Method Implementation Document for BS EN 1948: Parts 1-3: 2006 Stationary source emissions - Determination of the mass concentration of PCDDs/PCDFs and dioxin-like PCBs

Foreword

The Environment Agency recognises that European and International standards may need supplementing by Method Implementation Documents (MIDs) to make sure they are being implemented consistently.

This document supplements EN 1948: parts 1-3. The clause numbers in this document follow those of EN 1948: parts 1-3, although the text from the standard is not repeated in this document.

The Environment Agency has specified that EN 1948: Parts 1-3 is used for the measurement of polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs). Additional information on sampling and analysis of polybrominated dioxins (PBDDs) and furans (PBDFs) are specified in this MID.

Part 1: Sampling of PCDDs/PCDFs

1 Scope

This MID is applicable to the filter/condenser method, using solid absorbent, without flow division. It specifies that the requirements of this method (See Annex B of the standard) shall be met.

The scope of EN 1948: Parts 1-3 can be extended to include PBDDs and PBDFs, provided additional requirements for PBDDs and PBDFs that are specified in this MID are followed. This means a test carried out to measure PCDDs and PCDFs can also be used to measure, PBDDs and PBDFs.

EN 1948-1 specifies quality assurance criteria for a method validation trial, the limit of quantification of individual congeners and the overall field blank. These requirements are applied to values determined using international toxic equivalence factors for PCDDs and PCDFs. These are not applied to the measurement of PBDDs and PBDFs, so are not applicable to their measurement.

A test carried out to measure PCDDs and PCDFs cannot also be used to measure polyaromatic hydrocarbons.

2 Normative references

EN 13284-1:2001 has been replaced by EN 13284-1:2017.

3 Terms and definitions

No additional information

4 Symbols and abbreviations

No additional information

5 Principle of the complete PCDD/PCDF measurement procedure

No additional information

6 Sampling device and materials

6.1 General sampling device and sub sections

No additional information

6.2 Materials

6.2.1 General

No additional information.

6.2.2 Sampling system

Commercial titanium is made to different specifications based on the purity of the titanium. An appropriate grade of titanium shall be used. Titanium will degrade in gas streams with a fluoride content of greater than 20ppm. Titanium may degrade at temperatures greater than 350^{o}C (refer to supplier's information).

The sample system shall be designed to allow a measurement that is representative of the gas temperature within the condenser or resin trap to be made.

Note: different approaches can be used to enable the gas temperature within the condenser or resin trap to be measured. The following approaches are used:

a) a thermocouple is fitted directly in the gas stream. This will give a very accurate reading of the gas temperature. However, there is potential for leaks around the fitting. Also, the thermocouples and seals will require cleaning to ensure they do not cause contamination. The requirements on materials of construction in section 6.2 of EN 1948 apply because the thermocouple is inserted into the gas stream.

b) the thermocouple is placed in an indentation in the sidewall of the condenser or resin trap (this may have to be added by a glass blower).

c) a surface temperature measurement sensor is used to provide a very good contact between the thermocouple and the surface of the condenser or resin trap.

6.2.3 Sealings (in contact with flue gas)

PTFE must not be used in temperatures above 200^{o}C (refer to supplier's information).

6.2.4 Filter

Quartz filters are recommended.

6.2.5 Quartz wool (if used)

The use of quartz wool is not recommended.

6.2.6 Solid adsorbent

An XAD-2 resin filled container (resin trap) is used for the method described by this MID.

6.2.7 Cooling fluid

Filter/condenser method uses an ice bath, with a re-circulating pump submerged in iced water for cooling the flue gas and resin trap.

6.2.8 Ice bath

No additional information

6.2.9 Silica gel

Indicating silica gel shall be used to ensure moisture does not break through to the control box and dry gas meter.

6.2.10 Reagents

No additional information

6.3 Cleaning the sampling device

The standard gives 3 examples of cleaning procedures. Cleaning procedure (1) shall be used, unless the analytical laboratory provides evidence to UKAS that an alternative procedure is equivalent.

Note: consistently low field blank results help demonstrate that an alternative cleaning procedure is effective.

When using cleaning procedure number (1), the sampling equipment shall be kept in a muffle oven for at least 3 hours. Due the length of probe linings, it is not practical to treat them in a muffle oven. The probe liners shall be heated within their outer sheaves to the maximum temperature practical for the probe.

The first impinger (condensate flask) shall also be cleaned.

