

DL-PCB EMISSION FROM SHREDDER PLANT PROCESSING MIXED SCRAP MEASURED ACCORDING TO EN 1948-4

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Abstract

The European Standards EN 1948 for measuring the emission of PCDD/F from stationary sources is going to be extended with a Part 4 for measuring DL-PCB. Validation measurements for EN 1948-4 were performed by three sampling teams at a state of the art incinerator. Because of the very low measured values, which were close to the level of the field blanks, an extra validation measurement was performed by one of the sampling teams at a shredder plant, where high concentrations were expected. The concentrations were indeed very high, and it caused severe analytical problems, and resulted in some adjustments of the European Standard. The results from this extra validation measurement are presented in this paper.

Introduction

The WHO limit values for dioxins in food and feed include dioxin and furans (PCDD/F), as well as dioxin-like PCB (DL-PCB) using WHO-TEF factors, while the EU emission limit value for dioxin in the directive for waste incineration is valid for PCDD/F using I-TEF factors. The WHO- and I-TEFs for the 17 PCDD/F are slightly different for five congeners. Four of the WHO-TEFs are lower than the I-TEFs and one is higher, resulting in only minor differences in the sum of toxicity (TEQ) for PCDD/F calculated with WHO-TEF or I-TEF. In food and feed the DL-PCB can contribute to a substantial part of the toxicity, but so far it seems to be a minor contributor in stack emissions, at least from combustion processes.

The standardization group CEN/TC 264/WG 1 Dioxins and PCB was in 2003 entrusted to establish a standard measurement method for the determination of dioxin-like PCBs from stationary source emissions. The new method was published in 2007 as Technical Specification CEN/TS 1948-4:2007 /1/. Within the framework of the EU/EFTA mandate M 388 the validation of the method in order to transfer the Technical Specification to the European Standard EN 1948-4 was financed by the European Commission and EFTA, and took place in 2007 and 2008. The validation of the new method was performed in three parts:

1. An inter laboratory calibration study in 2007, where the analytical section of the method was validated through the distribution of two ash samples, two standards solutions, one ash extract and two sets of complete calibration standards to 8 expert laboratories.
2. Validation of the combined sampling and chemical analysis, performed at a full scale facility by 3 sampling teams in combination with 3 analytical laboratories selected from the inter calibration 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 in June 2007.
3. An additional validation was performed at a shredder plant in February and March 2008, because of very low concentrations measured at the incinerator. 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.

All the results from the validation are reported in /2/ and the results from the additional validation measurements at a shredder plant are presented in this paper.

The plant is a normal shredder plant for metal scrap, with a capacity of processing of approximately 100 t/h mixed scrap, with a production of approximately 80 t/h metal fractions. All sorts of metal scrap are processed e.g. used cars, white goods (refrigerators, washing machines, cookers, etc.), industrial metal waste and residues, demolition iron, etc. The white goods are collected and processed separately one day a week. Examples of the varying content of the scrap process at the plant are illustrated in figure 1 and 2.

The scrap is feed to the shredder via a chute, and from the shredder it is transported to sorting by a conveyer. Waste gas/air from ventilation of the shredder and from the separation process, is first treated in cyclones to remove coarse particles, and followed by a venturi scrubber to remove smaller particles.



Figure 1. Example of white goods



Figure 2. Example of mixed scrap

The off gas is discharged through a 20 m stack, where the measuring site is situated in the level of 10-14 meters. The inside diameter of the stack is 1.4 m and the flow is app. 65,000 m³(s,d)/h with 1- 4 % H₂O and temperature of 20-40°C depending of the outdoor temperature. The sampling was made through two sampling ports 90° apart, and the sampling points were placed inside a circle with a diameter of approx. 0.2 m in the centre of the stack. Gas velocity was measured continually through a third sampling port in the same area as the sampling points. Previously emission concentrations up to 22 µg/Nm³ marker-PCB have been measured from the plant and consequently relatively high concentrations of DL-PCB were expected.

