

**Technical Guidance Note  
(Monitoring)**

**M2**

**Monitoring of stack emissions to air**

Environment Agency  
Version 12  
August 2017

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## Foreword

This Technical Guidance Note (TGN) is one of a series providing guidance to our staff, monitoring organisations, industry and other parties interested in monitoring stack emissions to air. It is also a technical reference for our Monitoring Certification Scheme (MCERTS) and Operator Monitoring Assessment (OMA) scheme.

It describes our overall approach to stack-emission monitoring and provides guidance on methods used for regulatory purposes. It focuses on areas where practical guidance is necessary. This includes:

- the legislative framework
- the role of MCERTS
- different approaches to stack-emission monitoring
- sampling strategy
- the hierarchy of different methods
- an index of monitoring techniques and methods

The index of monitoring techniques and methods will be particularly useful for operators with installations falling under our Environmental Permitting Regulations (EPR). Under EPR:

- applications for permits have to include proposals for monitoring emissions
- permits include conditions setting out suitable emission-monitoring requirements, specifying the measurement methodology and frequency, and evaluation procedure

To support the implementation of monitoring methods, the European Integrated Pollution Prevention and Control Bureau in Seville has published a reference document<sup>1</sup> on the principles of monitoring. This recognises that, wherever possible, emissions should be monitored using standards produced by recognised standards-making organisations and sets out a hierarchy of standards making organisations. This TGN builds on the general principles in the reference document. It specifies the index of monitoring techniques and methods, providing the user with the standards and methods to meet our monitoring requirements under EPR.

Measuring stack emissions can involve exposure to many safety hazards. TGN M1<sup>2</sup> draws attention to relevant health and safety legislation.

### How to use this TGN

This TGN is divided into two parts: general guidance on monitoring and an index of monitoring techniques and methods. The latter has been structured to help the user to find a solution to a monitoring problem or query. The most likely situation is that the user will be very specific about the substance, less confident about the general approach to use, and less confident still about which particular technique, method or equipment to employ. Accordingly, the index of monitoring techniques and methods is initially classified by substance. For each substance, the index is grouped according to the monitoring approach - Continuous Emissions Monitoring systems (CEMs) and periodic measurements. Then, for each approach a list of methods is given. Where a periodic method is required, use the section describing the hierarchy of methods to select the appropriate one.

## Amendments

Version number	Date	Amendment
12	August 2017	Section 2.2: Added reference to the MCERTS performance standard for laboratories testing samples from stack emissions monitoring.
		Section 5.4 Added information on BS EN 15267-4 (Portable-AMS).
		Table S2.5 Added reference to EA TGN M9: Monitoring bioaerosols from regulated facilities.
		Table S2.6 Added ISO 18466 (Determination of the biogenic fraction in CO <sub>2</sub> in stack gas using the balance method).
		Table S2.13 Added reference to PD CEN TR 17078 (Guidance on EN 16911-1 – Velocity and volume flow rate).
		Table S2.27 Deleted reference to MID for EN 14792 (measurement of NO <sub>x</sub> ). Added information on application of EN 14792 and completion of the converter efficiency check.
		Table S2.42 Added CEN TS 17021 and specified the date of the withdrawal of TGN M21 (measurement of SO <sub>2</sub> ).
		Section 9: Updated CEN/TS 14793 to EN 14793.

## Status of this document

This TGN may be subject to review and amendment following publication. The latest version is available on our website at:

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

## Feedback

If you have any comments on this standard please contact our National Customer Contact Centre at:

Email: [enquiries@environment-agency.gov.uk](mailto:enquiries@environment-agency.gov.uk)

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# 1. The regulatory framework

## 1.1 Legislative framework relevant to stack emission monitoring

### 1.1.1 Why carry out stack-emission monitoring?

The main reasons for carrying out stack emission monitoring are:

- compliance with environmental legislation
- collecting data for emissions-inventory compilation
- calibration of continuous emission monitoring systems (CEMs)
- collecting data for environmental impact assessments
- collecting data to assess process efficiency and process control
- assessing the performance of a pollution-control device (abatement system)

The current legislative framework affecting the monitoring of stack emissions is outlined below.

