

Method Implementation Document (MID 1948)

BS EN 1948 Parts 1-3: 2006

Stationary source emissions - Determination of the mass concentration
of PCDDs/PCDFs and dioxin-like PCBs

Part 1: Sampling of PCDDs/PCDFs

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

Part 3: Identification and quantification of PCDDs/PCDFs

Environment Agency

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Version 3

Record of amendments

Version number	Date	Amendment
3	Draft 2013	6.2.2 – added clarification about measuring resin trap temperature
		9.3.5.2 – added information about transport of samples

Status of this document

This MID may be subject to review and amendment following publication. The most recent version of this MID is available from our website at:

www.mcerts.net

It is also available on the Source Testing Association web site at:

www.S-T-A.org

Implementation date

It is expected that organisations, which hold MCERTS accreditation for BS EN 1948-1, will have met the requirements of this MID by March 2010.

Feedback

If you have any comments on this document please contact Rupert Standing at rupert.standing@environment-agency.gov.uk

Role of Method Implementation Documents

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

We have established our Monitoring Certification Scheme: MCERTS to deliver quality environmental measurements. Organisations wishing to include a standard in their schedule of MCERTS accreditation shall follow the requirements of the standard and, where available, the associated MID.

It may not be necessary to produce a MID for every standard but where required they will be used to supplement standards called up by Technical Guidance Note M2. MIDs provide details on how the preferred standards shall be used for regulatory monitoring.

MIDs are produced in collaboration with the Source Testing Association (STA) and its members.

Further information on MCERTS including copies of performance standards and guidance can be obtained from our web-site at:

www.MCERTS.net

Copies of MIDs are available from the STA web-site at:

www.S-T-A.org

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Foreword

This MID follows the numbering in the standards and like the standard is split into three parts. However, unlike the standard these are combined in the same document. The three standards must be read and used in conjunction with one another. It is also necessary for the sampling organisation to liaise with the analytical laboratory.

Introduction

No additional comments

Part 1: Sampling of PCDDs/PCDFs

1 Scope

BS EN 1948 Stationary source emissions — Determination of the mass concentration of PCDDs/PCDFs and dioxin-like PCBs (referred to in this document as EN 1948) is published in three parts:

- Part 1: Sampling of PCDDs/PCDFs
- Part 2: Extraction and clean-up of PCDDs/PCDFs
- Part 3: Identification and quantification of PCDDs/PCDFs

Part 1 of the standard includes several different approaches to sampling:

- Filter/condenser method
- Dilution method
- Cooled probe method

The standard also includes the following approaches to the filter condenser method:

- Liquid absorbent downstream of the condensate flask
- Solid absorbent downstream of the condensate flask
- Solid absorbent upstream of the condensate flask
- Flow division to enable side stream sampling to be carried out

This MID provides information on the filter/condenser method¹, using a solid absorbent upstream of the condensate flask, without flow division.

In order to obtain MCERTS accreditation to measure PCDDs/PCDFs it is necessary to meet the requirements of EN1948 Part 1 and this MID. This MID specifies that the requirements of the filter condenser method (See Annex B, section B4) of the standard shall be met.

Furthermore, it is necessary for the analytical laboratory to be accredited for the analysis specified in EN1948 Part 2 -3 and in this MID. This should be stated on the analytical laboratory's schedule of accreditation.

A test carried out to measure PCDDs/PCDFs cannot also be used to measure PAHs¹.

¹ In 2006 the STA carried out a questionnaire of its members with UKAS accreditation to use BS EN 1948. This confirmed that sampling organisations in the UK use the filter condenser method. The equipment used follows the specifications outlined in US EPA method 23.

2 Normative references

MID 13284-1, Environment Agency.

MCERTS for manual stack emission monitoring - performance standard for organisations, Environment Agency.

3 Terms and definitions

No additional information

4 Symbols and abbreviations

No additional information

5 Principle of the complete PCDD/PCDF measurement procedure

5.1 Sampling

5.1.1 General

This MID specifies the use of the filter/condenser method, using solid absorbent upstream of the condenser, without flow division.

5.1.2 Filter/condenser method

No additional comments

5.1.3 Dilution method

This approach is not relevant to this MID.

