Continuous Monitoring of Dioxins in Accordance to EN 1948

H. D. Schepers, Deventer/NL; **B. Leysen, K. Smets**, Lokeren/B

Introduction

Ever since the 'Lickebaert' case in the Netherlands in 1989, strict attention has been paid to dioxins (PCDD and PCDF) in the Dutch environment. This is also true for the standards set for dioxins in air. In the Netherlands, emissions of dioxins to air are fall under a minimisation duty, which means that the involved industrial plants must at least meet the Netherlands Emissions Regulations Guidelines (NeR)'. Certain types of installations fall under legal emission requirements, such as the Waste Incinerators Emissions Decree (Bla)".

Eight years after the trouble in the Netherlands waste incineration in Flanders (Belgium) had also become discredited due to the commotion in 'Neerlandwijk' in Antwerp. This was another incident that led to sharper supervision and enforcement of the waste incineration sector. Flanders has even gone to extra lengths with their explicit supervision of the ferro and non-ferro industries, crematoriums, refineries, etc.

Supervision and enforcement of the set requirements is attained through standard measurement methods where possible. Dioxin measurements are carried out in accordance with EN 1948. In Flanders (Belgium) there is also continuous sampling of the flue gases from domestic waste incineration installations, besides the regular separate emission measurements. However, there is no standard measuring method available for the continuous sampling of dioxins. Therefore a method based on EN 1948 is used.

The EN 1948 standard has been developed to measure dioxin concentrations at about 0.1 ng I-TEQ/m³ in stationary source emissions by single measurements lasting a maximum of 8 hours. This paper describes the Tauw by experience with EN 1948 in the Netherlands and Belgium and gives an analysis of deviations and bottlenecks in using EN 1948 for continuous monitoring.

Experience in using EN 1948

The EN 1948 consists of three components, sampling (1), extraction and clean-up (2) and identification and quantification (3).

Sampling

The EN 1948 contains three different methods for dioxin sampling. This paper deals with the cooled probe method. In general, standard measuring methods often have a certain degree of freedom. The EN 1948 is such a method. This degree of freedom may lead to essential differences in practice as the complex sampling matrix for air and the impossibility of carrying out a fundamental, statistical approach complicate the matter. It is therefore of the utmost importance that any standardisation has a dynamic nature and that past experience is shared and put into the standardisation process. Sampling and dioxin analysis are sensitive matters. Given the low detection level, high demands are imposed on the knowledge and expertise of the measuring body. This applies to both the equipment and the technical competence of employees. A uniform quality of dioxin measurements may be enhanced by accreditation.

One of the main things when using the standard is to *avoid contamination* between separate measurements and, if necessary, to prove whether contamination was transferred or not. One's track record is very important for the outcome of measurements here. The EN 1948 only provides a general framework for the prevention of contamination. For instance, repeated use of the same gas sample carrying parts is allowed, provided that they are rinsed 'clean'. However, this rinsing is not always quantitatively possible in practice. Certain isomers 'cling' to the surface material. The possible effect is demonstrated for a fictitious situation below.

Two measuring rounds are carried out; the first one at an industrial plant measuring untreated flue gas with a PCDD/PCDF concentration of 70 ng I-TEQ/m³. The second measuring round is done at an industrial plant measuring the treated exhaust gases with a concentration level of 0.1 ng I-TEQ/m³. In this specific case the overall rinsing efficiency (obligatory rinsing with acetone and subsequently with toluene) is about 99.5%. This means that if the sample gas carrying parts are not all replaced there is a large risk that the sampling system contains 0.5% of 10 ng (0.05 ng per m³) of contamination per sampled volume.

Within this context it is very important to use blanks for the measurement and rinsing samples between the different samplings on one and the same location. A blank is unambiguous and therefore guarantees that sampling train is free of contamination from another area. The intermediary rinsing samples can indicate at any given moment whether a high concentration is found again in the next measurements. It is highly recommended to use a surplus of rinsing liquid because a volume that is too small may leave dioxins behind. The use of acetone and toluene at Tauw has not resulted in any noticeable effects.