### 1.1.2 European directives

The European Union (EU) has drawn up directives stating the objectives that must be achieved to control pollution. The requirements of these directives must be adhered to by member states of the EU.

The Air Framework Directive 84/360/EEC<sup>3</sup> sets out plans for a number of daughter directives, which seek to control emissions from a wide range of processes in a number of industrial categories.

Of particular significance to stack emission monitoring is the Industrial Emissions Directive (IED)<sup>4</sup>. It replaces a number of directives including the Integrated Pollution Prevention and Control Directive (IPPCD)<sup>5</sup>, the Waste Incineration Directive<sup>6</sup> (WID) and the Large Combustion Plant Directive<sup>7</sup> (LCPD). The IED specifies the use of Comité Européen de Normalisation (CEN) standards for monitoring and calibration.

The IED has been transposed into law in England, via the Environmental Permitting Regulations. It applies to all new installations. Existing installations have implementation dates depending on the type of industrial activity and whether they are subject to the current IPPC Directive.

### 1.1.3 Environmental Permitting Regulations

The Environmental Permitting (England and Wales) Regulations (EPR) came into force in April 2008. EPR replaced the Pollution Prevention Control (PPC) and Waste Management Licensing (WML) regimes. All PPC Permits and WML automatically became environmental permits. EPR was revised in 2010<sup>8</sup> to extend it to cover water discharges and groundwater activities, radioactive substances, mining installations and waste and has been amended again in 2013 to implement the IED.

## 1.2 The importance of this guidance in the MCERTS context

This TGN covers the correct choice of monitoring approach, technique, method and equipment. TGN M1 covers sampling and safety requirements. Encompassing all of this is our Monitoring Certification Scheme: MCERTS (see Box 1.1), which provides performance

standards to improve the quality of regulatory monitoring. TGNs M1 and M2 are key reference documents underpinning MCERTS for stack emission monitoring.

**Box 1.1 MCERTS**

MCERTS is our Monitoring Certification Scheme for instruments, monitoring and analytical services. The scheme is built on proven international standards and provides industry with a framework for choosing monitoring systems and services that meet our performance specifications. MCERTS reflects the growing requirements for regulatory monitoring to meet European and international standards. It brings together relevant standards into a scheme that can be easily accessed by manufacturers, operators, regulators and test houses. Further information on MCERTS is available at [www.mcerts.net](http://www.mcerts.net).

The general requirements for the competence of testing laboratories are described in International Standard EN ISO/IEC 17025<sup>9</sup>. This contains the general requirements laboratories have to meet if they wish to demonstrate that they operate a quality system, are technically competent, and are able to generate technically valid results. EN ISO/IEC 17025 recognises that it may be necessary to supplement EN ISO/IEC 17025 for some testing activities, for example, specific types of monitoring, such as stack emission monitoring. As such, CEN has published CEN TS 15675<sup>10</sup>. Measurement of stationary source emissions - Application of EN ISO/IEC 17025 to periodic measurements.

MCERTS for stack emission monitoring requires organisations to meet the requirements of both EN ISO/IEC 17025 and CEN TS 15675. Some sections of CEN TS 15675 require the competent authority to make decisions on how best to implement the standard in their member state. For example, two different approaches are given for demonstrating personnel are competent; one is to use a personnel competency scheme the other is to use a combination of academic qualifications and assessment of work carried out. Under MCERTS the approach is to use a personnel competency scheme.

The main areas defined in the MCERTS performance standard<sup>11</sup> are as follows:

- use of MCERTS certified personnel
- use of Agency Method Implementation Documents (MIDs)
- detailed requirements for a
  - risk assessment
  - site-specific protocol (measurement plan)
  - reporting of results
- use of alternative methods based on instrumental techniques

TGN M2 is a key reference document for MCERTS for manual stack emissions monitoring in selecting appropriate methods following, where possible, international standards.

