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Field Test Experiments and Validation for EN 1948-4

Standardisation mandate to CEN for standard
measurement methods for the determination of
dioxin-like PCBs from stationary sources

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Air Quality
Stationary Source Emissions
CEN/TC 264 /WG 1 Dioxins and PCBs (Emission)

**Standardisation mandate to CEN for standard measurement methods for the
determination of dioxin-like PCBs from stationary sources**

Final Report

November 2008

We would like to thank the numerous experts dealing with the validation measurements and evaluation for their fruitful co-operation.

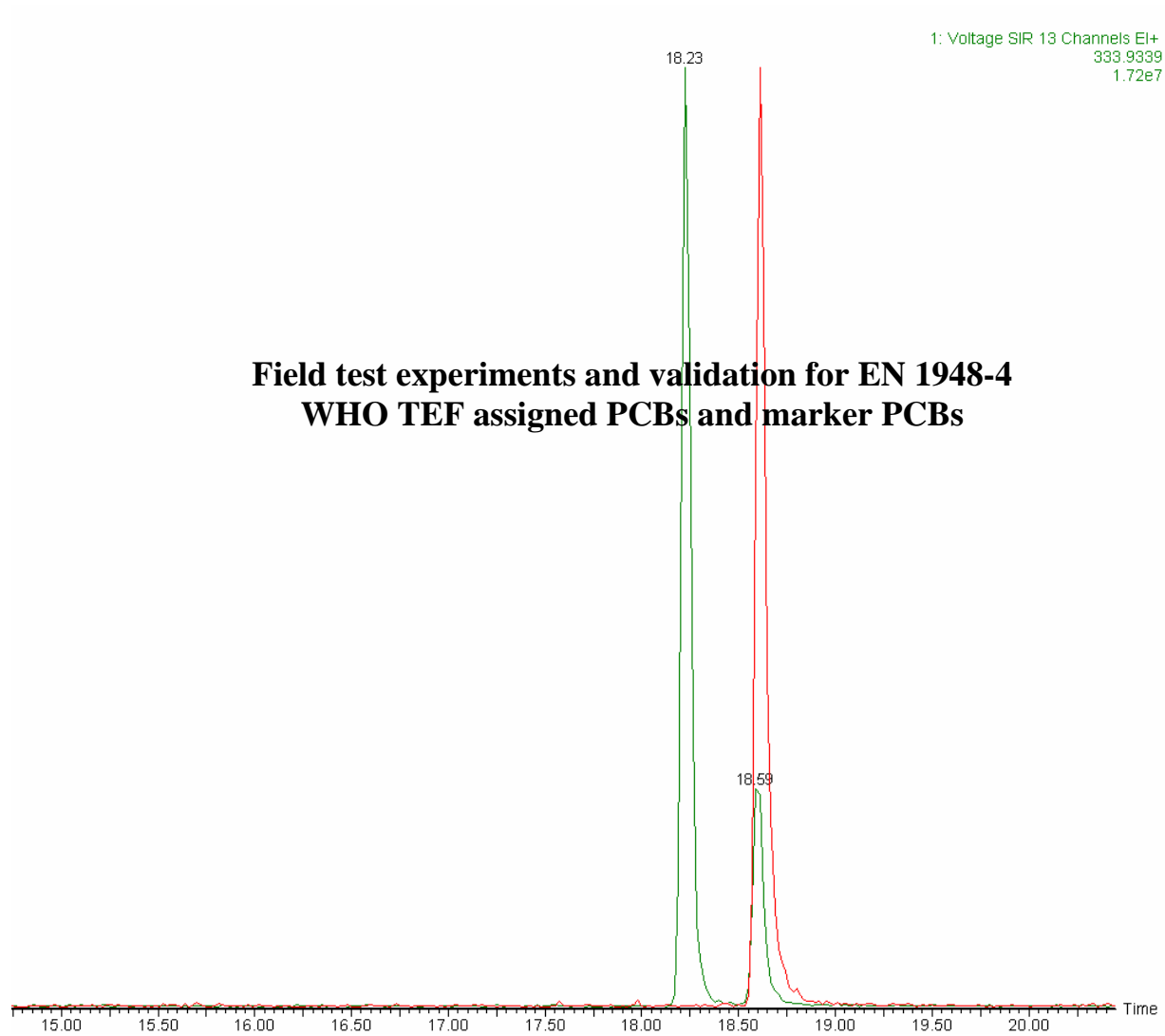
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**Field test experiments and validation for EN 1948-4
WHO TEF assigned PCBs and marker PCBs**

Bert van Bavel
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Content	Page
Section 1: Introduction.....	3
Section 2: Interlaboratory comparison study of the analytical method.....	4
Section 3: Field validation measurements at a waste incinerator.....	5
Section 4: Results of the validation measurements at the waste incinerator.....	9
Section 5: Recovery at the waste incinerator.....	17
Section 6: LOD and LOQ at the waste incinerator.....	18
6.1 LOD.....	18
6.2 LOQ.....	18
Section 7: Evaluation of the field blank samples at the waste incinerator.....	20
Section 8: Breakthrough during sampling at the waste incinerator.....	21
Section 9: Accuracy of the measurement methods at the waste incinerator.....	21
Section 10: Additional measurements at a shredder plant.....	25
10.1 Results.....	25
10.2 Break through.....	26
Section 11: Conclusion.....	27
 Annex 1: Interlaboratory comparison study	
Annex 2: Plant description and sampling conditions at a municipal waste incinerator	
Annex 3: Measurement data and graphs of municipal waste incinerator measurements	
Annex 4: Recovery of the ¹³ C ₁₂ -labelled standards at municipal waste incinerator measurements	
Annex 5: LOD and LOQ calculation of municipal waste incinerator measurements	
Annex 6a: Measurement report cooled probe method	
Annex 6b: Measurement report filter/condenser method	
Annex 6c: Measurement report dilution method	
Annex 7a: Additional measurements at a shredder plant	
Annex 7b: Additional measurement data and break through investigations at the shredder plant	

1. Introduction

Within the framework of the EU/EFTA mandate M 388 CEN/TC 264/WG 1 was entrusted to establish a standard measurement method for the determination of dioxin-like PCBs from stationary source emissions (Grant Agreement for an Action SA/CEN/ENV-EFTA/388/2006/30 and Supplementary Agreement n°1 to Grant Agreement for an Action; 070402/2006/445241/SUB/C4).

1 million tons of PCBs have been produced and used during 20th century until their ban in 1985. PCBs are not as toxic as dioxins, but the quantities of PCBs released to the environment are several times higher. The following legal acts will benefit from a standardised method for PCBs:

- Regulation (EC) No 850/2004 on persistent organic pollutants (POPs) includes PCBs as one of 16 substances or group of substances to be subject for prohibition and/or release reduction provisions.
- Regulation (EC) No 166/2006 concerning the establishment of a European Pollutant Release and Transfer Register includes PCBs as one of 91 parameters of which releases to air, water and land from industrial facilities have to be reported.
- Council Conclusions on the Dioxin Strategy (COM(2001) 593)) emphasizes that WHO has derived toxicity equivalency factors for dioxin-like PCBs and has stressed the importance of integrated standards for dioxins and dioxin-like PCBs.

Therefore, the methods for determination of PCDD/PCDF described in EN 1948 Part 1, 2, and 3 are expanded to the measurement of the WHO TEF assigned PCBs and marker PCBs. The measurement method for PCBs was also developed by CEN/TC 264/WG 1 and published as Technical Specification CEN/TS 1948-4:2007. The validation of the method in order to transfer the Technical Specification CEN/TS 1948-4:2007 to a European Standard EN 1948-4 has taken place from 2006 to 2008 financed by the European Commission and EFTA (Grant Agreement for an Action SA/CEN/ENV-EFTA/388/2006/30). The validation of the new method was performed in three parts.

The first part of the validation consisted of an interlaboratory comparison study in December 2006 to February 2007. Here the analytical section of the method was validated by distributing two ash samples, two standards solutions, one ash extract and two sets of complete calibration standards to 8 expert laboratories. The results of this study are summarized in Section 2 and are described in detail in Annex 1 of this report.

The second part of the validation of the combined sampling and chemical analysis at a full scale facility was performed by 3 expert sampling teams in combination with 3 analytical laboratories selected from the interlaboratory comparison study to cover all three sampling techniques; the cooled probe method, the filter/condenser method and the dilution method. Sampling took place at a state of the art incinerator facility in Vienna, Austria from the 20th of June until the 26th of June 2007 (sampling conditions and plant description see Section 3 and Annex 2).

The sampling campaign included 6 sampling days and samples were taken in duplicate using all three methods in the same duct, in addition 3 field blanks and 3 breakthrough samples were taken. These samples were analyzed during the following 2 months. This report contains a detailed evaluation of the results of the sampling campaign (see Section 4 to Section 9 and Annex 3 to Annex 6a, 6b, 6c).

The third part of the validation was performed at a shredder plant in the period from the 25th of February until the 5th of March 2008. This sampling campaign included five duplicate emissions measurements and two field blanks. In addition PCB break through was validated at two occasions by adding an extra adsorption unit to the sampling equipment. The adsorption units were analyzed separately from the emission samples. This additional validation was performed only for the filter/condenser method in order to validate the method at higher concentrations with emphasis on break through and within method variation (Details see Section 10 and Annex 7a, 7b).

2. Interlaboratory comparison study of the analytical method

Before the sampling campaign at a full scale incineration facility, an interlaboratory comparison study was organized. The results of this study were used to estimate the variance of the chemical analysis both between the expert laboratories and within laboratories. The details of the interlaboratory comparison study are given in Annex 1.