Extraction and identification

The implementation of EN 1948 has had a large impact on the performance of analyses. For instance, the standard has created a better insight in the critical steps of the analysis process. It also clearly shows which criteria apply. Treatment of a rough extract into a measuring extract is a complicated process. For the time being, insiqht in this will remain incomplete due to the enormous variation in the sample matrix. However, the use of labelled extraction standards has led to a feasible uniform quality. The recovery rate of sampling standards has a fixed lower threshold of 50%. Contrary to the extraction standards this may sometimes give problems. The properties of the sampling standard during analysis are not always the same as the properties of the extraction standard used for quantification. During cleanup, sampling standard 1,2,3,4,7,8,9-HpCDF and extraction standard 1,2,3,4,6,7,8-HpCDD (against which the recovery of 1,2,3,4,7,8,9-HpCDF is tested), do not behave completely the same way. Due to the (occasional) larger losses during clean up of 1,2,3,4,7,8,9-HpCDF compared to 1,2,3,4,6,7,8-HpCDD, a lower sampling standard recovery is calculated. If the recovery of 1,2,3,4,7,8,9-HpCDF subsequently drops to below the set criterion, it could be falsely concluded that the criteria of EN 1948 for sampling are not being met.

In addition to the standard, a cleanup standard is added prior to cleanup. The recovery of this standard ((13 C 12 1,2,3,4,7-PeCDD) in combination with the recovery of the extraction standard can indicate whether a problem has occurred during the cleanup or the extraction. The criterion for this outcome lies between the 75 and 125%. The recovery from the combination of sampling, extraction and cleanup standards provides a clear picture of how the analysis process has transpired.

Another problem that may occur during extraction is that the specific nature of the sample material makes it hard to release dioxins quantatively. Previous experience has pointed out that samples loaded with active carbon (used in flue gas treatment systems to trap dioxins) require a longer extraction time.

Suggested supplements supplements to EN 1948

1. The standard could benefit from the following supplements: A more explicit regime to prevent contamination by replacing essential flue gas carrying components in the sampling ducts between each measurement (i.e., the glass liner in the cooled probe, glass condensate impingers, glass curves between the liner and impingers and glass nozzle) and by applying a preventative contamination criterion in case of reuse of the XAD-2 cartridge;
2. The use of an extra spike during treatment will make it easier to sea during which phase of the measurement (sampling, preparation or treatment) a problem may have occurred.
3. Specific extraction times when using a high active carbon load on the sample material.

Continuous monitoring of dioxins according to EN 1948

Introduction

In Flanders, domestic waste incineration plants are legally bound to continuously sample and analyse dioxins’’’ This enables the government to get a clear picture on the average dioxin emission during a sampling period of a fortnight.

Differences between the continuous sampling of dioxins and the discontinuous sampling of dioxins accorrjing to EN 1948.

The continuous sampling of dioxins is carried out by means of a sampling system based on the cooled probe method as proposed in EN 1948.

Figure 1 represents the cooled probe method as given in the standard. Figure 2 presents the sampling method for continuous sampling of dioxins used by Tauw.

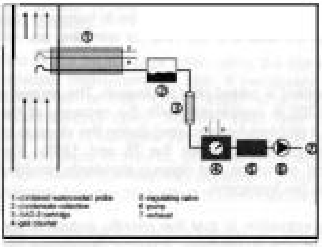

Figure 1 Ovenview of the discontinuous cooled probe method

Differences are:

- Condensate interception after the XAD-2 instead of before: the amount of condensate that is trapped during a sampling round of a fortnight is too large for preparation and analysis. If the condensate is first led through the XAD-2, all dioxins are adsorbed and analysis of the condensate is no longer necessary;
- A sampling period of a fortnight instead of 6-8 hours;
- Although sampling is done through isokinetics, this only involves one point instead of several points over the entire measuring section.

Because the sampling takes a fortnight, an automated isokinetic sampling system is used. Additional checks are built in to ensure a proper functioning of the system:

- Temperature measurement before the XAD-2: checking the proper cooling of the exhaust gases to below 20°C;
- Measuring the oxygen surplus within the installation including feedback to the continuous sampling: checking whether incineration is still taking place and, if not, the system will automatically turn itself off.