## 2. The different approaches to monitoring stack emissions

### 2.1 Types of approach

Stack emissions monitoring approaches can be classified into two types:

- a) **Periodic measurements** – a measurement campaign is carried out at periodic intervals, such as once every three months. The sample is usually, but not always, withdrawn from the stack and analysed away from the site (extractive sampling). An instrumental/automatic technique may be used, where an on-line analyser carries out the sampling and analysis. Alternatively, a manual technique may be used where a sample is extracted on site and analysed later in a laboratory. Samples may be obtained over periods of several hours, or may be so-called spot samples or grab samples collected over a period of seconds to a few minutes.
- b) **Continuous emissions monitoring systems (CEMs)** – automatic measurements carried out continuously, with few - if any - gaps in the data produced. Measurement may be carried out in the stack (in situ) or extractive sampling may be used with an instrument permanently located at or near the stack. CEMs are also referred to as automated measuring systems (AMS), particularly in a European context.

### 2.2 Advantages and disadvantages of CEMs and periodic monitoring approaches

The main characteristics of the two approaches are summarised in Box 2.1. One approach is not inherently superior to the other; both have their own strengths and weaknesses depending upon the application. In general, it is recognised that CEMs provide increased confidence for both regulatory purposes and process control.

**Table 2.1 Important characteristics of CEMs and periodic monitoring**

<b>Characteristic</b>	<b>CEMs</b>	<b>Periodic monitoring</b>
Sampling period.	Monitoring covers all or most of the period that substances are emitted.	Snapshots of the long-term emissions profile.
Speed of results generation.	Almost always real-time output of results.	Real-time results if instrumental analysers used; delayed results if manual method with laboratory end-method used.
Averaging of results.	Results continuously averaged, typically over one hour or 24 hours.	Result over period of test, typically 30 minutes to several hours.
Calibration and traceability.	CEMs require calibration against a standard reference method (SRM) and with certified reference materials.	Standard reference methods can be used for periodic monitoring; also instruments calibrated with certified reference gases can be used.
Capital cost.	Tends to be higher than the cost of periodic monitoring equipment.	Tends to be lower than the cost of CEMs.
Operating cost.	Tends to be lower than periodic approach, as not usually labour intensive. Requires routine maintenance and calibration only.	Tends to be higher than CEMs approach because labour intensive. Trained team on site for whole duration of monitoring campaign.
Certification of equipment.	MCERTS certification of equipment available.	MCERTS certification of transportable stack-monitoring equipment available.
Accreditation of monitoring.	Quality assurance of the calibration and maintenance of CEMs is covered in EN 14181 <sup>12</sup> .	UKAS accreditation to ISO 17025 for the MCERTS performance standard for organisations carrying out periodic monitoring. Accreditation to the MCERTS standard includes the requirement for individuals carrying out monitoring to be certified under MCERTS as competent. UKAS accreditation to ISO 17025 for the MCERTS performance standard for laboratories testing samples from stack emissions monitoring <sup>13</sup>

### 3. The main elements of successful monitoring

#### 3.1 The importance of representative sampling

Whichever monitoring technique, method or equipment is chosen, the fundamental principle of sampling must be adhered to. This principle is that a small amount of collected material should be a representative sample of the overall character of the material. The number and locations of samples that need to be taken to make up a representative sample depends on how homogeneous the bulk material (the stack gas) is. If the stack gas is very homogeneous, only a few samples may be required. If it is not homogeneous, many more samples will be required. Our requirements for representative sampling are covered in TCN M1. Since sampling uncertainty is frequently much greater than analytical uncertainty, it is crucial that this guidance on sampling is followed.

#### 3.2 The importance of isokinetic sampling for particulates

Due to the wide range of particle sizes normally present in process emission streams, it is necessary to sample isokinetically to ensure that a representative sample of the particulate emission is obtained.

If the sampling velocity is less than the isokinetic ratio (usually expressed as a percentage), the actual volume sampled will be less than it should be. Thus, at first sight, it would appear that the emission will be underestimated (see Box 3.1). However, because the sampling rate is too low, there is a divergence in flow around the sampling inlet. Small particles are able to follow the flow and a percentage of them will not be sampled. Larger particles, on the other hand, are not able to follow the flow because of their greater inertia and more of these particles will enter the sampler. Thus a sub-isokinetic sampling ratio will lead to a bias in the sampled particle-size distribution towards the larger particles. This could lead to an overestimate of the particulate concentration, depending on the original size distribution.