In summary the result of the 9 expert laboratories of which 8 were able to submit data before the set deadline were very good for standard solutions, a fly ash extract and two fly ash samples. Based on a z-score evaluation three validation teams representing each sampling method were selected.

Surprisingly the relative standard deviations (RSDs) for the analysis of the marker PCBs were somewhat larger than the RSD for the WHO TEF assigned PCBs, which is generally assumed to be a more difficult analysis. The between laboratory variance of the 8 participating expert laboratories and the within laboratory variance of the final 3 selected laboratories for the validation measurements are given in Table 1. The between laboratory variance for the chemical analysis for the standard solutions and the extract were all below 11 %, the corresponding within laboratory variance was below 5 %. For the fly ash samples the between laboratory variance for the WHO PCBs was 12 % and 16 % for the low and high level sample respectively, the corresponding within laboratory variance was 4 % and 8 %. Unexpectedly the variance for the sum of the marker PCBs were significantly higher both between and within the laboratories varied from 17 % to 47 %. All data on a congener specific basis is given in Annex 1. Standard solutions according to EN 1948-3:2006 were purchased from two suppliers. The supplied QA/QC information states a variation of 5 % for the concentration in the standard solutions and calibration curves.

Table 1. Between and within laboratory variance for the chemical analysis of the WHO PCBs (pg/μl or pg/g) and the sum of marker PCBs (ng/μl or ng/g) for the chemical analysis according to CEN/TS 1948-4:2007.

		Mean	Between laboratories			Within laboratories	
			n	SD	RSD	n	
Standard high	WHO PCB TEQ ¹	2,27 pg/μl	7	0,078	3%	2	5%
Standard low	WHO PCB TEQ ¹	0,45 pg/μl	8	0,048	11%	2	1%
Extract	WHO PCB TEQ ¹	0,18 pg/μl	8	0,018	10%	2	4%
	Sum Marker PCBs	8,16 ng/μl	8	0,77	9%	1	5%
Ash high	WHO PCB TEQ ¹	0,53 pg/g	8	0,09	16%	3	4%
	Sum Marker PCBs	4,60 ng/g	8	0,96	21%	3	21%
Ash low	WHO PCB TEQ ¹	0,008 pg/g	8	0,001	12%	3	8%
	Sum Marker PCBs	1,447 ng/g	8	0,682	47%	2	17%

¹ WHO TEF according to van den Berg et al. (Environmental Health Perspectives 1998, Vol. 70, pp. 775-792)

3. Field validation measurements at a waste incinerator

The field validation emission measurements with three sampling methods (cooled probe method, filter/condenser method and dilution method) were performed at a municipal waste incinerator. The sampling location consisted of 3 lines of a Martin grate incinerator equipped with a fabric filter with the addition of carbon, a two stage wet scrubber and a selective catalytic reduction unit. The bag house filter in combination with the catalytic reduction unit normally reduces 'dioxin' emission to less than 10 % of the regulation limit of 0,1 ng/m³. A detailed description of the operating conditions is given in Annex 2 and is summarized below in Table 2. The active carbon addition was stopped on sampling day 2 to day 6. On day 4 line 2 was started up after being shut down on day 1 to day 3.

Table 2. Operating conditions of the waste incinerator.

	Operation condition	Carbon injection
Day 1	Line 1,3 normal, Line 2 only fan	1 kg/h carbon
Day 2	Line 1,3 normal; Line 2 only fan	No carbon*
Day 3	Line 1,3 normal; Line 2 only fan	No carbon
Day 4	Line 1,3 normal; Line 2 start up	No carbon
Day 5	Line 1,2,3 normal	No carbon
Day 6	Line 1,2,3 normal	No carbon

* Recirculation but no active carbon

A wide variety of operating parameters were measured during the sampling campaign. The average values of a selected number of parameters of importance for the sampling are given in Table 3. The average oxygen levels from this table are used to normalize the data according to EN 1948-1:2006. All individual measurements and a detailed description are given in Annex 2.

Table 3. Average operating conditions during the sampling period.

	O ₂ Vol % (dry)	CO ₂ Vol % (dry)	CO mg/m ³ (s,d)	Flue gas temperature °C	Velocity m/s	Flue gas flow m ³ /h	Flue gas flow m ³ (s,d)/h
Day 1	14,3	5,7	11	132,5	16,5	268 900	151 300
Day 2	14,4	5,32	17	132,3	16,5	269 100	150 900
Day 3	11,3	8,3	23	125,9	10,70	174 300	99 400
Day 4	9,7	9,7	42	132,9	14,36	233 900	131 200
Day 5	9,3	10,2	36	133,8	14,30	232 900	130 000
Day 6	9,1	10,4	27	132,9	14,30	232 900	129 700

s,d standard conditions, dry gas

The measurements were performed on a horizontal sampling platform on the ‘west’ and ‘east’ side of the horizontal duct. The position of the sampling probes is given in Table 4 and Figure 1, all details are given in Annex 2.

Table 4. Position of the probes in the duct.

Flange	Method	Probe length in duct	X (mm)	Y (mm)	Z (mm)	Position
C	Cooled probe	1750 mm	700	0	2150	West
D1		700 mm	900	0	2150	East
E	Filter/condenser	570 mm	570	+300	4300	East
B		1750 mm	900	-400	1800	West
F	Dilution	400 mm + 600 mm	400, 600	0	5500	East
A		1750 mm	600	0	0	West
B2	Oxygen	600 mm	600	0	2150	East

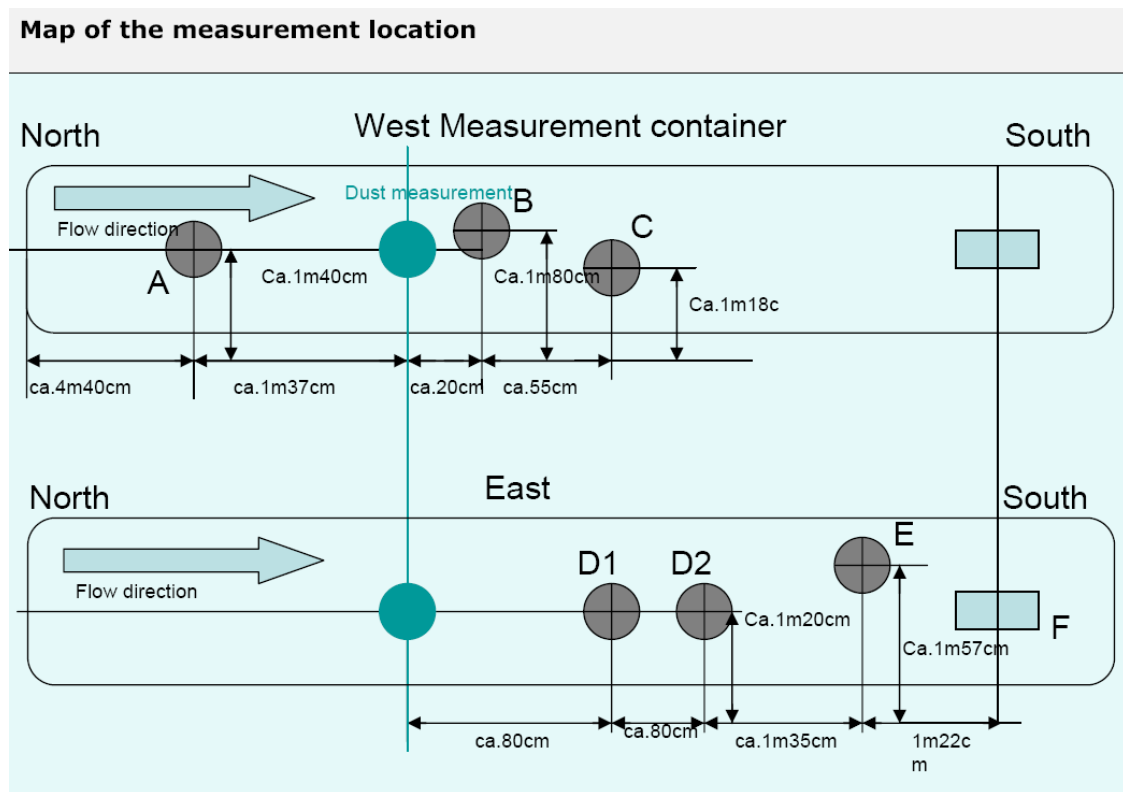
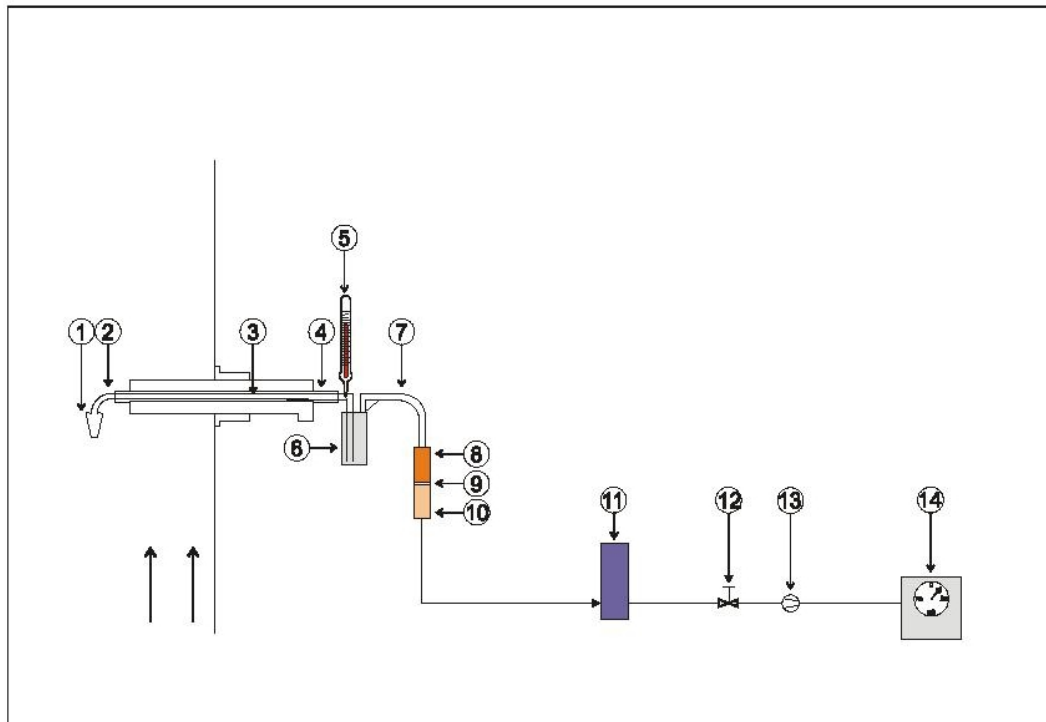


