

## Method Implementation Document for BS EN 14385:2004

### Stationary source emissions – Determination of the total emission of As, Cd, Cr, Co, Cu, Mn, Ni, Pb, Sb, Tl and V (including an option to measure mercury)

#### Foreword

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 ensure 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.

MIDs are not produced 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.

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

[www.mcerts.net](http://www.mcerts.net)

Or from the STA web-site at:

[www.S-T-A.org](http://www.S-T-A.org)

Any comments or suggested improvements to this MID should be e-mailed to Rupert Standing at [rupert.standing@environment-agency.gov.uk](mailto:rupert.standing@environment-agency.gov.uk).

#### Record of amendments

Version number	Date	Amendment
5	Sept 18	Deleted information on nozzle size limitations (5.1.2.1), leak check requirements (8.2.4) and field blank leak check (8.5), following the publication of EN 13284:2017.
		Added statement about the use of alternative cleaning procedures (section 7)

This document supplements BS EN 14385:2004 (referred to in this document as EN 14385). However, it does not re-state all the provisions of EN 14385 and organisations are reminded of the need to comply with the criteria detailed in EN 14385. The clause numbers in this document follow those of EN 14385 although the text from the standard is not repeated in this document.

## 1. Scope

European Standard BS EN 14385:2004 may be used to determine other metals than those named in the scope of the standard.

In order to extend the scope of metals it is necessary for the analytical laboratory to carry out validation for the analysis of the additional metals. The filter, rinsing solutions and absorption solutions can be spiked with certified reference materials and analysed to determine recoveries and limits of detection<sup>1</sup>.

This MID includes two approaches. One for measuring metals including mercury and one for measuring metals without mercury.

EN 14385 allows BS EN 13211 - *Manual method of the determination of the concentration of total mercury* (referred to in this document as EN 13211) to be carried out using a side stream sampling technique. In the UK custom and practice does not normally include the use of side stream sampling techniques.

This MID therefore includes the option of measuring mercury in the main sampling train. When carrying out this option it is important that all provisions specific to EN 13211 are met.

Measurement of metals including mercury differs from measurement of metals, according to EN 14385, in the following ways:

- a different absorber (also known as impinger) train configuration to that specified by EN 14385 is used;
- the absorbants / analytical requirements of BS EN 13211 are included; and
- extra analytical requirements are employed to ensure the combination of both methods does not affect the reliability of the measurement.

This approach follows the principles established by a validation exercise carried out by the Environment Agency<sup>2</sup>.

In order to obtain MCERTS accreditation for measuring metals including mercury it is necessary to meet the requirements of this MID and be accredited to use EN 13211. If accreditation is sought for metals excluding mercury it is not necessary to be accredited for EN 13211. The UKAS schedule of accreditation will specify whether mercury is included or excluded.

EN 14385 has been validated on stacks with a gas composition given in Table 1 of the standard. The standard can be used on processes with other gas compositions.

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<sup>1</sup> The analysis of tin (Sn) may be problematic due to the formation of "tin stone" (a mixed valence oxide). However, validation work carried out by a UK laboratory has shown acceptable results.

<sup>2</sup> Agency document: Monitoring mercury at the same time as other heavy metals (2004)  
MID EN 14385, Version 5, September 2018

Note 1: practical experience shows that the standard can be used on a wide range of processes and stack gas conditions.

It is not acceptable to combine the measurement of metals and particulates.

## **2. Normative references**

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

## **3. Definitions, symbols and abbreviations**

No additional information

## **4. Principle**

No additional information

## **5. Apparatus, chemicals and gases**

### **5.1 Apparatus**

Commercial titanium is made to different specifications based on the purity of the titanium. As the other materials present may contain the specific elements being determined during the measurement it is important that an appropriate grade of titanium is used.

Titanium will degrade in gas streams with a fluoride content of greater than 20ppm.

Titanium may also degrade at temperatures greater than 350°C.

When using this MID to sample for metals including mercury it is important that parts of the sampling equipment in contact with the mercury containing flue gas, or with liquid containing mercury, shall be made of materials shown in Table 1 of EN 13211.