Sampling at a rate in excess of the isokinetic ratio will lead to a bias in the sampled particle-size distribution towards the smaller particles. This could lead to an underestimate of the emission rate, depending on the original size distribution.

**Box 3.1 Determining the isokinetic ratio**

To perform isokinetic sampling, it is necessary to calculate the required sampling flow rate to ensure that the velocity of the gas entering the nozzle is the same as the velocity of the stack gas at the sampling plane. This takes into account the velocity of the gas in the stack at the sampling point and the effective diameter of the sampling nozzle.

Sampling flow rate = area of nozzle x velocity of gas entering nozzle

By comparing the velocity of the gas at the nozzle with the velocity of the stack gas at the sampling plane, the isokinetic ratio is determined.

Isokinetic ratio (%) =  $\frac{\text{velocity at the nozzle}}{\text{velocity of stack gas}} \times 100$

It is also possible to check for isokinetic sampling compliance by comparing the required sampling flow rate to the actual sampling flow rate performed during the monitoring.

Isokinetic ratio (%) =  $\frac{\text{actual sampling flow rate}}{\text{required sampling flow rate}} \times 100$

BS EN 13284-1:2001 for the determination of low range mass concentration of dust states that if the mean actual isokinetic ratio during the sampling at the sampling plane differs by more than -5 to +15% the measurement is not valid.

With the exception of in-situ CEMs, the collected sample is usually conditioned in some way before it is analysed. This conditioning may occur at the probe, during transport to the analysis stage, or just prior to analysis. Some examples of sample conditioning during extractive monitoring of gases are:

- the use of a particulate filter in the sampling probe to prevent particulate matter depositing further downstream and/or carrying over to the analysis stage;
- the use of a heated sample line to prevent condensation during transport from the probe to the analysis stage;
- the use of a system to remove moisture from the sample using, for example, a cooling system or permeation drier; the use of a dynamic system to dilute the sample by a known factor to below its dew point.

It is important that any conditioning undertaken to make the gas compatible with the analysis method should not alter the substance being monitored.

**3.4 Reporting of results****3.4.1 Reporting requirements**

Reports of results for regulatory purposes must meet the conditions placed in the permit. For periodic monitoring, reports should meet the requirements outlined in the MCERTS performance standard for organisations carrying out manual stack-emission monitoring.

**3.4.2 Calculating concentration and mass emissions**

Permits require results to be reported as concentrations or mass emission rates (see Box 3.2).

**Box 3.2 Calculation of concentrations and mass emissions**

To calculate a concentration, the mass of the substance collected during sampling is divided by the volume of stack gas sampled.

$$\text{Concentration} = \frac{\text{mass of substance}}{\text{sample volume}}$$

To convert a concentration to a mass emission, it is necessary to know the volume flow rate of gas discharged from the stack.

$$\text{Stack gas volume flow rate (m}^3 \text{ s}^{-1}\text{)} = \text{velocity of stack gas (m s}^{-1}\text{)} \times \text{cross-sectional area of stack (m}^2\text{)}$$

$$\text{Mass emission rate (mg s}^{-1}\text{)} = \text{concentration measured (mg m}^{-3}\text{)} \times \text{stack gas volume flow rate (m}^3 \text{ s}^{-1}\text{)}$$

$$\text{Mass emissions (mg)} = \text{Mass emission rate (mg s}^{-1}\text{)} \times \text{time period (s)}$$

Note 1: volume flow rate and concentration must be at the same reference conditions (see section 3.44).

Note 2: measurement uncertainties are not subtracted from mass emission results.

Normally, when continuous monitoring is used the half-hourly or hourly mass emission is calculated from the half-hourly or hourly average concentration and the average stack gas volume flow rate. The concentration and flow rate should be at the same reference conditions. These values can be summed over longer periods, such as, monthly or annually. Larger mass units, such as kg, tonnes or kilotonnes, are used for these longer time periods.