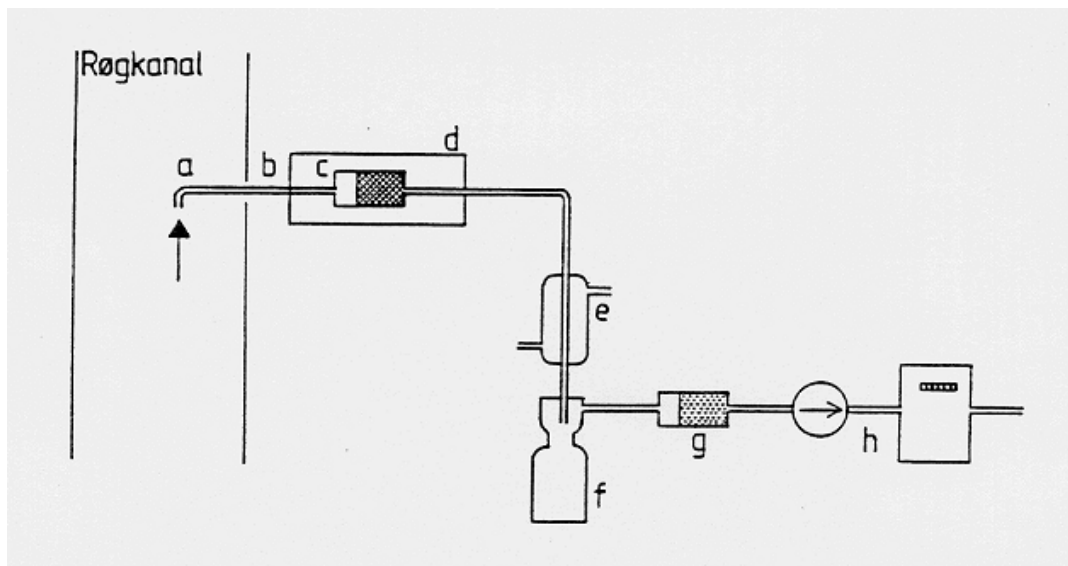
Figure 1. Arrangement of sampling ports and their use for sampling
A: Dilution method; B: Filter/condenser method; C: Cooled probe method
D1: Cooled probe method; E: Filter/condenser method; F: Dilution method

All sampling was performed in agreement with EN 1948-1:2006. A schematic of all three methods is given below in Figure 2 to 4. All details are described in Annex 6a, 6b and 6c. All nozzles were of the same diameter except for the dilution method. For practical and technical reasons two nozzle diameters (6 mm East, 8 mm West) were used.



- | | | |
|------------------|-----------------------|----------------------------|
| 1 Nozzle | 6 Condensate flask | 11 Silica gel drying tower |
| 2 Elbow | 7 Glass connection | 12 Control valve |
| 3 Titanium liner | 8 Glass wool | 13 pump |
| 4 Cooled probe | 9 Plane filter GF10HY | 14 Dry gas meter |
| 5 Thermometer | 10 XAD-2 resin | |

Figure 2. Schematic of the cooled probe sampling train (Annex 6a).



- | | | |
|-----------|---------------------------|-------------------------------------|
| a: Nozzle | d: Heated filter box | g: XAD-2 adsorbent |
| b: Probe | e: Water cooled condenser | h: Drying tower, pump and gas meter |
| c: Filter | f: Condensate bottle | |

Figure 3. Schematic of the filter/condenser sampling train (Annex 6 b).

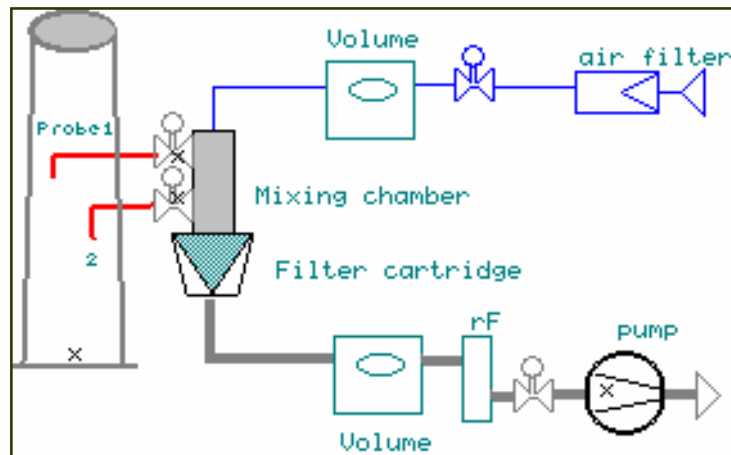


Figure 4. Schematic of the dilution sampling train (Annex 6c).

4. Results of the validation measurements at the waste incinerator

The individual results for the 4 planar PCBs (#77, #81, #126, #169), the 8 mono ortho substituted PCBs (#105, #114, #118, #123, #156, #157, #167, #189) and the 6 marker PCBs (#28, #52, #101, #138, #153, #180) for the 6 duplicate measurements, the 3 blank samples and the 3 breakthrough samples are given in Annex 3. In addition indicative values for HCB are given in this Annex 3. Chemical analysis and quantification was performed according to CEN/TS 1948-4:2007. All values are normalized on the same O₂ values measured in the duct given in Table 2, to avoid individual variation caused by different O₂ measurements. From this data the total WHO TEQ was calculated according to CEN/TS 1948-4:2007 Clause 8.8.2 and Table A.1. The TEQ values and the sum of the 6 marker PCBs are summarized in Table 5. Both an upper bound (non detected congener concentration = reported detection limit) and lower bound (non detected congener concentration = 0) TEQ values were calculated.

As an example the data is graphical represented in Figure 5 and 6 where the individual results of the PCB TEQ values for each of the three methods (cooled probe, filter/condenser and dilution) are given in relation to the field blank levels calculated on the same sample volume. For the dilution method due to the relatively large difference between the volume sampled at the east and west side of the duct, two blank values are included corresponding to the respective sample volumes at the east and west sampling locations.

The levels calculated on TEQ basis according to the 1998 WHO TEFs¹⁾ were extremely low ranging from 0,19 pg TEQ/m³ to 0,41 pg TEQ/m³ and very close to the levels in the field blank samples. This corresponds to 0,0002 ng TEQ/m³ to 0,0004 ng TEQ/m³ which is at the lower end of the calibration curve of the method and well below the advised level of 0,01 ng TEQ/m³ which is 10 times below the European limit value of 0,1 ng TEQ/m³.

The standard deviation is calculated according to the following equation considering all 6 measurements (three duplicates at different locations in the duct) on one specific day.

$$s_D = \sqrt{\frac{\sum_{i=1}^N (x_i - \bar{x})^2}{N - 1}}$$

s_D = Standard deviation of all measurements on the respective day

x_i = Measurement on the respective day

\bar{x} = Average of all measurements (3 methods, two duplicates) on one day

N = Total number of measurements on one day ($N = 6$)

Table 5. Summary of the results of the measurements day 1-6, WHO TEQ in pg/m³ and marker PCBs in ng/m³.

	Day 1			Day 2		
	Mean	SD	% RSD	Mean	SD	% RSD
WHO-TEQ PCB (pg/m³, nd =0)	0,29	0,16	55%	0,28	0,27	95%
WHO-TEQ PCB (pg/m³, nd =lod)	0,34	0,12	34%	0,34	0,26	75%
Sum 6 Marker PCBs (ng/m³)	4,43	1,71	39%	7,46	6,10	82%
	Day 3			Day 4		
	Mean	SD	% RSD	Mean	SD	% RSD
WHO-TEQ PCB (pg/m³, nd =0)	0,25	0,25	97%	0,41	0,27	64%
WHO-TEQ PCB (pg/m³, nd =lod)	0,29	0,22	78%	0,41	0,27	64%
Sum 6 Marker PCBs (ng/m³)	4,91	4,31	88%	10,51	10,22	97%
	Day 5			Day 6		
	Mean	SD	% RSD	Mean	SD	% RSD
WHO-TEQ PCB (pg/m³, nd =0)	0,37	0,31	82%	0,14	0,12	86%
WHO-TEQ PCB (pg/m³, nd =lod)	0,37	0,31	82%	0,19	0,12	65%
Sum 6 Marker PCBs (ng/m³)	4,96	3,42	69%	7,29	9,27	127%

A graphical representation of the data for the duplicate measurements by each of the three methods for each day and the field blank samples are given for the WHO PCBs in Figure 5 and 6, the sum of the marker PCBs in Figure 7 and 8 and for HCB in Figure 9 and 10. All figures for the individual PCBs are given in Annex 3. In the figures the duplicate samples which were taken simultaneously are represented by the blue symbols, and the field blank samples by the red symbols. Levels under the analytical detection limit are represented by the open symbols.