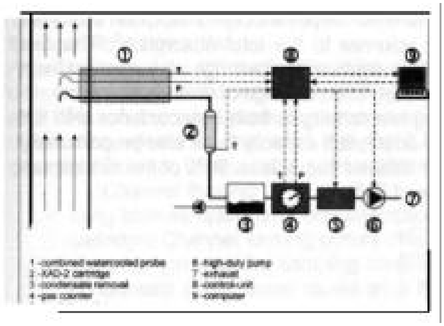

Figure 2 Diagram of the modified cooled probe method as applied to continuous sampling of dioxins.

Inventory of possible problems with continuous sampling of dioxins

Specific problems that can be expected during continuous sampling of dioxins always involve the longer measuring period and/or not separating the moisture before the adsorbent. Some of the possible problems are:

1. Difficulties with dioxin adsorption to the adsorbent due to
    - a limited adsorption capacity of the XAD-2;
    - channel forming in the adsorbent due to extended sampling;
    - slower mass transfer from liquid phase to resin;
    - the water washing away dioxins from the adsorbent;
2. Contamination in the sample carrying parts that is harder to rinse;
3. A clogging of the continuous rate measuring device (pitot) that will inhibit isokinetics;
4. Unauthorised manipulation by unauthorised personnel.

Tauw's verification of the sampling system[IV,V,VI,VII,VIII,IX]

Besides the previously discussed problems, the system should be assessed for possible deviations in practice. The issues below were investigated within the framework of such assessment.

<u>1. Checking the adsorption capacity of the used XAD-2 cartridge.</u>
For continuous sampling of dioxins, Tauw uses an adsorption cartridge in accordance with EN 1948.

Any adsorption problems are checked by means of a double test (for results, see Table 1). The first part of the test involves splitting up the cartridge into two parts (front and back). The front contains a cartridge in conformity with EN 1948 and the back a cartridge of 5g XAD-2. This test points out to which depth effective adsorption still takes place in the cartridge and compares the volumes to the total adsorption’. The test shows that it is not necessary to use the entire depth of the cartridge very often; at least 90% of the dioxins can be found in the front part, at an average of 98%.

The second part of the test involved placing two cartridges, both in accordance with EN 1948. behind each other. This doubles the adsorption capacity but it also proportionally increases the pressure drop. This test also showed that at least 90% of the dioxins can be found in the first cartridge, at an average of 98%.

	Front	Back
	ng TEQ.Nm^{-3} (%)	ng TEQ.Nm^{-3} (%)
extra compartment (+5g)	0.01 (99)	0.0001 (1)
	0.004 (100)	0.00001 (0)
	0.01 (96)	0.0004 (4)
	0.003 (100)	0.00001 (0)
	0.012 (100)	0.00001 (0)
	0.003 (100)	0.00001 (0)
	0.004 (99)	0.00003 (1)
	0.01 (91)	0.001 (9)
double cartridge	0.002 (100)	0.00001 (0)
	0.003 (98)	0.00007 (2)
	0.001 (100)	<0.00001 (0)
	0.002 (97)	0.00007 (3)

Table 1 Tests with a divided XAD-2 cartridge, the front in accordance with EN 1948 and the back consisting of 5g XAD-2. The second part of the Table gives the result of two XAD-2 cartridges in accordance with EN 1948 placed behind each other.

The above tests verify the mathematical dimensioning of the carhidge and show that the capacity is adequate[2].

As a final test of the thorough adsorption of the XAD-2 cartridge the condensate of 12 different measurements was analysed[3]. The recovered concentrations lie between 0 and 35% of the total content of recovered dioxins, at an average of 20%. This observation seems to contradict that the XAD-2 cartridge has sufficient adsorption capacity. However, there are two valid explanations for this phenomenon.

- Channel forming

  Long term sampling over one adsorption cartridge creates small channels in the cartridge. Channel forming occurs over the entire length of the cartridge. These channels grow as the sampling continues because the exhaust gases and the condensate prefer these routes as a reaction against the pressure drop in the cartridge. This causes early saturation of the XAD-2 along the channels and adsorption will be minimised.

  In addition, during sampling dioxin adsorption will gradually move to the back of the cartridge. By the time adsorption has ended up in the back part of the cartridge, channel forming will have occurred to such an extent that the adsorption efficiency has become minimal.
- *Particle transfer*

  A second possible explanation for the sometimes high concentrations of dioxins in the condensate is the insufficient restraint of the fine-grained particles. The adsorption cartridge does have a glass wool wad for a depth filter. The excess of condensation led over this filter will strongly influence the filter action. This theory is confirmed by the visual observation of the discoloration of the top part of the adsorption cartridge by particle retention at the end of a fortnight of sampling, where the condensation also clearly contains suspended matter. If matter ends up in the condensation water, this could also happen to dioxins adsorbed to matter.