For combustion plants that do not have continuous monitoring (typically < 100 MW), the annual total stack gas volume can be calculated from annual fuel consumption (see Annex E of EN ISO 16911-1 – velocity and volume flow rate). The annual mass emission is determined from the annual average measured pollutant concentration multiplied by the annual stack gas volume. It is good practice to verify the calculation by measuring the stack gas volume flow rate using either a velocity or tracer injection method, according to EN ISO 16911-1.

**3.4.3 Converting results from parts per million to mg m<sup>-3</sup>**

Monitoring results can be expressed either in volumetric or in gravimetric units, ppm or mg m<sup>-3</sup>. Volumetric units have the advantage of being independent from temperature and pressure. Most calibration gases have concentration values given in ppm.

It is often necessary to convert results obtained as ppm to mg m<sup>-3</sup> to meet the conditions of permits or authorisations (see box 3.3).

**Box 3.3 Conversion of ppm to mg m<sup>-3</sup>**

To convert ppm to mg m<sup>-3</sup>, the following equation is required:

$$\text{Concentration (mg m}^{-3}\text{)} = \frac{\text{concentration (ppm)} \times \text{molecular weight (g)}}{\text{molar volume (l)}}$$

The molar volume is the volume occupied by one-gram mole of a gas at a specific temperature and pressure. The temperature and pressure that concentrations are usually reported at is 273K and 101.3 KPa. Under these conditions, the molar volume, for an ideal gas, is equal to 22.40 litres.

Concentration measurements must be reported to a standard set of conditions so that comparisons can be made with:

- emission limit values (ELVs);
- emission concentrations measured at different times on the same site;
- emission concentrations at different sites.

Only concentration measurements expressed as mass per unit volume, for example mg m<sup>-3</sup>, are affected by temperature pressure, moisture and oxygen concentration. Concentrations expressed as volume per unit volume, for example ppm, are unaffected by temperature and pressure. Mass emissions results, for example kg hr<sup>-1</sup>, are unaffected by temperature, pressure, oxygen and moisture levels.

The applicable reference conditions are specified in the authorisation or permit. Reference conditions are specified for temperature and pressure, and may also be set for moisture and oxygen content.

Concentration measurements are usually reported to 273 Kelvin (K) and 101.3 kilo Pascals (kPa). Since it is most unlikely that the concentrations, as measured, will be at these conditions, correction factors  $F_t$  and  $F_p$  for temperature and pressure respectively, need to be applied. These are described in Box 3.4.

**Box 3.4 Temperature and pressure corrections of mass per unit volume concentrations**

To convert the concentration as measured at a temperature of T K to the concentration at 273 K, multiply by  $F_t$  where

$$F_t = T/273$$

To convert the concentration as measured at a pressure of P kPa to the concentration at 101.3 kPa, multiply by  $F_p$  where

$$F_p = 101.3/P$$

For concentration measurements, P will be the pressure at the point where the sample volume is metered.

The level of water vapour and oxygen affects the as-measured concentration of a substance by adding to the volume that the mass of pollutant occupies. This is particularly relevant for

processes involving combustion, where oxygen will be consumed and water vapour produced during the combustion process.

The oxygen level can cause significant changes in measured concentrations. Many permits therefore require the concentration results to be expressed at a standard oxygen reference level. It is important that an oxygen reference level is set that is appropriate for the process. It should be based on the typical oxygen level of the process when it is running at normal conditions and the fuel type used. Different oxygen reference values are used for different fuels, for example 3 per cent for gas or liquid fuels, 6 per cent for solid fuels, 11 per cent for most incineration processes and 15% for gas turbines. However, some processes may be designed to run in an oxygen enriched atmosphere. Under these circumstances the results of the measured concentrations can be standardised at an oxygen content laid down by the competent authority reflecting the special circumstances of the individual case.

Moisture has a smaller, but still significant, effect and the correction is conventionally to zero moisture, that is, dry. The moisture content of the exhaust gas, H<sub>2</sub>O%, must be measured using an appropriate technique and method. Moisture and oxygen correction is described in Box 3.5.