¹⁾ van den Berg et al. (Environmental Health Perspectives 70 (1998) pp. 775-792)

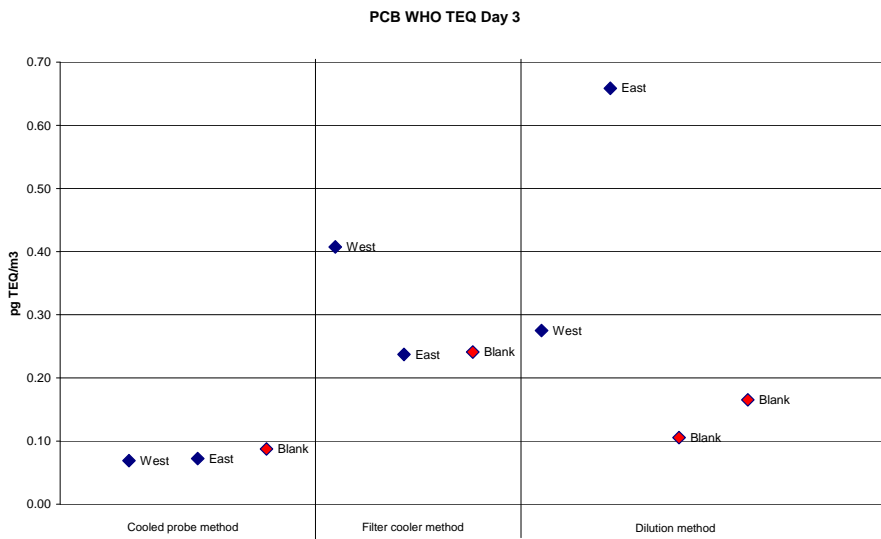
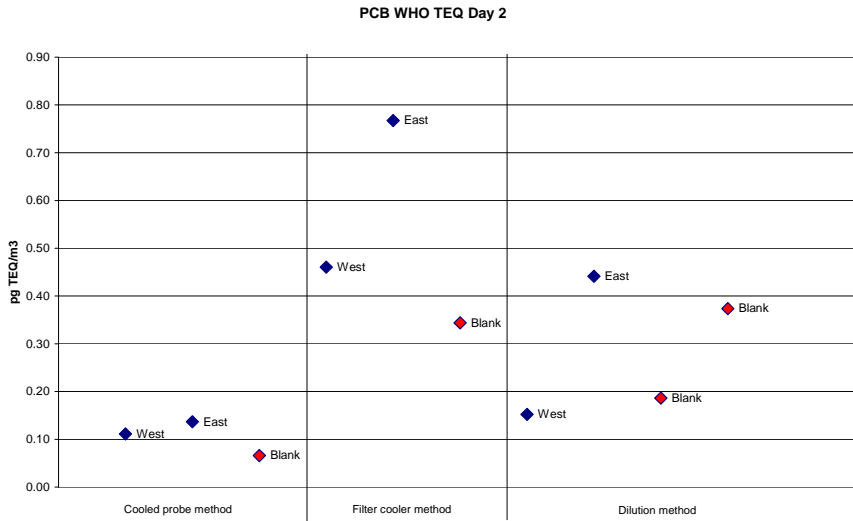
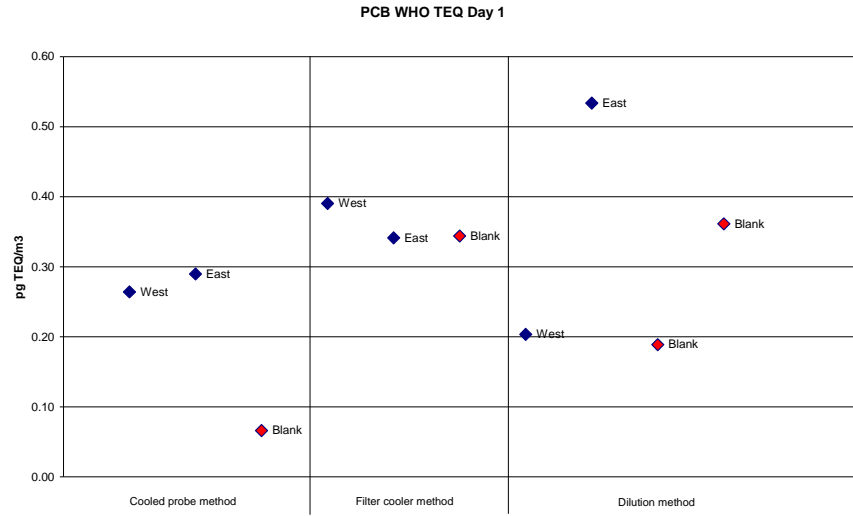


Figure 5. Graphical representation results total WHO PCB TEQ day 1,2,3.

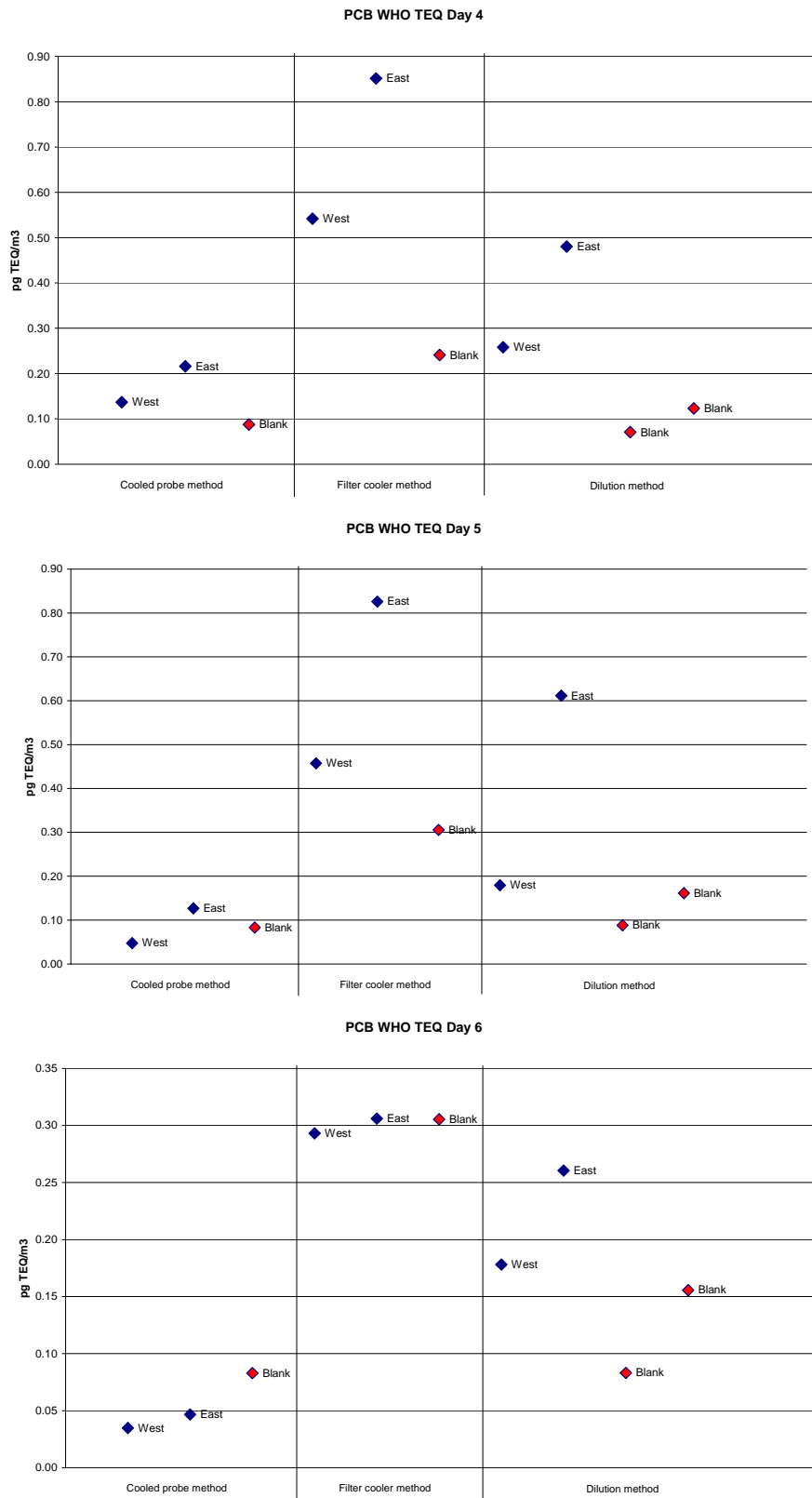


Figure 6. Graphical representation results total WHO PCB TEQ day 4,5,6.