Absorbers shall be kept below 30°C. This can be done by using ice.

PTFE is not suitable for temperatures in excess of 200°C.

### **5.2 Chemicals and filter material**

#### **5.2.1 General**

No additional information

#### **5.2.2 Filter**

A batch of filters for metals sampling are those prepared on a single occasion. This may include filters prepared prior to the sampling campaign for use exclusively on that campaign or a greater number of filters prepared on one occasion but stored for use in future monitoring campaigns.

At least one filter per batch should be analysed for metal content prior to use.

#### **5.2.3 Hydrofluoric acid**

No additional information

#### **5.2.4 Hydrogen peroxide**

No additional information

#### **5.2.5 Nitric acid**

No additional information

#### **5.2.6 Hydrochloric acid**

No additional information

#### **5.2.7 Water**

No additional information

#### **5.2.8 Absorption solution**

EN 14385 states that the absorption solution must be freshly made. The diluted nitric acid solution shall be prepared at a permanent laboratory. The addition of peroxide to the acid solution may be carried out at the laboratory or on site.

The elements being determined shall be below 1 µg/l in the absorption solution.

EN 13211 describes two absorption solutions that may be used for the absorption of mercury.

If a potassium permanganate / sulphuric acid solution is used it shall be prepared at a permanent laboratory, as it requires the addition of concentrated hydrochloric acid.

If a potassium dichromate / nitric acid solution is used the nitric acid solution shall be made in a permanent laboratory. The potassium dichromate solid can be added to the pre-prepared nitric acid solution at the laboratory or on site.

If a potassium permanganate / sulphuric acid solution is used it is important that the solution is not mixed with the absorption solutions for other gaseous metals. Mixing of the two may lead to the nitric and sulphuric acid causing a gas release, which results in high pressure and possible explosion of the bottle. The use of an empty absorber between the different absorption solutions will reduce the likelihood of mixing occurring (see Annex B).

#### **5.2.9 Boric acid solution**

No additional information

#### **5.2.10 Chemical blank solution for digestion**

At least one digestion blank shall be prepared with each batch of samples.

#### **5.2.11 Rinsing acid**

The standard states that the rinsing acid is used for rinsing the digestion equipment. The rinsing acid is used on site to rinse the nozzle probe and filter housing (see section 8.4.2)

EN 14385 specifies the use of 25% mass content nitric acid for rinsing glassware on site. Due to health and safety reasons 5% mass content nitric acid may be used.

The elements being determined shall be below 1 µg/l in this solution. This shall be confirmed before use.

#### **5.2.12 Standard solutions**

No additional information

#### **5.2.13 Certified reference material**

No additional information

#### **5.2.14 Gases**

No additional information

### **6. Sampling equipment**

#### **6.1 General requirements**

When performing the determination of mercury in conjunction with EN 14385 the first three absorbers in the sample train are the same as specified in EN 14385. The fourth absorber is empty. The fifth and sixth absorber contains absorbent solutions for gas phase mercury. It may be necessary to place an empty absorber at the start of the train and before the drier assembly (the use of these optional absorbers depends on the expected moisture content of the stack gas). An example sample train is provided in Annex B.

#### **6.2 Isokinetic sampling equipment**

No additional information

#### **6.3 Absorbers**

The absorber efficiency test compares the concentration of each element found in the third absorber with the concentration of that element in the total sample train.

Note 1: A number of metals are often measured together as a group and are summed for comparison with an ELV for total metals. For example, metals are typically reported in two groups:

- Cd and Tl
- Sb, As, Pb, Cr, Co, Cu, Mn, Ni, & V

The absorber efficiency test is applied separately to each group of metals.

If one of the individual metal elements in the last impinger (e.g. Sb) is more than 10% of the total combined metals for that individual element (i.e. the filter, probe rinse and impingers) collected, then the result for all the metals in that group shall be rejected.