#### **Box 3.5 Moisture and oxygen corrections**

Emissions of stack gases are often expressed on a dry gas basis, so that variation in the moisture of stack gas does not affect the assessment of the emissions.

To convert a concentration from wet gas to dry gas, the following is used:

Dry gas concentration = Wet gas concentration x 100 / (100 – H<sub>2</sub>O%)

To convert a concentration as measured to a concentration at reference oxygen level, multiply the concentration by F<sub>o</sub>, the correction factor for oxygen, given by:

$$F_o = \frac{21 - O_2\% \text{ reference}}{21 - O_2\% \text{ measured}}$$

The reference oxygen level will be specified in the authorisation, permit or process guidance

### **3.5 Access, facilities and services**

Access, facilities and services required will vary slightly from one approach to another and from one technique or type of equipment to another. However, all require:

- a safe means of access to, and a safe place of work at the sampling position
- a means of entry into the stack for sampling equipment
- sufficient space for the equipment and personnel
- essential services, for example, electricity, lighting and water

Reference should be made to TGN M1, which contains further details on such requirements. These factors may limit the choice of approach, technique, method and equipment.

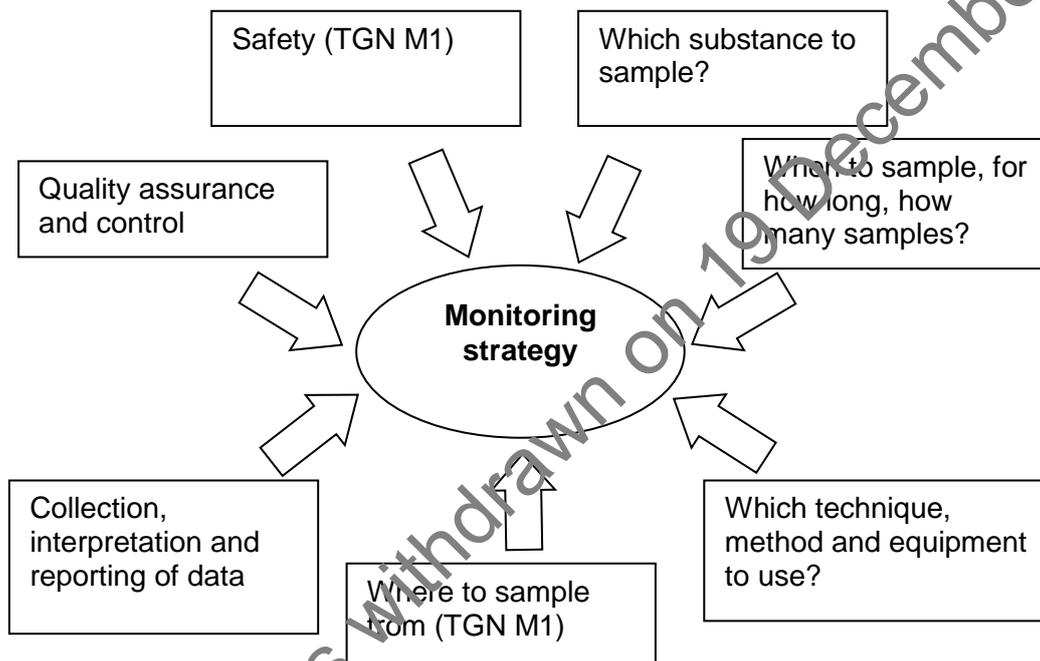
## 4. Monitoring strategy

### 4.1 General considerations

#### 4.1.1 The importance of a monitoring strategy

A monitoring strategy specifies what, where, and when to sample, how long to sample for, how many samples to take and by which method (Figure 4.1). Even the most sophisticated monitoring programme can provide unsuitable data if sufficient care is not taken to define the monitoring strategy. Also, an effective quality assurance (QA)/quality control (QC) system is essential to ensure high-quality results and to eliminate invalid data.

**Figure 4.1 Main elements of a monitoring strategy**



#### 4.1.2 Site-specific protocols

For CEMs the monitoring strategy is likely to be in place for the long term. In contrast, organisations carrying out periodic monitoring should be reviewing monitoring strategies every time a monitoring campaign is carried out. The monitoring strategy for a periodic monitoring campaign must be documented in a site-specific protocol (SSP). The requirements for SSPs are given in the MCERTS performance standard for organisations carrying out stack-emission monitoring.