Formation of PCB in the shredder process is not likely, and the emission of PCB must consequently be emission of existing PCB in the scrap processed in the plant. The PCB is believed to come from PCB containing materials, e.g. sealants and fire resistant surface treatment, but no knowledge and evidence for the source of PCB in scrap is present, and the scrap was not investigated for the PCB content.



Figure 3. Stack and sampling site below the upper platform



Figure 4. Sampling site with sampling equipments

Materials and Methods

Sampling and analyses of DL-PCB and marker-PCB was performed according to EN 1948-1, -2, -3 and CEN/TS 1948-4 /1/. Sampling was carried out by FORCE Technology using a filter/condenser sampling system. The concentration of particles at the plant is normally within the range of 10 -15 mg/Nm³, and consequently a pre-filter of quartz wool was used. For safety reasons, it is not allowed to stay at the sampling site, when the shredder is in operation. Two sampling devices for duplicate sampling were consequently mounted in the sampling ports for sampling in fixed points, and the pumps were placed outside the restricted area, where they could be watched over during the whole sampling period.

Seven duplicate samplings were performed, but two of the samples were not analyzed because of broken glass equipment caused by flying metal pieces from the shredder plant, demonstrating the difficult sampling conditions. Two of the samples were equipped with an extra XAD adsorption column for break through measurements, and also two blank samples were performed.

Analysis of the samples was carried out by Eurofins ERGO Forschungsgesellschaft GmbH in Hamburg. 50% of the extraction standard (100 µl of each of the EN 1948-4 WHO extraction standards CIL and the marker-PCB extraction standards (10 ng/ml)) was added to the filter and the other 50% were added to the XAD. After the spiking, the filter was treated by hydrochloric acid for at least 1 hour. The filter and the XAD were subsequently soxhlet extracted with the same toluene solution for at least 20 hours. Afterwards the combined condensate and rinsing solution were liquid/liquid extracted three times by using the same toluene as used for the extraction.

An aliquot of 40 % was used for the clean-up and analysis and the remaining 60 % were stored in sealed vials. The clean-up was done on the multicolumn system:

1. Silvercolumn (Silicagel doped with AgNO₃, H₂SO₄/KOH).
2. Supelco SPE carbon column to partition the marker and mono-ortho PCB fraction and the PCDD/F and non-ortho PCB fraction.
3. Final cleanup with an aluminiumoxide column.

The non-ortho PCB fraction was reduced to dryness and resolved in the syringe standard resulting in a final volume of 25 µl. The volume of the PCB fraction was reduced to 100 µl, and 5 µl recovery standard was added. Final analysis was done by means of high resolution gaschromatography and high resolution mass spectrometry (HRGC/HRMS) using a VGAutoSpec or a Finnigan MAT 95 XL on a DB-5 capillary column. The final injection volume was 2 µl for non-ortho PCB, and 1 µl for marker and mono-ortho PCB.

The PCB fraction could not be analyzed because of an oily fraction in the samples, which overloaded the HRGC/MS instrument. The oily fraction could not be removed by further clean-up procedures. Both the PCB fraction for the extra XAD to measure the break through and the field blanks did not contain the oily fraction, and were analyzed without any problem. In the two blank samples only the non-ortho PCBs (PCB#77, 81, 126 and 169) were just above the limit of quantification (LOQ), and the upper bound concentration was 0.0012 and 0.0011 ng WHO-TEQ/m³(s,d), which is well below 10 % of the measured values and in agreement with the European Standard EN 1948-4. At these extreme high concentrations the two break through measurements of the sampling train were 2.6 % and 5.3 % for the marker-PCBs and 0.38 % and 5.3 % for the WHO-PCBs, where EN 1948-4 specify less than 10 %.

This oily fraction was found to contain very high amount of PCB and a new aliquot only containing 0.02 % of the sample extract was taken from the remaining 60 % of the extract. The new aliquot was spiked again with 10µl of each of the two extraction standards. These samples were filled up with toluene to 50 µl and directly injected into the GC-MS without any clean-up procedure. This procedure gave acceptable results due to the extreme high levels of PCBs in the sample extracts. The planar PCB #169, was analyzed in the PCDD/F fraction after the active carbon chromatography, as described in the new European standard EN 1948-4. All other PCBs were analyzed and calculated from the aliquots without any clean-up.

