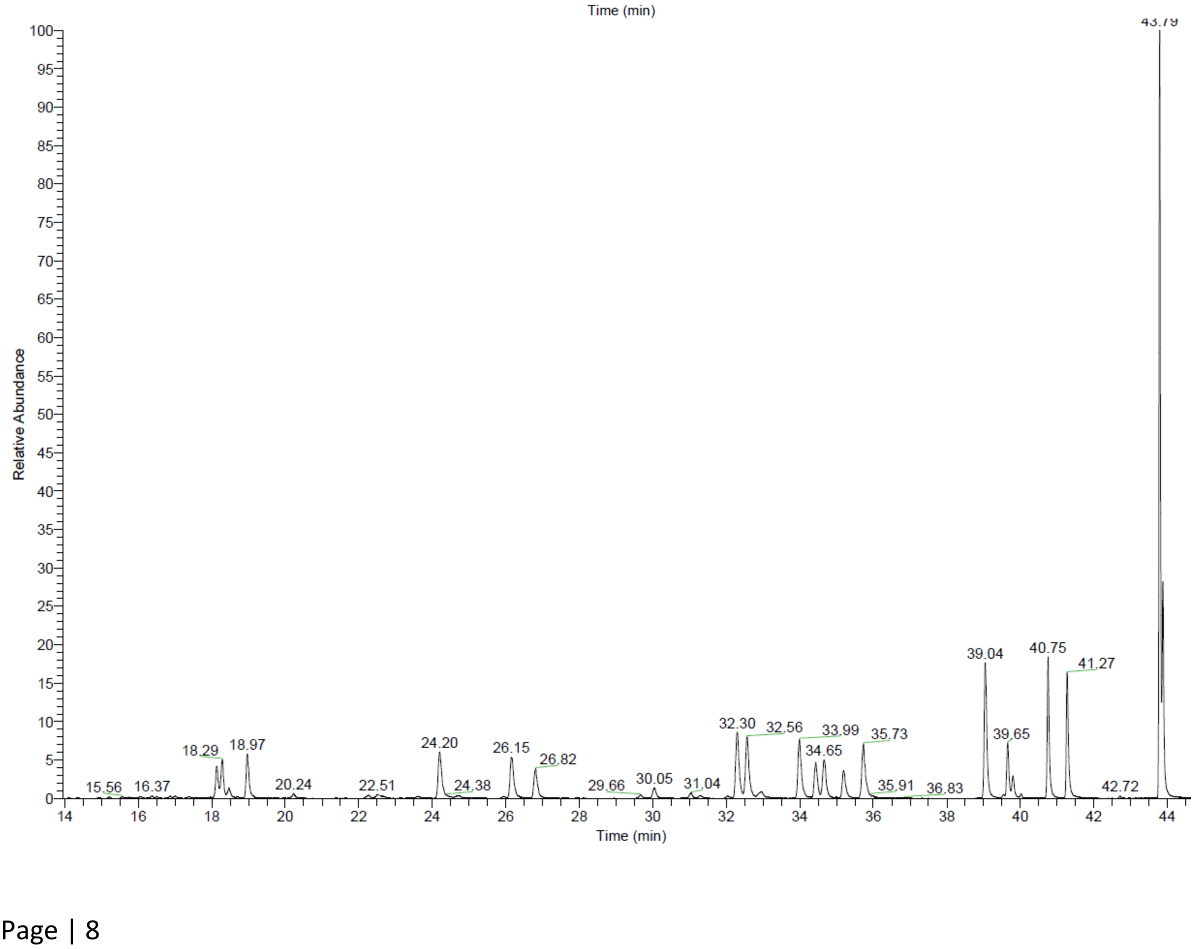
Congener	Assigend value	sd	Results	z-score
	µg/kg	µg/kg	µg/kg	
PCB77	125	22	132	0,3
PCB81	333	74	297	-0,5
PCB123	58	13	68	0,8
PCB118	325	57	321	-0,1
PCB114	38	8	48	1,2
PCB105	265	61	272	0,1
PCB126	111	25	129	0,7
PCB167	170	44	172	0,0
PCB156	234	64	219	-0,2
PCB157	297	90	291	-0,1
PCB169	232	54	225	-0,1
PCB189	43	9	49	0,7
PCB28	49	9	60	1,3
PCB52	48	9	34	-1,5
PCB153	149	19	131	-1,0
PCB180	161	31	121	-1,3
Total PCB	3129	362	2891	-0,7

Table 4 Results using GO-EHT (18mm column set) for PBDE testing.