Where monitoring is proposed using CEMs, factors such as calibration and maintenance arrangements should be summarised by the operator in a documented protocol.

## 4.2 Which substance to measure?

### 4.2.1 Targeting the substance

This appears straightforward for regulatory monitoring; the substances will normally be those specified in the authorisation or permit. However, even when the substance has been specified, it may still be necessary to consider what precise form of the substance should be measured.

### 4.2.2 Different phases

Particulates are sampled by extracting flue gas from a stack and collecting the material on a filter. When sampling for a gas, the sample is extracted and the required substance is collected into a solution, or absorbed onto a solid adsorbent, for example, activated carbon for volatile organic components (VOCs).

Some substances exist simultaneously in both gaseous and particulate phases. There are examples of this with both organic pollutants, such as polyaromatic hydrocarbons (PAHs), and inorganic pollutants, such as mercury. The monitoring method needs to be able to sample the selected phase or both phases, as appropriate. For example, mercury is mainly present in gaseous form, but can also be found in particulate phase and in water droplets. Therefore, a manual method for the determination of the concentration of total mercury requires a filter for the particulate phase and a series of absorbers for the gas phase.

### 4.2.3 Total or speciated measurements

For certain pollutants it is common to express the concentration as the sum total of the individual species present, for example, total heavy metals or total organic carbon (TOC). Alternatively, some members of a group of pollutants may be especially important and may require specific determination, such as cadmium and mercury. Similar to this concept is sampling for a particular physical fraction of particulate matter, such as particles less than 10µm in diameter (known as PM<sub>10</sub>).

## 4.3 Number and duration of samples

### 4.3.1 General considerations

The following questions need to be considered:

- can continuous monitoring be carried out or is periodic sampling required?
- what will be the averaging period (often specified in EC Directives) over which an individual measurement is made, or the averaging period over which the data are to be expressed?
- how many samples should be taken?

When monitoring is for comparison with certain release limits, some of these parameters may already be specified in the authorisation or permit. In other cases, the decisions will need to be based on how the pollutant concentration is expected to vary with time and the characteristics of the monitoring methods available.

### 4.3.2 Continuous versus periodic approach; manual or automatic monitoring

CEMs, supported by the appropriate checking and calibration (QA/QC) provide increased confidence for both regulatory purposes and process control.

However, periodic monitoring alone may be acceptable depending on the process or installation. For example, periodic monitoring is normally appropriate when sampling a batch process. A further choice then exists between carrying out periodic monitoring using automated instruments giving a real-time readout or manual monitoring giving a result averaged over the sampling period.

Generally, the more variable the emissions, the more frequently periodic monitoring is required. Where emissions levels vary so frequently and significantly that intermittent sampling would be unrepresentative, or would be required too frequently to be practicable, then sampling should be carried out using a continuous system, where available.

#### 4.3.3 Averaging periods and duration of sampling

The choice of a suitable averaging period is strongly influenced by the expected short-term variability in emission levels (concentrations and/or mass emissions) and whether such peaks are important. Also, the averaging period chosen must be consistent with the averaging period of the relevant release limit specified in the authorisation or permit, with which the data will be compared. For CEMs, the averaging time may be specified in legislation, such as IED.

It is important to recognise that a particular averaging period may limit the choice of measuring techniques and vice-versa. Some methods may be capable of operating only within a finite range of sampling averaging times. The points to consider differ between automated instrumental techniques and manual techniques.

Direct-reading analysers can provide vast quantities of data with a very fine time resolution. Selecting an appropriate averaging time is limited in principle only by the response time of the instrument. However, a minimum duration of at least half an hour or more per measurement would be expected. The minimum averaging time for a CEM to obtain so-called independent result is equal to at least four response times.