7 Minimum requirements for sampling

7.1 Method validation criteria

a) No additional information

b) The absorbent material (XAD-2) shall be sufficiently well packed and evenly distributed in the resin trap to prevent the formation of channels, which stack gas may pass through without coming into close contact with the absorbent.

c) In order to validate the adsorption stage efficiency for gaseous PCDDs and PCDFs, it is necessary to put two resin traps in sequence.

7.2 Minimum requirements for sampling

No additional information

Note: as measurements can be required for several hours it is good practice to have a system in place that will detect leaks during the sample run. This can be done on combustion processes by using an analyser to measure the oxygen concentration of the gas exiting the isokinetic sampling equipment and comparing it to the dry stack gas oxygen concentration. An increase in the oxygen concentration from the isokinetic sampling equipment relative to the dry stack gas oxygen may indicate a leak. If this occurs the sample run can be stopped, and the leak rectified before continuing with the measurement.

7.3 Field blank requirements

The field blank shall be performed before a measurement series (that is consecutive measurements on one stack). However, it is acceptable to apply a field blank to more than one stack provided the stacks are in the same location (that is the sampling platform) and the process conditions are the same. To apply a blank to more than one stack in the same location, the glassware used shall:

- be the same as used on the previous stack; or
- shall have been prepared/cleaned in the permanent laboratory at the same time and conditions as the glassware used on the previous stack.

7.4 Additional sampling minimum requirements for the filter/condenser method

To maintain the required resin trap temperature, the sampling team shall have planned where they will obtain ice and how much ice is required for the measurement.

Note: the amount of ice required is based on the stack gas temperature, the duration of the test and the moisture content of the stack gas.

7.5 Additional sampling minimum requirements for the dilution method

This approach is not applicable to this MID.

7.6 Additional minimum requirements for the cooled probe method

This approach is not applicable to this MID.

8 Safety measures and transport

No additional information.

9 Preparations and sampling

9.1 Advance preparations at the sampling site

No additional information

9.2 Advance preparations at the laboratory

No additional information

9.3 Sampling at the plant

9.3.1 Initial checks

No additional information

9.3.2 Preliminary survey

No additional information

9.3.3 Assembly of apparatus

The following components of the sample train shall be prepared/assembled and disassembled/recovered in a clean area:

- filter and filter holder
- condenser, resin trap and impinger train glassware

When transferring the sample train or train components from and back to the clean area, all openings shall be sealed.

Note: due to safety issues it may not be practical to assemble the entire sample train in a clean area before carrying the equipment to the sample location.

9.3.4 Sampling

No additional information

9.3.5 After sampling

9.3.5.1 Sample recovery from the sampling train

When working on a platform, only the probe and filter housing should be disconnected at a location other than the designated clean area. All other parts shall be disassembled at a designated clean area. An exposed working platform shall not be used as a designated clean area.

9.3.5.2 Sample storage

Samples shall be stored during transport in a cool dark place, such as a cool box packed with ice or plastic freezer packs. An appropriate temperature measurement / indication device shall be used to confirm that the temperature is maintained below 25°C. Samples shall be extracted within 30 days of collection and shall be analysed within 45 days of extraction.

Note: BS EN 1948 does not specify time limits on extraction and analysis, so the requirement specified in US EPA M23 has been specified in this MID.

9.4 Calculation of flue gas sample volume

No additional information

9.5 Sampling report

No additional information for PCDDs and PCDFs

Typically, the sum of the following PBDDs and PBDFs congeners shall be reported using the associated toxic equivalent factors:

Brominated congeners (PBDD/F)	**I-TEF[a]**
2,3,7,8-TBDD	1
1,2,3,7,8-PBDD	0.5
1,2,3,7,8,9-HxBDD	0.1
1,2,3,4,7,8-HxBDD / 1,2,3,6,7,8-HxBDD (co-elutes)	0.1
1,2,3,4,6,7,8-HpBDD	0.01
OBDD	0.001
2,3,7,8-TBDF	0.1
2,3,4,7,8-PBDF	0.5
1,2,3,7,8-PBDF	0.05
1,2,3,4,7,8-HxBDF / 1,2,3,6,7,8-HxBDF[b] (co-elutes)	0.1
1,2,3,7,8,9-HxBDF[b]	0.1
2,3,4,6,7,8-HxBDF[b]	0.1
1,2,3,4,6,7,8-HpBDF	0.01
1,2,3,4,7,8,9-HpBDF[b]	0.01
OBDF	0.001

[a] The I-TEF values are from table A.1 of EN 1948-1. They are for PCDD and PCDFs. They have been applied to PBDDs and PBDFs that have equivalent structures in terms of halide atom positions. This is based on the expectation that the toxic effects are equivalent.