However, for each group the requirement to pass the absorber efficiency check shall not apply:

- to individual metal element(s), where the individual mass of the element in the final result is less than 1% of the result for the total mass of metals in the group; or
- if the total combined result for the metals in the group is less than 30% of the ELV.

Note 2: the absorber efficiency check becomes less effective as the concentration of the pollutant in a stack gas decreases.

Note 3: For example:

- Cd and TI combined – 0.05 mg/m<sup>3</sup>
- Sb, As, Pb, Cr, Co, Cu, Mn, Ni, V combined – 0.5 mg/m<sup>3</sup>

For Cd and TI combined it would not be necessary to comply with the less than 10% in the last impinger criteria, if the overall combined Cd and TI result for the sample train was below 0.015 mg/m<sup>3</sup> (i.e. <30% of the ELV).

For combined metals (Sb, As, Pb, Cr, Co, Cu, Mn, Ni, V) it would not be necessary for each individual element to comply with the less than 10% in the last impinger criteria, if the overall combined result for the sample train was below 0.15 mg/m<sup>3</sup> (i.e. <30% of the ELV).

For mercury the requirements on the absorber efficiency in EN 13211 shall be followed. However, when EN 14385 and EN 13211 are combined, the mercury in the last absorber is compared to the total mercury in both the mercury absorbers and the absorbers used for metals.

## 7. Cleaning of the sampling equipment prior to sampling

The following is a proven cleaning procedure:

- Rinse all sampling train glassware with hot tap water and then wash in hot soapy water. Next, rinse glassware three times with tap water, followed by three additional rinses with HPLC water. Then soak all glassware in a 10 percent (v/v) nitric acid solution for a minimum of 4 hours, rinse three times with water and then rinse a final time with acetone and allow to air-dry. Cover all glassware openings until the sampling train is assembled for sampling<sup>3</sup>.

Note 1: the grade of water is defined in section 5.2.7 of the standard.

The above procedure also includes glass and titanium probe liners. However, it may not be practical to soak probe liners for 4 hours in a nitric acid solution. An alternative is to circulate the rinsing solution for 15 minutes.

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 above.

Note 2: consistently low field blank results help demonstrate that an alternative cleaning procedure is effective.

Although it is acceptable to re-use glassware on different stacks, it may not be advisable due to the risk of contamination.

## 8. Procedure

### 8.1 General requirements

There are several temperature criteria required depending on the stack gas temperature, the type of equipment being used and whether sampling for mercury is being undertaken.

EN 14385 states that the sampling probe and out-stack filter shall be maintained at a temperature of at least 20°C above stack gas temperature. However, due to limitations

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<sup>3</sup> This procedure is specified in US EPA method 29  
MID EN 14385, Version 5, September 2018

on the equipment, it is not necessary to heat the sampling probe and out-stack filter to temperatures above 180°C.

The following applies when sampling for metals including mercury:

- the sampling probe and the out-stack filter shall be maintained at a temperature of at least 20°C above stack gas temperature (it is not necessary to heat the sampling probe and out-stack filter to temperatures above 180°C).
- when using titanium equipment the temperature shall be maintained at 180°C or higher.

Details of the probe and filter temperature shall be included in the report.

When measuring mercury it is important that the absorption solutions do not mix. Mixing of the solutions will result in manganese contamination.

## **8.2 Preparation and installation of equipment**

### **8.2.1 Filter installation**

Filters should not be installed or recovered on exposed platforms.

### **8.2.2 Nozzle installation**

No additional information

### **8.2.3 Installation of absorbers**

Due to the possibility of pressure caused by stored absorber solutions, it may be appropriate to consider the use of pressure-relief devices on absorber solution storage bottles.

### **8.2.4 Leak test**

No additional information

### **8.2.5 Installation of equipment at chimney or duct**

No additional information

## **8.3 Performance of the sampling**

No additional information

## **8.4 Disassembling the equipment**

Aluminium foil shall not be used to cap sample trains.

## **8.5 Field blanks**

A blank shall be taken at each stack during a sampling campaign. A campaign is defined as one site visit.