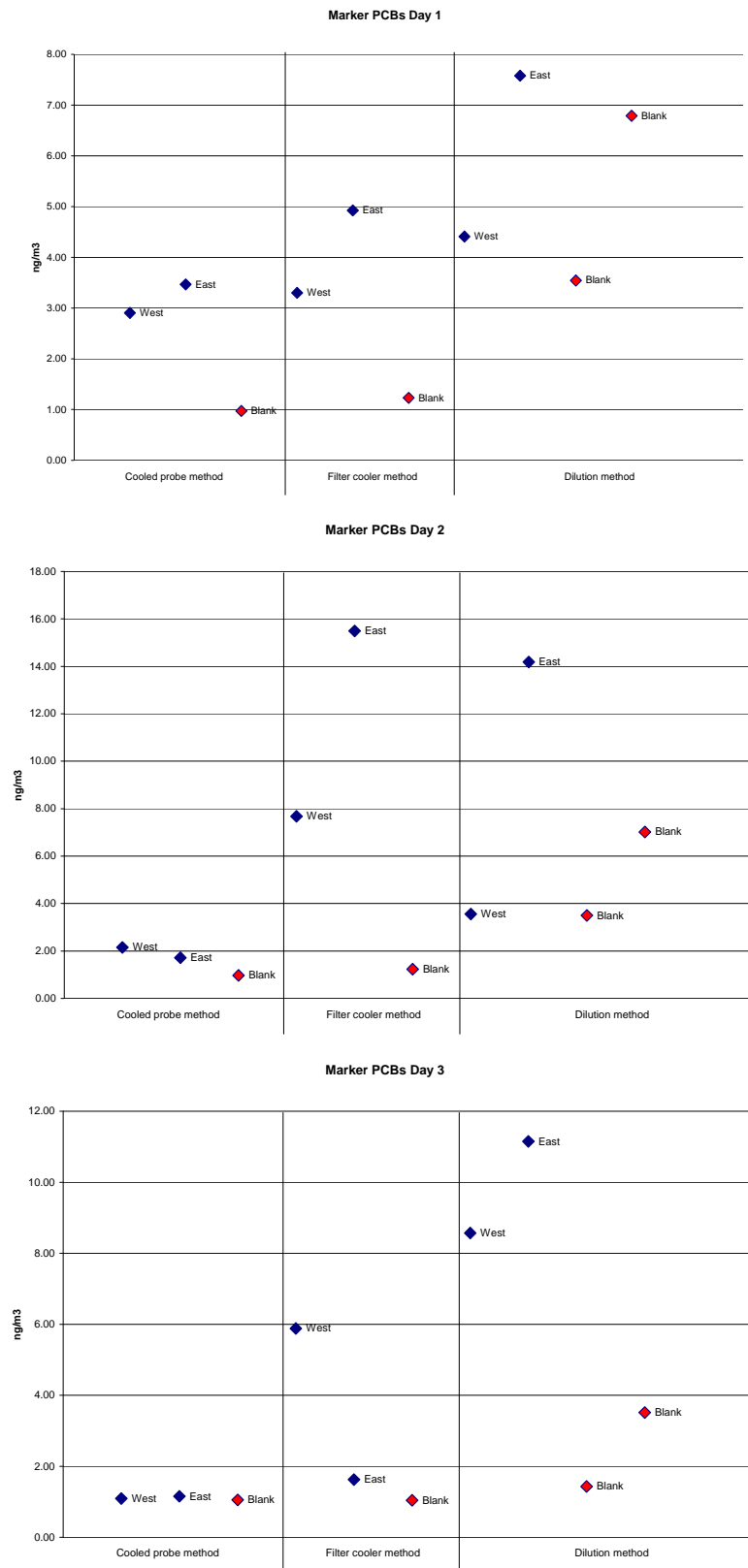


Figure 7. Graphical representation results sum of the marker PCBs day 1,2,3.

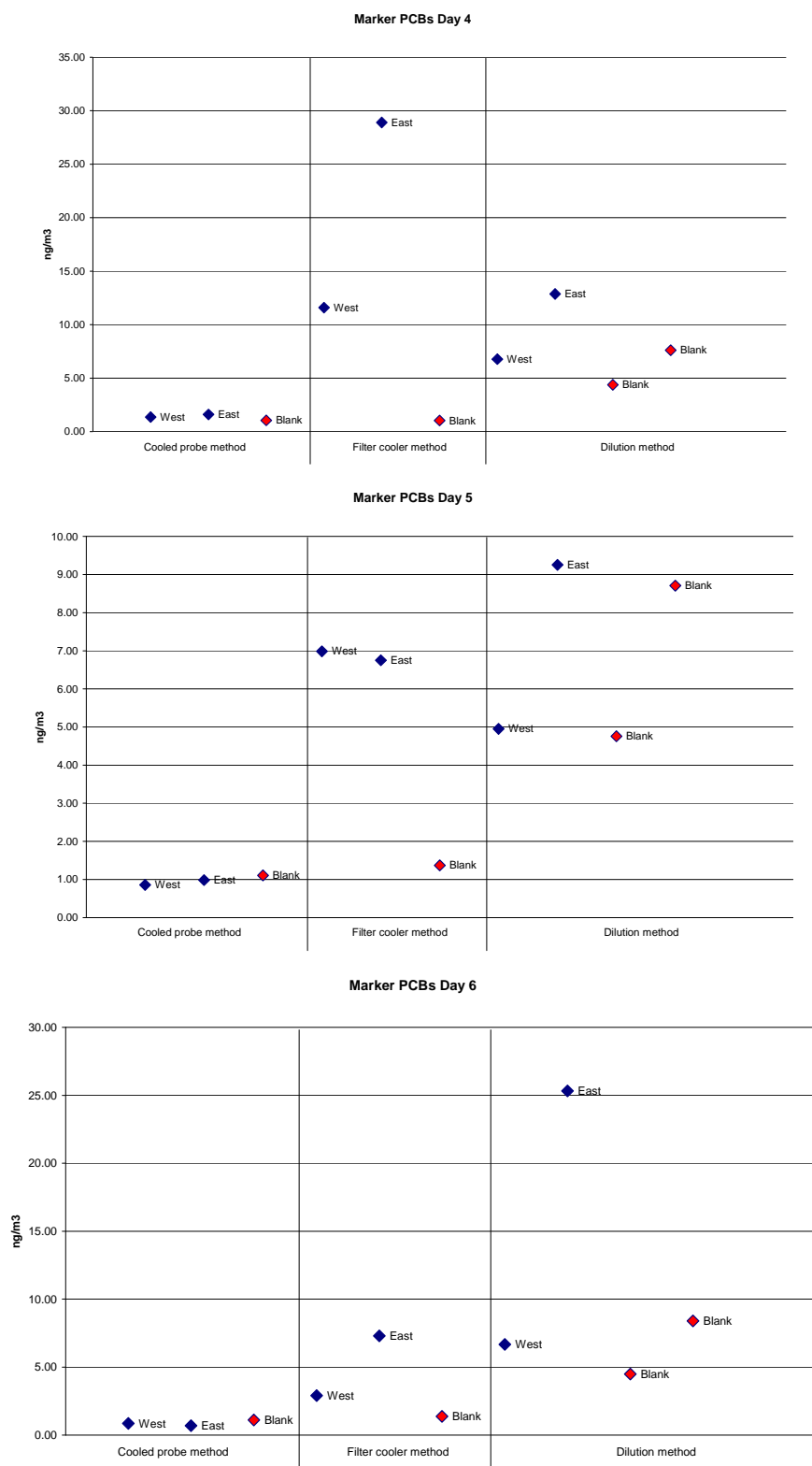


Figure 8. Graphical representation results sum of the marker PCBs day 4,5,6.

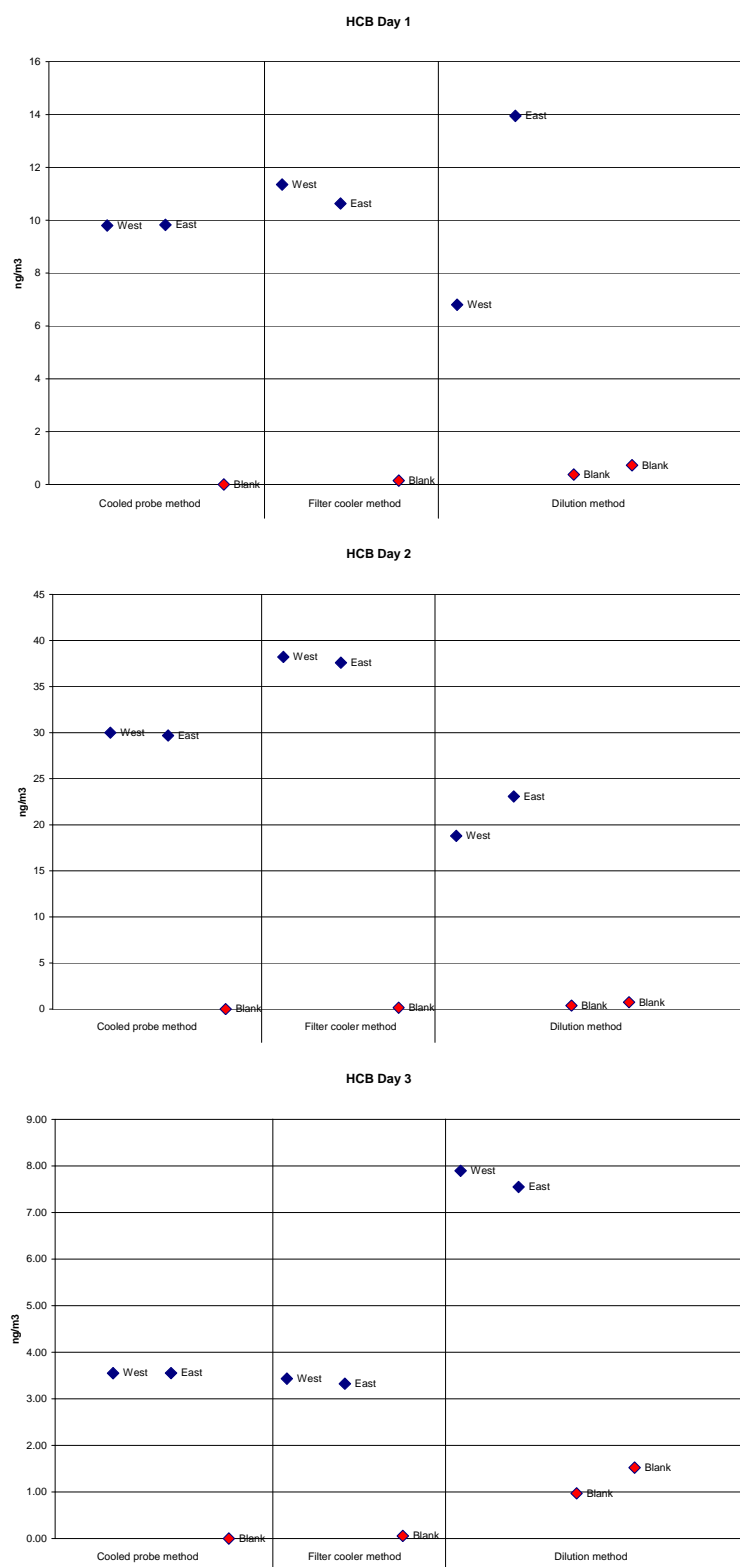


Figure 9. Graphical representation results HCB day 1,2,3.