5.1.4 Cooled probe method

This approach is not relevant to this MID.

5.2 Extraction and clean-up

No additional comments

5.3 Identification and quantification

No additional comments

6 Sampling device and materials

6.1 General sampling device and sub sections

¹There is currently no CEN or ISO procedure that combines the measurement of PCDDs/PCDFs with PAHs. Without validation evidence and an agreed industry wide procedure it is not possible to obtain MCERTS accreditation for a combined method. PAH should be measured using ISO 11338.

No additional requirements

6.2 Materials

6.2.1 General

No additional requirements

6.2.2 Sampling system

Titanium may be used. 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°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 thermocouple is fitted directly in the gas stream. This will give a very accurate reading of the gas temperature. However, it may cause leakage around the fitting. Also the thermocouples and seals will require cleaning to ensure they do not cause contamination.

- 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).

- a surface temperature measurement sensor is used to provide a very good contact between the thermocouple and the surface of the glass.

6.2.3 Sealings (in contact with flue gas)

PTFE must not be used in temperatures above 200°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 requirements

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 requirements

6.3 Cleaning the sampling device

The standard gives three cleaning procedures. Cleaning procedure number (1) shall be carried out before a sampling campaign. The solvent wash and treatment in a muffle oven shall be carried out.

The muffle oven shall be at 400 to 480°C, except when using titanium. When using titanium the temperature shall be between 300 to 380°C.

The sampling equipment shall be kept in the muffle oven for at least three hours. Due the length of probe liners 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.

Note: due to limitations on the probe heaters it is not usually practical to heat probes to between 300 to 380°C.

It is permissible to use an alternative cleaning procedure if an analytical laboratory provides evidence to UKAS that the procedure is equivalent to the procedure specified in this MID.

Note 1: consistently low field blank results help demonstrate that an alternative cleaning procedure is effective.

Note 2: an alternative cleaning procedure may, for example, include prolonged exposure to UV light.

7 Minimum requirements for sampling

7.1 Method validation criteria

a) No additional requirements

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/PCDFs, it is necessary to put two resin traps in sequence.

7.2 Minimum requirements for sampling

a) BS EN13284-1 states that nozzles with an internal diameter of less than 6mm shall be avoided. The sample train used for the filter condenser method* (see Annex B4) is designed to have a sample gas flow rate of around 5 – 25 l/min. At high stack gas velocities (typically above 25 m/s) it may be necessary to use a nozzle with a diameter of less than 6mm in order to remain within the designed flow rate of the sampling train.

If a nozzle with a smaller diameter than 6mm is used:

- sufficient sample volume shall be extracted to meet the limit of detection required by the analytical laboratory;
- justification for the deviation from EN 13284-1 shall be provided in the monitoring report.

b) No additional requirements

c) No additional requirements

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.

d - k) No additional requirements

7.3 Field blank requirements

The field blank shall be performed before a measurement series (i.e. 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 (i.e. sampling platform) and the process conditions are the same. In order 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

During the production of a Site Specific Protocol¹ it is important to specify whether an in or out of stack filter will be used.

In the UK it is general custom and practice to use an out of stack filter system to measure PCDDs/PCDFs. Annex B of this document shows the sample train with an out of stack filter configuration.

* Variant with solid absorbent upstream of the condensate flask

¹ Refer to MCERTS for manual stack emission monitoring - performance standard for organisations

The resin trap temperature shall be kept below 20°C throughout the measurement. The sampling team shall have planned in advance where they will obtain ice and how much ice is required for the measurement. The amount of ice required shall be recorded in the SSP.

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.

Note: it is strongly recommended that the sampling team have access to an ice making machine to ensure they have sufficient ice available throughout the measurement.

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 requirements

9 Preparations and sampling

9.1 Advance preparations at the sampling site

9.1.1 Selection of suitable sampling location

No additional requirements

9.2 Advance preparations at the laboratory

9.2.1 Preparation of equipment

No additional requirements

9.2.2 Preparation of parts of the sampling train in contact with the sample

No additional requirements

9.3 Sampling at the plant

9.3.1 Initial checks

No additional requirements

9.3.2 Preliminary survey

No additional requirements

9.3.3 Assembly of apparatus

See section 7.2 of this MID for information on selecting nozzle sizes.