When carrying out a sampling campaign with multiple tests over a number of days it is advisable to carry out several blanks.

When measuring mercury it is necessary to carry out analysis of mercury upstream of the mercury absorbers. This analysis shall also form part of the field blank.

## **8.6 Requirements for storage of the samples**

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.

Note: this approach is based on the requirements in US EPA M29 and VDI 3869.

## **8.7 Pre-treatment before analysis**

No additional information

### **8.7.1 General**

No additional information

### **8.7.2 Pre-cleaning of the digestion equipment**

No additional information

### **8.7.3 Treatment of CRM and filter**

No additional information

#### **8.7.3.1 General procedure**

No additional information

#### **8.7.3.2 Heating in oven or heating plate**

No additional information

#### **8.7.3.3 Heating in microwave oven**

When analysing metals including mercury the requirements of EN 13211 shall be met.

Note: EN 13211 specifies that the filter should be heated during digestion for a greater length of time than specified in EN 14385.

### **8.7.4 Pre-treatment of absorption solutions**

No additional information

### **8.7.5 Pre-treatment of rinsing solutions**

When measuring mercury it is necessary to carry out the pre-treatment according to EN 14385. However, before carrying pre-treatment for metals analysis a portion shall be quantitatively removed for mercury analysis.

## **8.8 Analysis**

When measuring mercury it is necessary to meet the requirements of EN 13211. For the filter and probe wash the following approach shall be used:



- the filter shall be digested/heated and analysed as one sample following the requirements in BS EN 14385. This gives the result for both the mercury and metals on the filter;
- the probe rinse volume shall be measured. This shall be split into two samples A and B (B being a measured small aliquot);
- Sample A shall be digested/heated and analysed according to BS EN 14385. This gives the result for metals in the sample A portion of the probe rinse. The metals concentration in sample A shall be used to determine the metals mass in sample B. The results from samples A and B shall be combined to give the total metals in the probe rinse.
- Sample B shall be analysed according to BS EN 13211. This gives the probe rinse mercury result for sample B. The mercury concentration in B shall be used to determine the mercury mass in Sample A. The results from samples A and B shall be combined to give the total mercury in the probe rinse.

Besides these requirements it is also necessary to analyze the absorber solutions in the first three absorbers, which are primarily in place to capture other gas phase metals. In total five absorbers shall be measured for mercury by taking a known volume from each. The analytical method for measuring all five absorbers is the same. At least once per sampling campaign it shall be proven that less than 5% of the total gas phase mercury absorbed is in the final absorber (see section 7.33 of EN 13211).

Linearity shall be checked and the correlation coefficient should be 0.98 or better. Analyte additions can be used as an alternative calibration technique and internal standards may be added to correct for transport effects and instrument drift.

Suitable quality checks (QCs) should be prepared and measured with each batch of samples. For filters, a suitable certified reference material (CRM) can be used if available. If no CRMs are available then a spiked filter may be exposed to the digestion process instead. For adsorption and rinsing solutions, spiked solutions can be used. For all QCs a recovery of  $100 \pm 20$  % of the expected or certified value is acceptable. If any QC results are outside this range then this must be highlighted in the final report. If recoveries are outside the required range sampling and analysis stages may have to be repeated.

Note: adsorption and rinsing solutions are tested as part of the blank solution for digestion and, consequently, do not need to be done separately.

## 9. Expression of results

If results are at or below the limit of detection then they shall be reported as being at the detection limit.