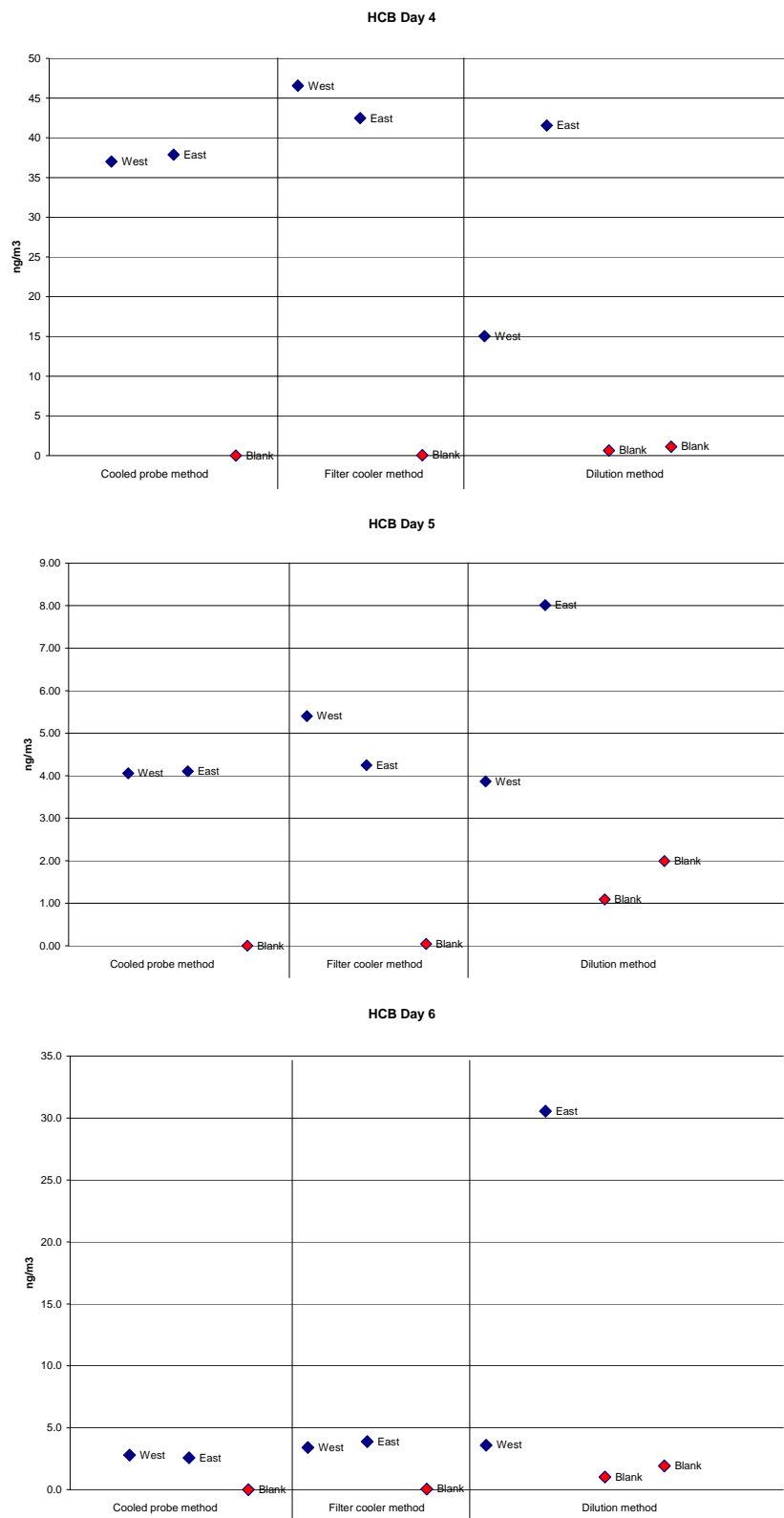


Figure 10. Graphical representation results HCB day 4,5,6.

5. Recovery at the waste incinerator

The recovery of the sampling standards and the extraction standards added to the samples according to CEN/TS 1948-4:2007 Clause 6.2 and Table 1 and calculated according CEN/TS 1948-4:2007 Clause 8.8.2 and 8.8.3 are summarized below for each of the three methods. All individual recoveries are given in Annex 4.

All recoveries were within the minimum requirements as outlined in Clause 10.3 of CEN/TS 1948-4:2007 except for one occasion for the cooled probe method (PCB #167, 151 %), two occasions for the filter/condenser method (PCB #157, 18 % and 19 %) and 5 occasions for the dilution method (PCB #52, 14 % and 19 %, PCB #169, 154 % and 159 % and PCB #28, 157 %). For all recoveries lower than 40 % or over 120 % but higher than 20 % or lower than 150 % the contribution of this congener to the total WHO PCB TEQ was less than 10 % as outlined in the method and in agreement with the requirements of the method. According to this quality criterion, these data were therefore included in the calculation of the WHO-TEQ values.

Table 6. Summary of the recovery of the three methods during the sample campaign.

Sampling Standards	Cooled Probe				Filter/condenser				Dilution			
	min	max	mean	n*	min	max	mean	n	min	max	mean	n**
13C-PCB 60 [%]	87	103	94	24	23	134	111	14	63	92	73	14
13C-PCB 127 [%]	66	107	92	24	72	105	92	15	51	102	66	14
13C-PCB 159 [%]	71	112	90	24	43	106	85	15	53	88	66	14
Extraction Standards												
13C-PCB 28 [%]	73	99	81	24	52	69	61	15	35	157	86	14
13C-PCB 52 [%]	63	81	74	24	48	68	56	15	14	150	66	14
13C-PCB 101 [%]	79	97	85	24	57	75	64	15	20	136	54	14
13C-PCB 138 [%]	78	136	95	24	45	67	60	15	21	91	45	14
13C-PCB 153 [%]	75	133	92	24	36	66	54	15	45	142	91	14
13C-PCB 180 [%]	67	122	86	24	53	76	66	15	36	97	60	14
13C-PCB 77 [%]	52	94	83	24	26	64	50	15	35	143	89	14
13C-PCB 81 [%]	86	109	95	24	25	66	51	15	51	149	96	14
13C-PCB 105 [%]	87	147	104	24	27	63	49	15	26	114	56	14
13C-PCB 114 [%]	91	145	103	24	25	61	48	15	21	101	54	14
13C-PCB 118 [%]	68	117	84	24	20	47	36	15	22	95	55	14
13C-PCB 123 [%]	91	146	102	24	24	49	41	15	23	91	55	14
13C-PCB 126 [%]	55	102	76	24	22	50	39	15	27	147	68	14
13C-PCB 156 [%]	97	144	113	24	23	53	40	15	29	107	56	14
13C-PCB 157 [%]	94	145	111	24	18	42	34	15	29	98	58	14
13C-PCB 167 [%]	95	151	114	24	20	38	31	15	27	89	54	14
13C-PCB 169 [%]	82	106	94	24	20	43	34	15	32	159	75	14
13C-PCB 189 [%]	79	121	96	24	20	39	33	15	37	145	94	14

* All data included all field blanks, breakthrough samples.

** Two samples not included which had been run through an additional clean up.

Values in red bold italic are outside the specified recovery range (40 % to 120 %) but comply with the recovery quality criterion.

6. LOD and LOQ at the waste incinerator

6.1 LOD

The LOD is defined in Clause 3.10 of CEN/TS 1948-4:2007 as the average analytical blank value (b_{ave}) plus 3 times the standard deviation of the analytical blank (s_b).

$$LOD = b_{ave} + 3 s_b$$

In this report the field blank values were used for calculation of LOD representing possible sources of contamination during the complete measurement procedure. The LODs of the individual congeners are given in Annex 5. Due to the relatively large differences between the sampling volumes of the East (low volume) and West (high volume) sampling points of the dilution method two LOD have been calculated related to the larger volume and the smaller volume.

The LODs for the individual WHO TEF assigned PCBs were very low and in the pg/m^3 range (Table 7). Consequently the WHO-TEQ calculated from the individual results was well below the suggested 0.01 ng/m^3 ranging from 0.00011 ng/m^3 to 0.00057 ng/m^3 .

Table 7. LOD of the different methods based on 3 field blanks.

	Cooled Probe	Filter/condenser	Dilution 1*	Dilution 2*
WHO-TEQ PCB (pg/Nm^3)	0,11	0,47	0,29	0,57
Sum 6 Marker PCBs (ng/Nm^3)	1,25	1,71	8,30	14,22

*Two values for the dilution method are given based on the two different sampling volumes.