[b] Currently, commercially available calibration standards for these congeners are not available. 1,2,3,4,7,8-HxBDF and 1,2,3,6,7,8-HxBDF can be reported as a combined result as they co-elute. For the other 3 congeners the analytical laboratory may not be able to provide a result or if they can provide a result, it will not be accredited, which means for both situations the overall result will not be accredited.

Annex A (informative) Toxicity and toxic equivalency

No additional information

Annex B Examples of operation

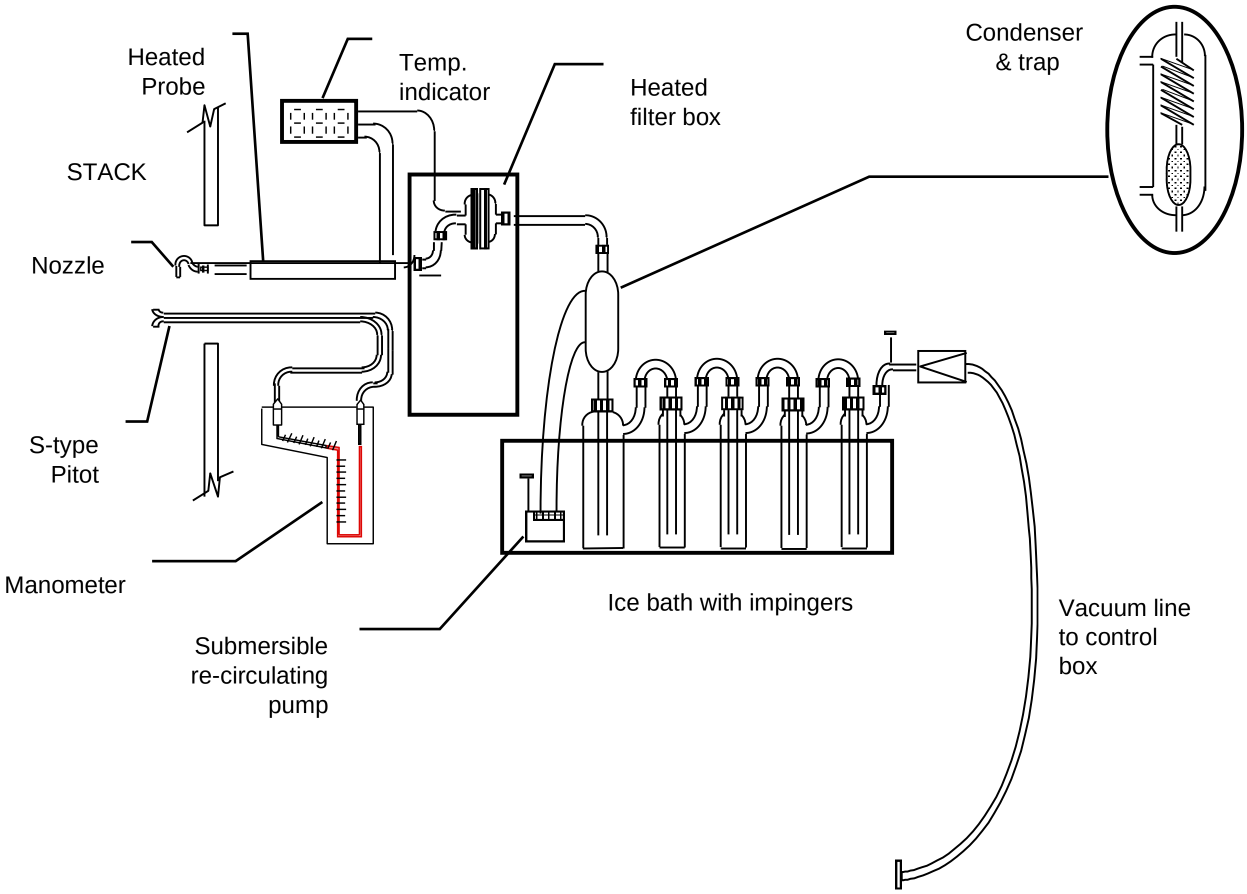
B4 Filter/condenser method - Variant with solid adsorbent upstream of the condensate flask

B4. 1. Summary of apparatus design

Equipment used in the UK to sample PCDDs/PCDFs differs from the example shown in Figure B5 of the standard. Figure 1 below shows the configuration of equipment commonly used in the UK. This equipment has a solid absorbent upstream of the condensate flask. A sample train with a solid absorbent downstream of the condensate flask may also be used.

Section B.4.1 of the standard specifies the use of a glass-lined probe. It is also acceptable to use titanium (see Section 6.2.2).