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 a clean area.

9.3.4 Sampling

9.3.4.1 Record keeping

No additional requirements

9.3.4.2 Changing sampling line

No additional requirements

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 should 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.

9.4 Calculation of flue gas sample volume

No additional requirements

9.5 Sampling report

If carrying out MCERTS accredited work the monitoring report shall be submitted in the report format specified in the Manual stack emission monitoring performance standard for organisations (Annex H) available from www.mcerts.net. The report shall also include specific requirements required by EN1948 and this MID.

Annex A (informative) Toxicity and toxic equivalency

No additional information

Annex B Examples of operation

B1 General

Annex B in the standard is informative, as it contains several different examples of operation. These examples have been validated by CEN. This MID specifies that the requirements of Section B4 shall be followed.

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 UK¹.

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).

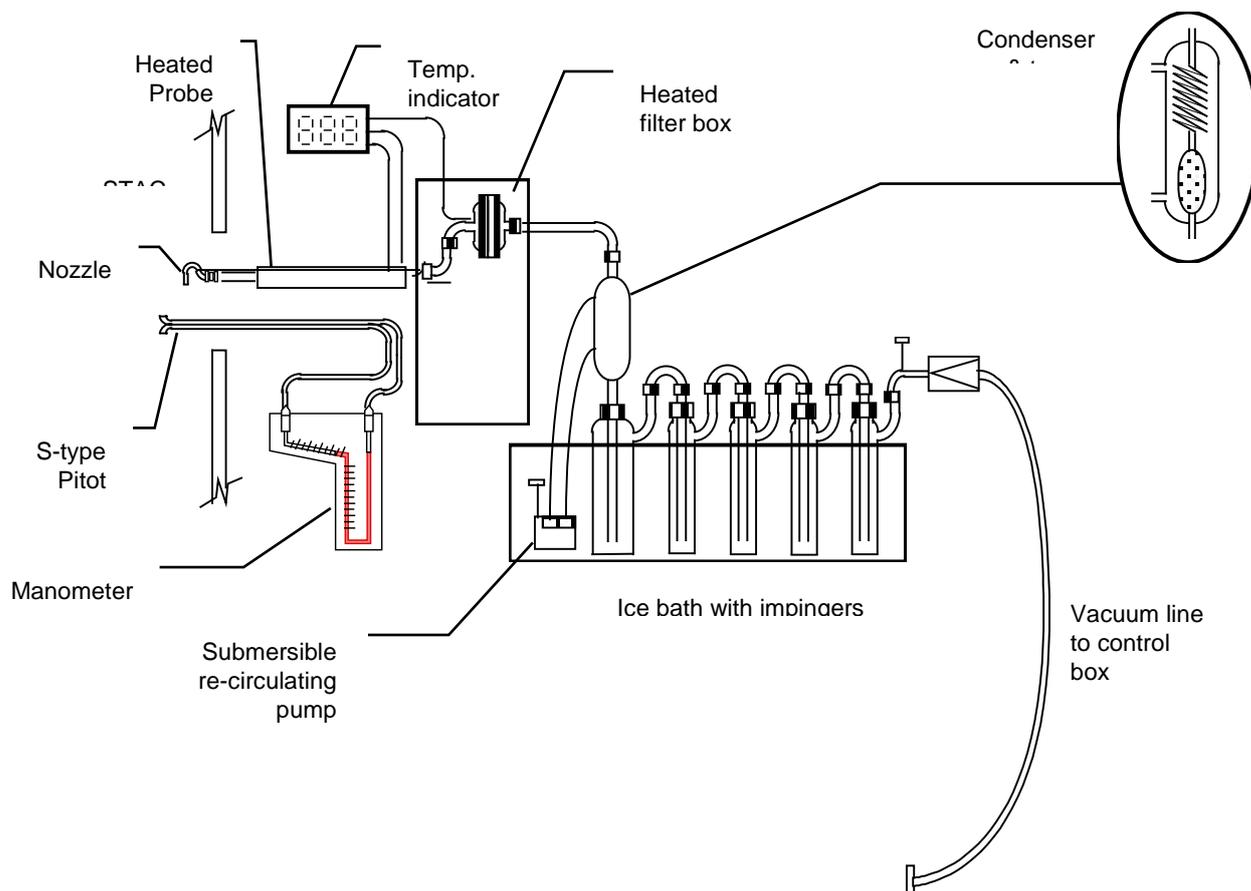


Figure 1 Dioxin sample train

¹ Equipment used in the UK follows the specifications outlined in US EPA method 23.