6.2 LOQ

The LOQ is defined in Clause 3.11 of CEN/TS 1948-4:2007 as the average analytical blank value (b_{ave}) plus a factor F ranging from 5 – 10 times the standard deviation of the analytical blank (s_b).

$$LOQ = b_{ave} + F s_b$$

In this report the field blank values were used for calculation of LOQ representing possible sources of contamination during the complete measurement procedure. The LOQs of the individual congeners, calculated with $F = 10$, are given in Annex 5. A summary of the LOQ for the sum of the marker PCBs and the WHO-TEQ PCB are given in Table 8.

Table 8. LOQ of the different methods based on 3 field blanks.

	Cooled Probe	Filter/condenser	Dilution 1*	Dilution 2*
WHO-TEQ PCB (pg/Nm³)	0,20	0,87	0,67	1,37
Sum 6 Marker PCBs (ng/Nm³)	1,72	2,85	20,08	32,62

*Two values for the dilution method are given based on the two different sampling volumes.

In Table 9 the individual LODs of the WHO TEF assigned PCBs are compared to the quantification limits in Table 5 of CEN/TS 1948-4:2007. Note that the indicative values specified in CEN/TS 1948-4:2007 are based on laboratory blank values and are not given for the field blank values which were measured during the sampling campaign at the full scale operating incineration facility.

The LOQ calculated from the field blanks for the planar PCBs were in the same range as recommended in CEN/TS 1948-4:2007 except for PCB #77. The LOQ for PCB #77 was significantly higher for both the filter/condenser and dilution method. The LOQs for the mono ortho PCBs for the cooled probe method were all within the recommended range. For the filter/condenser method PCB #105, #114, #118, and #156 were outside the recommended range. The dilution method showed LOQ above the recommended LOQ for all mono ortho PCBs for both the smaller and the larger sampling volume.

Because of the relatively high blank levels of PCB#77 which has a high TEF factor, caution should be taken with respect to blanks values for this PCB congener.

Table 9. Individual LOQs WHO PCBs of the different methods compared to suggested LOQ in CEN/TS 1948-4:2007.

	Cooled Probe	Filter/condenser	Dilution 1*	Dilution 2*	TS 1948-4**)
Unit	ng/m ³	ng/m ³	ng/m ³	ng/m ³	ng/m ³
3,3',4,4'-Tetra-CB #77	0,027	0,081	0,164	0,250	0,008-0,015
3,4,4',5-Tetra-CB #81	0,003	0,003	0,004	0,008	0,003-0,01
3,3',4,4',5-Penta-CB #126	0,001	0,007	0,005	0,010	0,002-0,004
3,3',4,4',5,5'-Hexa-CB #169	0,001	0,007	0,003	0,006	0,003-0,01
2,3,3',4,4'-Penta-CB #105	0,039	0,118	0,243	0,498	0,04-0,08
2,3,4,4',5-Penta-CB #114	0,004	0,021	0,033	0,048	0,008-0,015
2,3',4,4',5-Penta-CB #118	0,124	0,545	0,900	1,705	0,08-0,15
2',3,4,4',5-Penta-CB #123	0,004	0,004	0,030	0,045	0,008-0,015
2,3,3',4,4',5,-Hexa-CB #156	0,036	0,020	0,131	0,299	0,008-0,015
2,3,3',4,4',5'-Hexa-CB #157	0,009	0,004	0,030	0,063	0,008-0,015
2,3',4,4',5,5'-Hexa-CB #167	0,007	0,005	0,088	0,182	0,008-0,015
2,3,3',4,4',5,5'-Hepta-CB #189	0,006	0,004	0,022	0,049	0,008-0,015

*) Two values for the dilution method are given based on the two different sampling volumes.

**) Analytical blank data

7. Evaluation of the field blank samples at the waste incinerator

Field blank samples were measured at day 0, day 3 and day 5. The field blank sample of day 0 (19/6) was compared with the measurements of day 1 and day 2, the blank sample measured on day 3 (22/6) with the measurements on day 3 and day 4 and finally the field blank from day 5 (25/6) with the measurements at day 5 and day 6.

Because of the extreme low levels of PCBs during the sampling period, even low levels in the field blank samples are problematic. In Table 10, the percentage present in the field blank samples relative to the amounts found in the samples are summarized. In addition the same percentages for hexachlorobenzene are given. The data did indicate that all measurements were very close to the field blank levels, and varied on the different sampling days, independent of the method. It also indicates that PCBs are present in field blank samples at levels close to the low levels to be expected in state of the art incineration facilities in contrast to HCB.

Table 10. Relative percentage of the field blanks to the measured concentrations day 1-6.

	Cooled Probe	Cooled Probe	Filter/ Condenser	Filter/ Condenser	Dilution	Dilution
Sample Location	West	East	West	East	West	East
Day 1						
WHO-TEQ PCB	25%	23%	88%	101%	93%	68%
Total marker PCB	33%	28%	37%	25%	80%	90%
HCB	< 1%	< 1%	1%	1%	6%	5%
Day 2						
WHO-TEQ PCB	59%	48%	75%	45%	122%	85%
Total marker PCB	45%	57%	16%	8%	98%	49%
HCB	< 1%	< 1%	< 1%	< 1%	2%	3%
Day 3						
WHO-TEQ PCB	127%	121%	59%	102%	38%	25%
Total marker PCB	96%	91%	21%	78%	76%	92%
HCB	< 1%	< 1%	2%	2%	12%	20%
Day 4						
WHO-TEQ PCB	64%	41%	44%	28%	27%	26%
Total marker PCB	77%	66%	9%	4%	65%	59%
HCB	< 1%	< 1%	< 1%	< 1%	4%	3%
Day 5						
WHO-TEQ PCB	175%	65%	67%	37%	49%	26%
Total marker PCB	129%	113%	20%	20%	96%	94%
HCB	< 1%	< 1%	1%	1%	28%	25%
Day 6						
WHO-TEQ PCB	238%	178%	104%	100%	47%	60%
Total marker PCB	129%	162%	47%	19%	67%	33%
HCB	< 1%	< 1%	1%	1%	29%	6%

All field blank complied with criteria specified in Clause 10.2.b of CEN/TS 1948-4:2007, as indicated below in Table 11. None of the field blank samples exceeded 10 % of the actual limiting value (0,1 ng TEQ/m³). In relation to this value the levels found in the field blank are still several orders of magnitude lower.

Table 11. WHO TEQ PCB levels in the field blank (taken at day 0, day 3 and day 5), all below 10 % of the limiting value (0,1 ng TEQ/m³).

Field blank	Considered for samples of day	Cooled Probe	Filter/ Condenser	Dilution I	Dilution II
		ng/m ³	ng/m ³	ng/m ³	ng/m ³
1	1 and 2	0,00007	0,00034	0,00019	0,00037
2	3 and 4	0,00009	0,00047	0,00011	0,00017
3	5 and 6	0,00009	0,00030	0,00009	0,00016

8. Breakthrough during sampling at the waste incinerator

It is evident from Table 5 and Table 11 that the levels in the samples were extremely low and often in the same range as the field or laboratory blanks for the validation at the state of the art incineration facility. This results in an overestimation of the breakthrough while both the levels in the samples and in the break through samples are very close to the levels in the field blank samples.

9. Accuracy of the measurement methods at the waste incinerator

The accuracy of the methods was evaluated according the standard ISO 5725-2. This standard gives an estimate of the within laboratory variance (S_w^2), the repeatability variance (S_r^2), the between laboratory variance (S_L^2) and finally an estimate of the total reproducibility of the method. In addition the within method variance of the three methods (S_m^2) was calculated. The repeatability variance (S_r^2) was calculated according to Clause 7.4.5.3 of ISO 5725-2:1994. The between laboratory variance (S_L^2) was also calculated according to this clause but resulted in negative values, they were treated as described in Clause 7.4.5.4 of ISO 5725-2:1994. In order to estimate the between laboratory variance (S_L^2) the arithmetic mean of the within laboratory variance (S_w^2) between the laboratories was calculated. The total reproducibility (S_R^2) was calculated as $S_R^2 = S_L^2 + S_r^2$. The data of Table 12, 13 and 14 are calculated according the following equations:

$$S_L = \sqrt{\frac{\sum_{i=1}^n (\bar{x}_i - \bar{X})^2}{N - 1}}$$

S_L Standard deviation of duplicate measurements of the 3 laboratories

\bar{x}_i Mean of the duplicate measurements

\bar{X} Overall mean of the 3 laboratories

N Number of duplicate measurements (3 measurements) on each day

$$S_r = \sqrt{\sum_{i=1}^n \frac{(S_i)^2}{N}}$$

S_r Repeatability variance

S_i Standard deviation of the duplicate measurements of the 3 different methods on the same day

N Number of duplicate measurements (3 measurements)

$$S_m = \sqrt{\sum_{w=1}^n \frac{(S_w)^2}{N}}$$

S_m Within method variance

S_w Standard deviation of the duplicate measurements of the same method on each day

N Number of duplicate measurements (6 measurements)

A summary of the data of the 6 sampling occasions is given in Table 12. The total reproducibility is based on extreme low concentrations over a limited range from 0,19 pg TEQ/m³ to 0,41 pg TEQ/m³ for the WHO PCBs and from 4,43 ng/m³ to 10,51 ng/m³ for the marker PCBs.

Table 12. Summary of the repeatability standard deviation (S_r), between laboratory standard deviation (S_L) and the total reproducibility standard deviation (S_R)

Day 1-6		WHO-TEQ PCB (pg/m ³)	Marker PCBs (ng/m ³)
Repeatability standard deviation	S_r	0,151	4,33
Between laboratory standard deviation	S_L	0,196	5,27
Total Reproducibility standard deviation	S_R	0,247	6,82

Table 14 contains the data for each individual day. The reproducibility over the 6 days the measurements were performed varied between 41 % and 82 % for the WHO PCBs and ranged between 39 % and 128 % for the sum of the marker PCBs. The variation (RSD) for the WHO PCBs is in agreement with the theoretical Horowitz equation developed in 1980²⁾ to predict the between laboratory variation for the concentration range in the low ppt level. However the lower reproducibility of the higher concentrations of the marker PCBs is unexpected and the levels present in the blank samples might contribute to the larger variation.