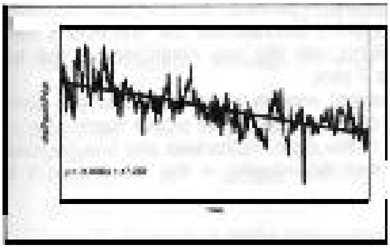

Figure 3 Diagram of the underpressure in the sampling system in relation to the kinetic pressure in the flue gas channel during a fortnight of sampling. The underpressure appears to decrease compared to the kinetic pressure, and this may indicate channel forming in the adsorption cartridge.

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[2] Because the measuring period is significantly longer with continuous sampling it seems logical to proportionally enlarge the adsorption cartridge in comparison to the cartridge used with discontinuous sampling. However, mathematical calculations show that the adsorption cartridge in conformity with EN 1948 has sufficient capacity.

[3] As described under the differences between continuous and discontinuous sampling. all condensate is first lad over the adsorption cartridge to hold back dioxins. The condensate is not normally part of the dioxin samples.

The problems described above are very likely to both take place. The various condensate measurements also make it clear that we are not dealing with a new breakthrough of dioxins each time. Possible explanation is a careful filling of the XAD-2 cartridge. This should be further investigated, however.

2.Verification of possible washing away of adsorbed dioxins.

A possible problem is the large quantity of water led through the cartridge washing away adsorbed dioxins. After all, the applied method significantly deviates from the cooled probe method as proposed in EN 1948. Instead of intercepting condensate before the adsorption cartridge, the moisture in continuous sampling is intercepted after the adsorption cartridge. The reason for this is that with a sampling period of a fortnight the intercepted moisture quantities are too large (-30 l) to allow for representative analysis.

The possibility of dioxins being washed away can be determined by checking the recovered sampling standards. In total, more than 50 samplings will be performed without the sampling standard dropping to below the criterion in the standard.

3. Rinsing the gas carrying Parts.

It is of the utmost essence to thoroughly rinse the entire sampling train after each sampling round[4]. There are two reasons for this. First, the result may be distorted because not all dioxins that are effectively sampled will be involved in the monitoring. Second, accumulated dioxins may be released from the system in a next round, thus also distorting the outcome.

Separate analyses of the rinsing sample show that the dioxin concentrations lies between 20 and 50% of the total content of sampled dioxins. It should therefore be obvious that a careful rinsing of the sample carrying parts is absolutely necessary.

4. Problems with continuous rate measurement.

In order to be able to control the system isokinetically the continuous rate measurement must be reliable. Problems with the rate measurement can be avoided by using an S pitot instead of a P pitot.

It is also important to continuously record enough parameters and any error messages during the entire sampling cycle. This way, the proper functioning of the system can be verified at the end of the cycle. Authorised and unauthorised manipulations are also recorded so that the integrity of the measurement is secured.

5. Checking consistency between discontinuous and continuous measurements.

The aim of the continuous sampling of dioxins is to arrive at a measurement that generates a sufficiently reliable outcome within the limitations of current technology. As it is not possible to test the method in relation to a reference point, it was decided to compare the continuous measurements with the discontinuous measurements. These tests were performed at the domestic waste incineration en Regional Environmental Care in Belgium.

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[4] Despite the logic of this proposition it turns out that in the majority of performed continuous sampling of dioxins, the sampling train are never rinsed. This paper proves that results will be heavily distorted by this fact.

Tauw has over 100 results from discontinuous measurements, performed between January 1998 and December 2000. Assessment of these results shows that the domestic waste incineration plant has its dioxin emissions well under control with an average of less than 0.015 ng TEQ/Nm³- (except during the test phase for active carbon dosages. The results presented in Figure 4 clearly indicate this.