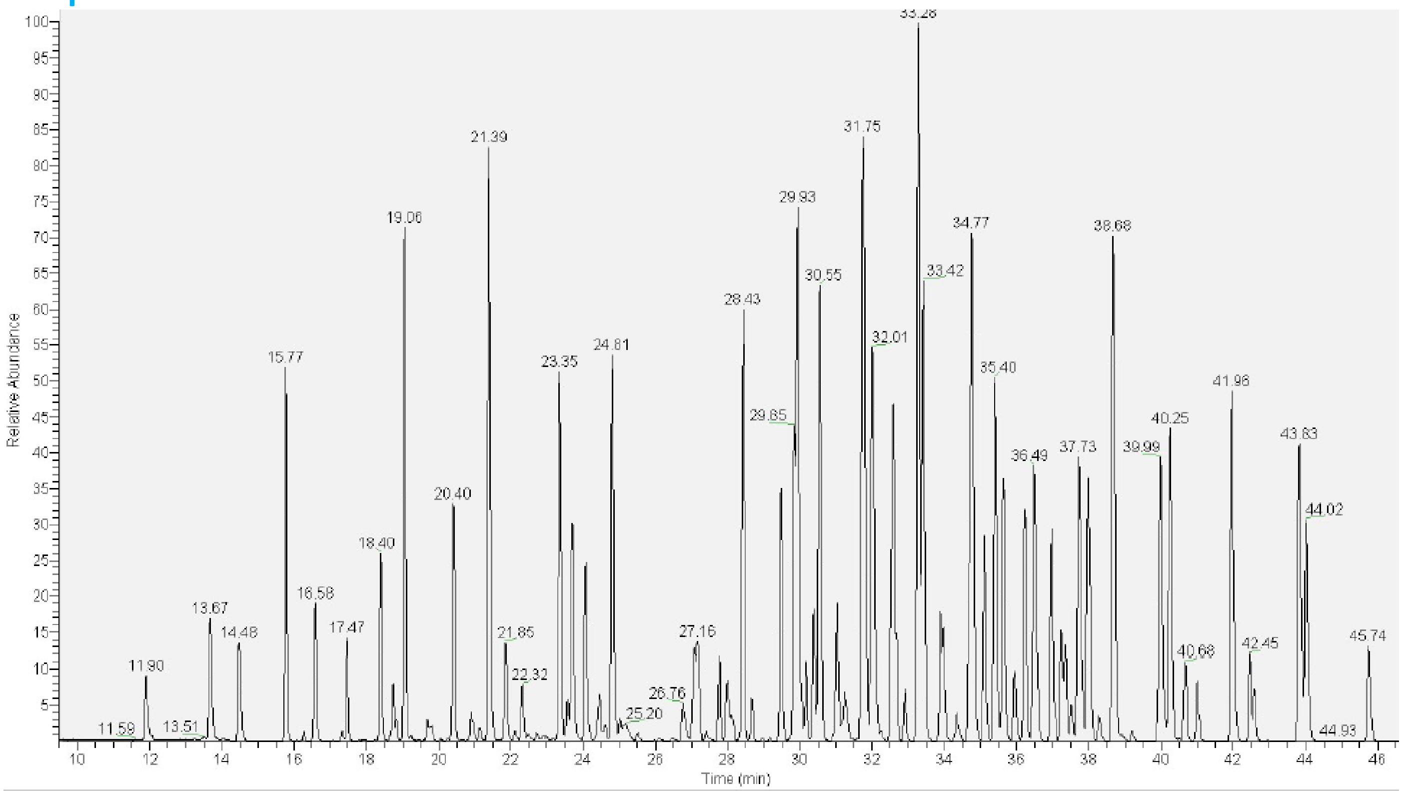
Congener	Canola oil 0,3g	solvent	Solids	Solids	lipid 0,35g	Canola oil 1g	Average recovery	SD
PBDE7	45	66	63	50	70	59	59	10
PBDE8/11	89	95	104	85	92	93	93	6
PBDE10	18	38	31	29	46	32	32	9
PBDE15	101	104	103	98	102	102	102	2
PBDE17/25	101	102	98	96	99	99	99	2
PBDE28/33	93	94	90	92	92	92	92	1
PBDE30	56	73	66	54	75	65	65	9
PBDE32	91	92	87	87	89	89	89	2
PBDE35	113	114	115	99	109	110	110	6
PBDE37	106	107	104	101	110	106	106	3
PBDE47	120	119	112	116	114	116	116	3
PBDE49	95	96	96	89	91	93	93	3
PBDE51	93	94	87	91	93	91	91	2
PBDE66	108	107	102	105	102	105	105	2
PBDE71	96	89	87	89	94	91	91	3
PBDE75	100	100	105	98	100	101	101	2
PBDE77	97	101	94	95	95	96	96	2
PBDE79	113	110	86	98	75	96	96	14
PBDE85	99	105	84	101	105	99	99	8
PBDE99	100	103	102	101	105	102	102	2