²⁾ Horowitz et al. Assoc. Off. Anal. Chem. 1980, 63, 1344-1354

The within method variance is given in Table 13. The within method reproducibility is clearly better for the cooled probe method. However, the location of the sampling point should be taken into account here (see Table 4 and Figure 1 in Section 3). For practical reasons the two sampling points were located very close to each other, this was in contrast for the duplicate sampling points for the other methods. Because of the extreme low levels the concentration in the duct might not have been homogeneously distributed through the duct.

Table 13. Within method variance (S_m^2) calculated for the 6 sampling days at low concentration (range 0,19 – 0,41pg TEQ/m³WHO PCBs and 4,43 – 10,51 ng/m³ Marker PCBs).

Method		WHO-TEQ PCB (pg/m ³)	Marker PCBs (ng/m ³)
Cooled Probe	S_m^2	0,0012	0,051
	S_m	0,0342 26%	0,225 14%
Filter/Condenser	S_m^2	0,0298	33,38
	S_m	0,1726 35%	5,78 67%
Dilution	S_m^2	0,0485	44,43
	S_m	0,2203 62%	6,67 69%

Footnote to Table 14

*) An estimate of the values of day 1 and day 2 were made by calculating the arithmetic mean of the within laboratory variance due to negative values of S_L^2 calculated according Clause 7.4.5.4 of ISO 5725-2:1994 (further explanation see Page 21). For day 1 and day 2 the mean values of the different methods are very similar and the between laboratory variance is smaller than the within laboratory variance which shows a large variance for the dilution method (see Figure 5 and Figure 7).

Table 14. The repeatability variance (S_r^2), the between laboratory variance (S_L^2) and the total reproducibility (S_R^2) calculated on each of the 6 sampling days

			WHO-TEQ PCB		Marker PCBs	
Repeatability variance	S_r^2	Day 1*)	0,0187		2,16	
Between lab variance	S_L^2		0,0027		2,05	
Total Reproducibility	S_R^2		0,0214		4,21	
Repeatability STD	S_r	Day 1*)	0,137	41%	1,47	33%
Between lab STD	S_L		0,052	15%	1,43	32%
Total Reproducibility STD	S_R		0,146	43%	2,05	46%
Repeatability variance	S_r^2	Day 2*)	0,0297		29,05	
Between lab variance	S_L^2		0,0616		24,78	
Total Reproducibility	S_R^2		0,0913		53,83	
Repeatability STD	S_r	Day 2*)	0,172	50%	5,39	72%
Between lab STD	S_L		0,248	72%	4,98	67%
Total Reproducibility STD	S_R		0,302	88%	7,34	98%
Repeatability variance	S_r^2	Day 3	0,0294		4,13	
Between lab variance	S_L^2		0,0402		20,10	
Total Reproducibility	S_R^2		0,0695		24,23	
Repeatability STD	S_r	Day 3	0,171	60%	2,03	41%
Between lab STD	S_L		0,200	70%	4,48	91%
Total Reproducibility STD	S_R		0,264	92%	4,92	100%
Repeatability variance	S_r^2	Day 4	0,0253		56,06	
Between lab variance	S_L^2		0,0691		88,40	
Total Reproducibility	S_R^2		0,0944		144,46	
Repeatability STD	S_r	Day 4	0,159	38%	7,49	71%
Between lab STD	S_L		0,263	64%	9,40	89%
Total Reproducibility STD	S_R		0,307	74%	12,02	114%
Repeatability variance	S_r^2	Day 5	0,0548		3,10	
Between lab variance	S_L^2		0,0772		12,28	
Total Reproducibility	S_R^2		0,1320		15,38	
Repeatability STD	S_r	Day 5	0,234	62%	1,76	35%
Between lab STD	S_L		0,278	74%	3,50	71%
Total Reproducibility STD	S_R		0,363	97%	3,92	79%
Repeatability variance	S_r^2	Day 6	0,0012		61,23	
Between lab variance	S_L^2		0,0175		61,56	
Total Reproducibility	S_R^2		0,0187		122,79	
Repeatability STD	S_r	Day 6	0,034	18%	7,82	107%
Between lab STD	S_L		0,132	71%	7,85	108%
Total Reproducibility STD	S_R		0,137	73%	11,08	152%

*) Footnote see Page 23

10. Additional measurements at a shredder plant

Due to the very low concentrations values measured during the validation campaign in summer 2007 at a municipal waste incinerator, additional measurements are performed in spring 2008 at a shredder plant, where higher PCB concentrations could be expected. The main topic of these additional measurements was the determination of break through values, which could not be determined based on the low concentration data of the municipal waste incinerator (see Clause 8). This sampling campaign included five duplicate emissions measurements with the filter/condenser method, two field blanks and two break through tests. In case of these high level samples from the shredder plant, analytical problems were experienced after testing several chromatographic clean up columns according to Clause 8.3 of CEN/TS 1948-4:2007. A dilution containing 0,02 % of 60 % of the sample was then taken for analysis (Details see Annex 7a).

10.1 Results of the shredder plant

The complete measurement data of the additional measurements at the shredder plant are given in Annex 7b. The levels calculated on TEQ basis according to the 1998 WHO TEFs are ranging from 0,29 ng WHO TEQ/m³ to 0,94 ng WHO TEQ/m³. For the sum of the 6 marker PCBs the levels are ranging from 3 500 ng/m³ to 26 100 ng/m³. The relative percentage of the field blanks to the measured concentrations were lower than 1 % for the WHO TEQ PCB and lower than 0,1 % for the sum of the 6 marker PCBs.

From the duplicate measurements of the five sampling days the standard deviation for duplicate measurements is calculated according the following equation (see Table 15):

$$S_D = \sqrt{\sum_{i=1}^n \frac{(c_{1,i} - c_{2,i})^2}{2N}}$$

S_D Standard deviation of duplicate measurements

$c_{1,i}$ Concentration of measurement 1

$c_{2,i}$ Concentration of measurement 2

N number of duplicate measurements (5 measurements)

Table 15. Summary of the results of the additional measurements averaged over 5 measurement days, WHO TEQ in and marker PCBs in ng/m³.

	n Number of duplicate measurements	Mean	SD of duplicate measurements	% RSD duplicate measurements*
WHO-TEQ PCB (ng/m ³ , nd =0)	5	0,55	0,10	17,3
WHO-TEQ PCB (ng/m ³ , nd =lod)	5	0,55	0,10	17,3
Sum 6 Marker PCBs (ng/m ³)	5	12 283	2 722	22

* Related to the mean value of the data collective

10.2 Break through

For validation of the break through of the method the data of the additional validation of the filter/condenser method at the high concentrations of the shredder plant was used as summarized below in Table 16 and described in detail in Annex 7b. During sampling an extra cartridge was placed after the original sampling cartridge to measure the break through of the PCBs.

The break through is below 1 % for WHO PCBs calculated as TEQ. For the marker PCBs the break through was below 3 %. For all individual PCB congeners the break through was below 5 % and in agreement with criteria specified in Clause 9.2 of CEN/TS 1948-4:2007 except for PCB #189. The level of this PCB was below the detection limit in the break through samples but due to a relatively high detection limit in combination with the low levels present in the samples, the 'upper bound' break through could be relatively high (>20 %). The contribution of PCB #189 was less than 5 % to the total TEQ.

Table 16. Break through at high levels sampling at the shredder facility for the filter/condenser method¹.

	Average Day 4	Break through	Average Day 6	Break through
WHO-TEQ PCB	368 pg/m ³	0,38%	212 pg/m ³	0,52%
Marker PCBs	8 364 ng/m ³	2,6%	281 ng/m ³	5,3%

¹ Breakthrough calculated on the individual sample with the extra cartridge

11 Conclusion

The overall method reproducibility for the WHO PCBs was 0,22 pg TEQ/m³ based on measurements at a full scale incinerator over an extreme low concentration range from 0,19 pg TEQ/m³ to 0,41 pg TEQ/m³, The corresponding reproducibility was 5,9 ng/m³ for the sum of the 6 marker PCBs over a concentration range from 4,4 ng/m³ to 11 ng/m³,

These concentrations were very close to the LODs based on the field blanks for the three methods which ranged from 0,11 pg TEQ/m³ to 0,57 pg TEQ/m³ for the WHO PCBs and 1,3 ng/m³ to 14 ng/m³ for the marker PCBs. Corresponding LOQ values based on the field blanks varied from 0,20 pg/m³ to 1,37 pg/m³ for the WHO PCBs and from 1,7 ng/m³ to 33 ng/m³ for the marker PCBs,

The levels in the field blank samples were at least two orders of magnitude below the EU limit value for dioxins, used in the absence of a limit value for PCBs, and thus in agreement with the requirement of CEN/TS 1948-4:2007 (see Clause 10.2),

Recoveries of the isotope labeled standards were in good agreement with CEN/TS 1948-4:2007,

The absolute amount of break through at levels just above the detection limit and field blank levels were at least two orders of magnitude below the EU limit for all three methods. At higher concentrations the break through was below 0,5 % for the WHO PCBs and below 4 % for the marker PCBs for the filter/condenser method.

The validation measurements demonstrated the applicability of CEN/TS 1948-4:2007 for the determination of PCBs from stationary sources. The results will be used for the transfer of the Technical Specification CEN/TS 1948-4:2007 to a European Standard EN 1948-4 which will then include the performance characteristics and important guidance for sampling and analysis over a broad concentration range.

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