## 10. Test report

No additional information

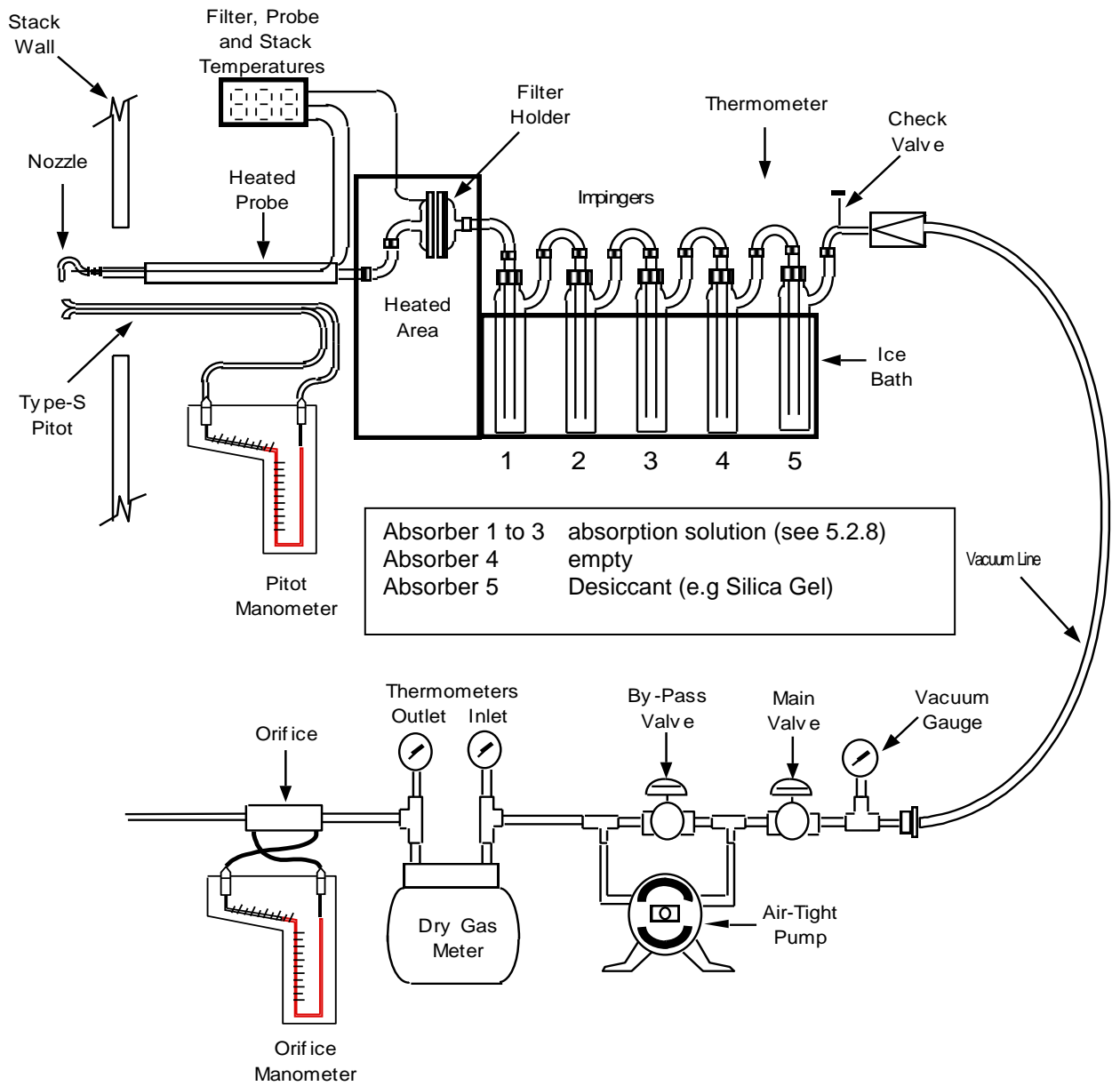
### Annex A: Examples of absorption vessels

Example B Greenburg-Smith impingers shall be used.