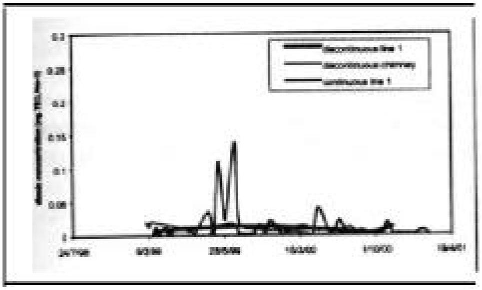

Figure 4 Diagram of dioxin measurements of line 1 of the domestic waste incineration plant in Houthalen. Discontinuous measurements are compared to continuous measurements. To stress the outcome, the resu/ts of the shared chimney is also given.

Since the first continuous monitoring of dioxins in July 1999 70 results have been obtained. As the investigation was based on 2 sampling systems, one for each incineration line, the results are assessed per incineration line. This drastically reduces the number of usable measurements as most discontinuous measurements were performed fort he shared chimney.

Measurement line 1	Number	Average	Variance
discontinuous	14	0.0086	0.0000055
continuous	34	0.0093	0.000063

Table 2 Basic data of the measurements performed on line 1 at the Houthalen Regional Environmental Care in Belgium.

Measurement line 2	Number	Average	Variance
discontinuous	3	0.028	0.00051
continuous	33	0.014	0.00031

Table 3 Basic data of the measurements performed on line 2 at the HouthalenRegional Environmental Care in Belgium, showing that the number of usable results for the discontinuous measurements on line 2 is too low.

Tables 2 and 3 give the basic data of measurements on lines 1 and 2. It appears that the results from line 1 can be used for a reliable statistical assessment, whereas there are not enough discontinuous results from line 2. Therefore, only line 1 will be discussed below

F-obs	*P value*	*Critical area F test*
0.012	0.73	4.05

Table 4 Variance analysis of the discontinuous and continuous measurements on line 1. The hypothesis was that the average of the discontinuous measurement corresponds t the continuous measurements. This was tested using a=0,05 The comparison between F-obs and F area shows that the hypothesis using this a is not rejected. The P value confirms this.

Table 4 gives the results from the variance analysis as applied to the continuous and discontinuous measurements on line 1 of the domestic waste incineration plant in Houthalen. The hypothesis ‘equality of averages for both types of sampling[5]. This equality was checked using *a*= 0.05. The comparison between F-obs and F area shows that the hypothesis is not rejected and this is confirmed by the P value.

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[5] Both groups of results represent a random check from one and the same basic group, although the latter is a dynamic factor in time. If the random check is large enough, it must be possible to detect the consistency between both groups.

Considerations

The rigorous implementation of the EN 1948 proves the benefit and reliability of the standard. But still the degree of freedom in using the EN 1948 can lead to essential differences in practice.

TAUW advocates an even stricter standard for the use of disposable sample carrying parts and the introduction of an additional cleanup standard.

All domestic waste incineration plants in Flanders (Belgium) must continuously sample dioxins. Because this significantly deviates from sampling as proposed in EN 1948, it is wise to incorporate this situation in the standard explicitly. This requires further investigation.

TAUW investigated the possible problems at the domestic waste incineration plant of the Houthalen Regional Environmental Care using a continuous sampling system designed by Tauw. The results are promising while at the same time revealing possible problems.

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Nederlandse emissie richtlijnen lucht, Infomil, 2000

[II] Waste Incinerators “Air Emissions” Decree, The Hague, 1993
Besluit luchtemissie afvalverbranding, Den Haag, 1993

[III] Decree on general and sectoral stipulations regarding environmental hygiene, art. 5.2.3.3.6. §1 Flemish Government, dated 1 June 1995, 1999
Besluit van de Vlaamse Regering van 1 juni 1995 houdende algemene en sectorale bepalingen inzake milieuhydiene, aft. 5.2.3.3.6.§ 1., 7999.

[IV] Leysen B. and Smets K., Dioxin assessment at Houthalen Regional Environmental Care, Tauw, Report no. R9501849, 1999. Houthalen Regional Environmental Care

[V] Leysen B. and Smets K., Emission measurement at Mouthalen Regional Environmental Care, Tauw, Report no. R9502283,1999.

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[VII] Leysen B. and Smets K., Emission measurements at Houthalen Regional Environmental Care domestic waste incineration plant, Tauw, Report no. R9502901, 2000.

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[IX] Leysen B. and Smets K., Continuous monitoring of dioxins at Houthalen Regional Environmental Care, Tauw, Report no. R9503994, 2001.