Because of the very high concentrations, the analysis was not done exactly according to the requirements of EN 1948-4 and its precursor document CEN/TS 1948-4, and consequently resulted in somewhat higher uncertainty. As a consequence of these analytical problems, an Annex D containing recommendations for measuring high concentrations of dioxin-like PCBs has been added to the new European standard EN 1948-4.

Results and Discussion

The result of the measurements results are shown in the table 1 below. Sampling time was 6 hours and sampling volume was around 8 m³.

Table 1. The result of the validation measurements at the shredder plant.

Sample No.	Marker-PCB µg/m³(s,d)		DL-PCB ng WHO-TEQ/m³(s,d)	
	Sample	Average	Sample	Average
1A	6.1	4.8	0.43	0.40
1B	3.5		0.36	
2A	19.1	22.6	0.81	0.88
2B	26.2		0.94	
4A	7.8	8.4	0.35	0.37
4B	8.9		0.38	
6A	5.3	7.3	0.29	0.42
6B	9.3		0.55	
7A	18.5	18.3	0.69	0.70
7B	18.2		0.70	
Total average	12.3		0.55	

PCDD/F was not measured, but in several previous and not published measurements at the same and other similar shredder plants, the concentration was slightly below 0.1 ng I-TEQ/m³(s,d), and in the same samples the concentration of marker-PCB was at the same level as the validation measurements /3/. In five of the latest of these measurements of marker PCB, the sampling conditions and analytical procedure were comparable to the validation measurements, and they were in the range of 2.9 to 22 µg/m³(s,d), with an average of 11.3 µg/m³(s,d) /3/. This average is very close to the average of the validations measurement of 12.3 µg/m³(s,d).

In a German investigation the concentration of PCDD/F from a few shredder plants in Sachsen-Anhalt was measured to be in the range from 0.002 to 0.43 ng I-TEQ/m³ with an average of 0.056 ng I-TEQ/m³ /6/.

In a Swedish investigation of the content of PCDD/F and PCB in light shredder waste sorted in the two fractions > 10-17 mm and < 10-17 mm, the PCDD/F were not detected in the coarse fraction and an average of 0.08 ng I-TEQ/g was found in the finer fraction /5/. The concentration for PCB was 20 and 134 µg/g respectively, but no information on the analyzed PCB congeners was given.

Francois et al. is reporting 10 measurements of DL-PCB and PCDD/F from three different shredder plants /4/. The DL-PCB vary from 0.025 to 1.06 ng WHO-TEQ/m³(s,d) with an average of 0.39 ng WHO-TEQ/m³(s,d), which is very close to the average of the validation measurement of 0.55 ng WHO-TEQ/m³(s,d). All the PCDD/F measurements except one were below 0.1 ng I-TEQ/m³(s,d), with an average of 0.06 ng I-TEQ/m³(s,d).

This conform the expectations, that levels of PCDD/F should generally be very low, because PCDD/F is neither used nor deliberately produced for any technical product or substance, and that the levels of PCB could be rather high, because PCB has been produced and used, and widely spread in products, where some of them are processed in shredder plants. Commercial PCB products always contained a little DL-PCBs and less PCDD/F, and the measured emissions can be explained by re-emission of former used PCB.

Shredder plants are not covered by the European IPPC Directive (unless they are a part of a larger installation which is covered), and consequently no common European regulation exist. National air emission regulations of shredder plant normally deal only with emission limit values for particles and sometimes also for some heavy metals. The validation measurements and the results in /4/ clearly demonstrate that shredder plant stack emissions may contribute to the overall re-suspension of PCB into the environment. The contribution of the DL-PCBs to the dioxin-like toxicity in emissions from shredder plants is evident and seems to be several times higher than the PCDD/F toxicity.

Based on the analytical problems in measuring very high concentrations of PCB, e.g. from shredder plants, it is recommended to carefully study the informative Annex D, Recommendations for measuring high concentrations of dioxin-like PCBs, in the new European Standard prEN 1948-4, and choose a sampling strategy to enable correct measurement and reliable results.

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