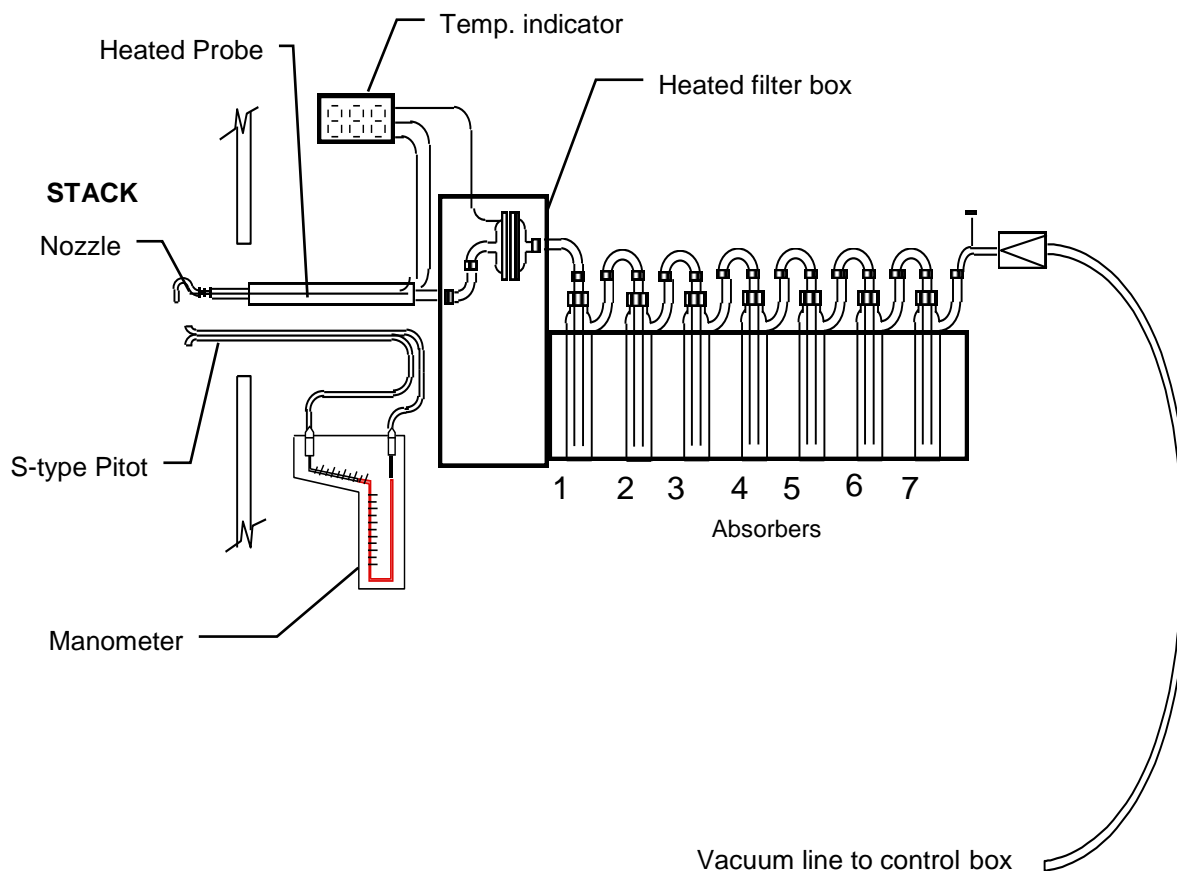
### Annex B: Types of isokinetic equipment

The examples shown below are shown with out of stack filtration.

**Figure 1: Sample train for metals (excluding mercury)**



**Figure 2: Sample train for metals and mercury**



Note: Absorber numbers 1-3 are analysed for all metals including mercury. Absorbers numbers 5 and 6 are analysed for mercury only. The amount of mercury in the final absorber should be less than 5% of the total amount of mercury in all absorbers or correspond to less than  $2 \mu\text{g}/\text{m}^3$  whichever is the greater.

Absorber 1 to 3	absorption solution (see 5.2.8)
Absorber 4	empty
Absorber 5 & 6	refer BS EN13211 clause 6.3
Absorber (optional)	empty
Absorber 7	desiccant (e.g. Silica Gel)

**Annex C: Pre-cleaning procedures of the sampling equipment at the laboratory and determination of the absorption efficiency**

No additional information

**Annex D: Measurement results of two field tests**

No additional information

**Annex E: pre-tests for determination of the efficiency, of the digestion and of the performance of the analytical procedure**

No additional information

**Annex ZA: Relationship with EU Directives**

No additional information