PBDE100	100	100	101	100	102	100	100	1
PBDE105	96	105	79	99	105	97	97	9
PBDE116	76	89	70	65	90	78	78	10
PBDE119/120	99	102	100	95	110	101	101	5
PBDE126	96	96	94	93	102	96	96	3
PBDE128	139	135	114	128	193	142	142	27
PBDE138/166	137	133	130	126	137	133	133	4
PBDE140	190	173	181	166	178	178	178	8
PBDE153	97	104	105	100	106	102	102	3
PBDE154	100	101	101	96	105	101	101	3
PBDE155	175	189	189	187	179	184	184	6
PBDE181	65	77	58	72	79	70	70	8
PBDE183	102	105	98	98	100	101	101	2
PBDE190	88	95	69	85	75	83	83	9
PBDE204/197	96	99	112	98	99	101	101	5
PBDE203	101	111	114	103	105	107	107	5
PBDE205	97	94	99	83	108	97	97	8
PBDE206	130	109	86	91	92	102	102	16
PBDE207	145	115	109	137	94	120	120	19
PBDE208	124	117	120	121	91	115	115	12
PBDE209	100	89	99	64	85	87	87	13
13C PBDE15	89	94	78	77	82	79	83	7
13C PBDE28	88	95	84	82	84	85	86	5
13C PBDE47	96	103	91	91	92	92	94	5
13C PBDE77	97	99	92	91	94	94	95	3
13C PBDE99	99	103	97	95	99	101	99	3
13C PBDE100	97	103	93	93	95	97	96	4
13C PBDE126	98	103	95	94	97	96	97	3
13C PBDE153	99	109	97	108	108	135	109	13
13C PBDE154	94	105	92	105	102	126	104	12
13C PBDE183	103	109	97	104	102	112	104	6
13C PBDE197	105	106	86	87	89	85	93	10
13C PBDE209	93	43	51	54	54	41	56	19
13C PBDE139	104	114	100	114	112	133	113	11

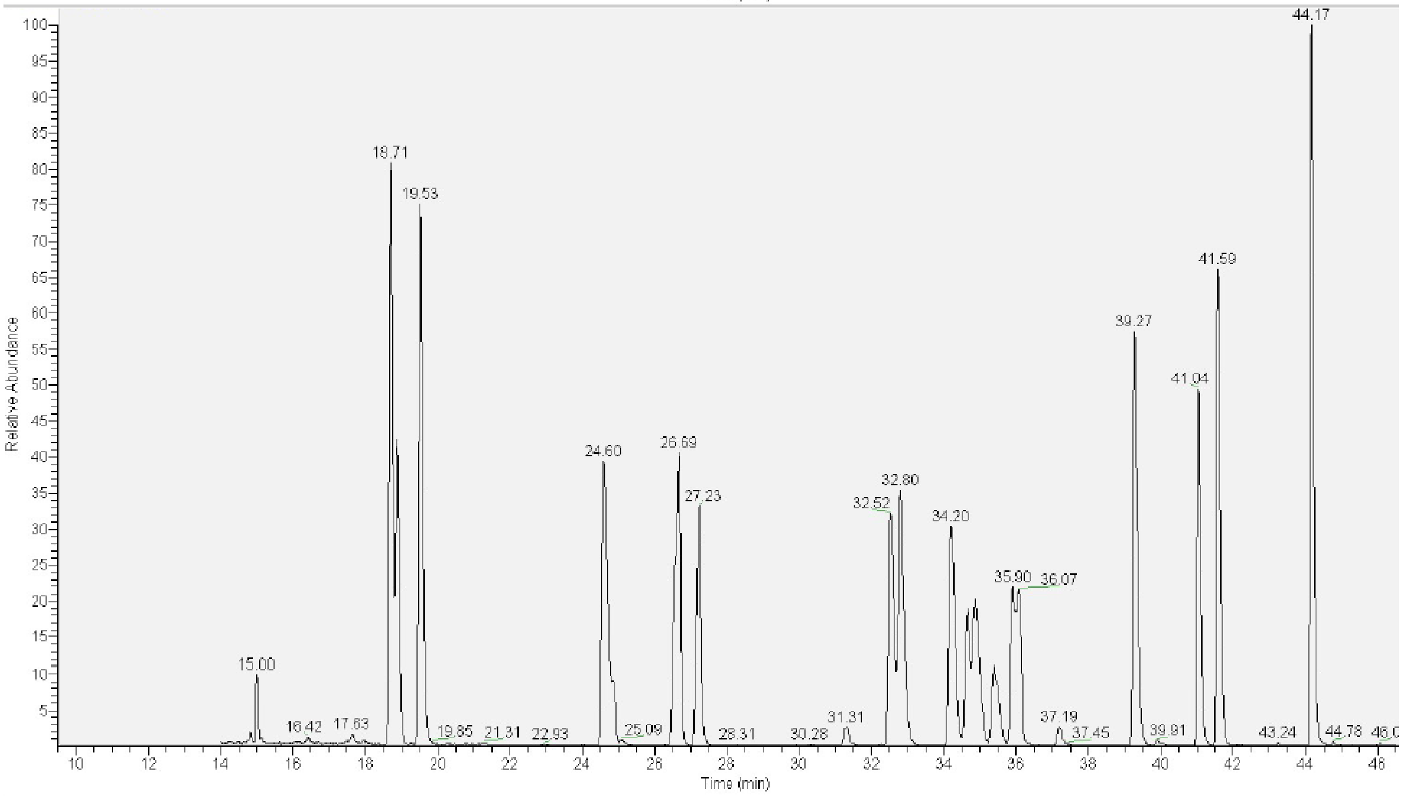
Annex 1 TIC chromatogram of PCBs (upper) and Dioxins and PCBs (lower)in a certified ash sample





Annex 2 TIC chromatogram of PCBs (upper) and Dioxins and Furans (lower) in a sludge sample





Annex 3 TIC chromatogram of PCBs (upper) and Dioxins and Furans (lower) in a undefined sample