Figure 1 Typical dioxin sample train



B4. 2. Adsorbent and cleaning procedure

No additional information

B4. 3. Sampling train cleaning procedure before sampling

No additional information

B4. 4. Spiking position

B4 specifies that the filter is spiked. It is acceptable to spike the resin trap only or to spike both the resin trap and the filter.

B4. 5. Equipment assembly procedure

The condensate flask may also be located before the solid absorbent.

B4. 6. Leak check procedure

No additional information

B4. 7. Sample gas flow rate control

No additional information

B4. 8. Sampling

No additional information

B4. 9. Equipment disassembly procedure

The condensate collected in the first impinger (condensate flask) shall be stored for analysis.

Annex C Examples of adsorbents and their preparations and cleaning

This MID specifies that the requirements of Section C.2 XAD-2 shall be followed.

Annex D (informative) Sampling measurement record

No additional information

Annex Za (informative) Clauses of this European Standard addressing essential requirements or other provisions of EU Directives.

No additional information

Part 2: Extraction and clean-up of PCDDs/PCDFs

1 Scope

No additional information

2 Normative references

No additional information

3 Terms and definitions

No additional information

4 Symbols and abbreviations

No additional information

5 Principle of the extraction and clean-up procedure

No additional information

6 Device, materials and $^{13}C_{12}$-labelled standards

No additional information

7 Method validation and quality control requirements

No additional information

8 Sample pre-treatment and extraction

8.1 Addition of extraction standards

Standards cannot be reliably split into different sampling train components based upon presence of native PCDDs/PCDFs, as there is unlikely to be any knowledge of how they are distributed. It is acceptable to use the masses provided in Table 1.

8.2 Sample storage

Brown glass bottles with screwcaps and PTFE-lined seals shall be used. Traps and filters may be wrapped in foil to exclude light.

When analysing PBDDs and PBDFs, the extraction and purification pre-treatment processes shall be conducted with a filter to remove UV light because of possible photolytic debromination of highly brominated congeners under UV irradiation during Soxhlet extraction.

8.3 Extraction

a) Some particulates on filters are extremely hydrophobic, which may mean that the pre-treatment with hydrochloric acid does not wet the entire surface but forms droplets on the surface of the filter.

8.4 Clean-up

Column chromatography on alumina may be used to separate PCBs from PCDDs/PCDFs.

8.5 Final concentration of the sample extract

No additional information

8.6 Addition of recovery standards

The text in the standard stating that recovery standards are used to measure the recovery of the sampling standards should state that recovery standards are used to measure recovery of the final quantification step.

9 Report

No additional information

Annex A – Zz

No additional information

Part 3: Identification and quantification of PCDDs/PCDFs

1 Scope

No additional information

2 Normative references

No additional information

3 Terms and definitions

No additional information

4 Symbols and abbreviations

No additional information

5 Principles of identification and quantification

No additional information

6 Reagents, materials and equipment

No additional information

7 Safety measures

No additional information

8 Quality control requirements for identification and quantification

8.1 Minimum requirements for identification of PCDF/PCDD congeners

No additional information

8.2 Isomer sums of PCDD/PCDF congeners

No additional information

8.3 Minimum requirements for quantification

a) no additional information
b) no additional information
c) the quantification requirement in this section applies to an initial system suitability check only. It is not necessary to carry out this step on each sample containing 2,3,7,8-TCDD.
d) no additional information
e) no additional information

f) this applies to native PCDDs/PCDFs only since labelled compound are present at the same concentration in the standards.
g) no additional information
h) the equation shown in the standard relates the minimum sensitivity of the measurement to the LOQ. In the original version of the standard this same relationship was presented with the LOD defined in the same manner. Meeting the terms of the original expression is acceptable when stating conformity with the standard.
i) the standard states one of the criteria for identifying a congener is if the isotope ratio between the ions matches the theoretical value. If interference results in only one ion being quantified the ion ratio limits would not have been met. However, it does allow quantification of a single ion if interference is unavoidable on the second trace. The use of one ion only must be reported.

9 Quality assurance criteria for extraction/clean-up/quantification procedure blanks

No additional information

10 Calibration of the analyser

If the calibration range is exceeded and the results are over range this shall be stated in the report.

11 Quantification of analysis results

No additional information

12 Calculation of the measurement results

Results should be reported to the toxic equivalency system specified in the Permit. If the Permit does not specify the system used, then the factors in Table A1 of the standard should be applied.

13 Analytical report

No additional information

14 Performance characteristics

No additional information

15 Interferences

No additional information

Annexes A - Zz (informative)

No additional information