B4. 2. Adsorbent and cleaning procedure

No additional requirements

B4. 3. Sampling train cleaning procedure before sampling

The cleaning procedure given in Section 6.3 of this MID shall be used.
The first impinger (condensate flask) shall also be cleaned using the procedure given in Section 6.3.

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

No additional requirements

B4. 6. Leak check procedure

No additional requirements

B4. 7. Sample gas flow rate control

No additional requirements

B4. 8. Sampling

No additional requirements

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

Annex C in the standard is informative, as it contains several different examples. 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

It is important that close co-operation takes place between sampling and analytical laboratories. Documented evidence for this shall be available.

2 Normative references

No additional requirements

3 Terms and definitions

No additional information

4 Symbols and abbreviations

No additional information

5 Principle of the extraction and clean-up procedure

5.1 Principles

No additional information

5.2 Minimum information prior to analyses

No additional information

6 Device, materials and ¹³C₁₂-labelled standards

6.1 Device and materials

No additional requirements

6.2 ¹³C₁₂-labelled 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.

7 Method validation and quality control requirements

7.1 Use of ¹³C₁₂-labelled standards

No additional requirements

7.2 Sample pre-treatment

No additional requirements

7.3 Clean-up

7.3.1 Method validation

No additional requirements

7.3.2 Minimum requirements for measurements

No additional requirements

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 screw-caps and PTFE-lined seals shall be used. Traps and filters may be wrapped in foil to exclude light.

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 requirements

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 requirements

Annex A (informative) Examples of operation of extraction and clean-up methods

No additional requirements

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

No additional information

Part 3: Identification and quantification of PCDDs/PCDFs

1 Scope

No additional information

2 Normative references

No additional requirements

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 requirements

7 Safety measures

No additional requirements

8 Quality control requirements for identification and quantification

8.1 Minimum requirements for identification of PCDF/PCDD congeners

No additional requirements

8.2 Isomer sums of PCDD/PCDF congeners

No additional requirements

8.3 Minimum requirements for quantification

a) no additional requirements

b) no additional requirements

- 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 requirements
- e) no additional requirements
- f) this applies to native PCDDs/PCDFs only, since labelled compounds are present at the same concentration in the standards.
- g) no additional requirements
- 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 requirements

10 Calibration of the HRGC/HRMS

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

11 Quantification of HRGC/HRMS results

11.1 Quantification of the sample

No additional requirements

11.2 Calculation of the recovery rates of the extraction standards

No additional requirements

11.3 Calculation of the recovery rates of the sampling standards

No additional requirements

12 Calculation of the measurement results

Results shall be reported to the reference conditions specified in the Permit. 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 requirements

14 Performance characteristics

14.1 General aspects

No additional requirements

14.2 Intra-laboratory results

No additional requirements

14.3 Inter-laboratory results

No additional requirements

14.4 Quantification limits

No additional requirements

15 Interferences

No additional requirements

Annex A - Zz (informative) Examples of operation of gas chromatography / mass spectrometry analysis of PCDDs/PCDFs in emission samples

No additional requirements

Annex B (informative) Estimation of the measuring uncertainty and precision of the determination of polychlorinated dibenzo-p-dioxins and dibenzofurans

No additional requirements

Annex C (informative) Mass of ions monitored for PCDDs and PCDFs

No additional requirements

Annex D (informative) Relative abundance of chlorine isotope ions and their ratio for PCDD/PCDF congeners containing 4 to 8 chlorine substituents

No additional requirements

Annex E (informative) Further general recommendations for separation, detection and quantification of PCDDs/PCDFs

No additional requirements

Annex F (informative) Variability determination based on the results of the validation tests

No additional requirements

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

No additional requirements