In contrast, the averaging time for a manual technique is often constrained by the need for a sampling run of appropriate duration (often half an hour or more). This is because manual techniques have an associated analytical end-method stage (for example, weighing of particulate samples), for which a sufficient mass of pollutant must be sampled to achieve an adequate limit of detection. For this reason, some standards specify that the sampling time is dependent on the expected concentration of the stack gas and the limit of detection and range of the analytical procedure used by the laboratory. It is therefore crucial that the sampling organisation considers the performance of the analytical end method when deciding on a suitable sampling time.

#### 4.3.4 Number of samples

CEM measurement standards describe in detail how to obtain a single valid periodic measurement. The decision on the number of samples required for compliance with environmental legislation is left to the regulatory authorities. However, the number of samples required when calibrating CEMs is specified in the European standard for Quality Assurance of CEMs (EN 14181). The number and duration of samples during a periodic monitoring campaign must be carefully considered. This is to ensure that a representative picture is obtained of the emission profile of the installation. In general, when measuring a stable emission best practice is to make a minimum of three measurements. In the case of unstable emissions, the number of samples should be increased. In the case of compliance

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\* The mass sampled is dependent on the pollutant flux to the sampler. The determining factor becomes the sampling time, since the sampling flow rate is constant or does not vary greatly.

monitoring for regulatory purposes, the number of individual measurements may be specified in the permit.

If a number of periodic measurements are taken during a sampling campaign (e.g. triplicate tests) these may be averaged to provide an overall result.

#### 4.4 Field blanks for manual sampling

Field blanks are an important part of quality control in manual sampling, as they are used to ensure that no significant contamination has occurred during the measurement. This includes the equipment preparation, transport and installation on-site, as well as the subsequent analytical work in the laboratory.

CEN methods and our Method Implementation Documents specify minimum requirements to carry out field blanks as part of a series of measurements. However, taking blanks more frequently than the minimum specified adds further confidence in the quality control of the measurements.

An overall blank is taken at the operator's site in an identical manner to the normal samples in the measurement series, except no gas is drawn through the sample train. The system is allowed to equilibrate to the temperature conditions that will be used for sampling. For all methods, with the exception of dioxins, PCBs, PAHs and speciated VOCs, the probe is placed in the stack for five minutes, with the nozzle at 180° to the direction of flow.

Generally, the field blank is acceptable if it does not exceed 10 per cent of the emission limit value (ELV).

When using CEN Standard methods, the field blank value obtained is not deducted from the sample result(s).

#### 4.5 Limit of detection of the method

A key aspect of stack emission monitoring is the Limit of Detection (LOD) of the method used, as the percentage uncertainty associated with a measurement increases the closer the result is to the LOD.

Some manual methods specify a LOD, in terms of a fixed percentage of the ELV (usually 10%). This provides a guide for selecting an appropriate sample time and helps minimise the uncertainty associated with a measurement result that is close to the ELV.

To ensure that the LOD of the method is met, monitoring organisations must liaise with the analytical laboratory to determine the detection limit of the analytical method. It is then possible, using an estimate of the expected concentration of the monitored substance in the stack gas, to calculate the sampling time required to ensure that the LOD of the sampling method is met.

#### 4.6 Instrument certified ranges

MCERTS provides criteria for selecting CEMs based on certified ranges. In general, the lower the certified range, the better the performance of the CEM is likely to be. This is because the majority of performance standards are expressed as a percentage of the range. A CEM is considered to have a suitable certified range when the certified range is less than 1.5x the daily average ELV for incineration processes and less than 2.5x the daily average ELV for large combustion plant and other types of process. More detailed guidance is available in TGN M20<sup>14</sup>.

In general, the certified range of the analyser for periodic instrumental techniques should be selected to ensure the MCERTS certified range is less than 1.5x the daily ELV for incineration processes and less than 2.5x the daily ELV for large combustion plant and other types of process. However, if a periodic instrumental technique is being used to calibrate a CEM it is important that the instrument has a certified range that is equal to or less than the CEM being calibrated. When periodic instruments are used on processes that do not have a daily ELV the MCERTS certified range should be less than 2.5x the periodic ELV.

#### **4.7 Instrument zero and span operations**

CEMs should be zeroed and spanned according to their maintenance requirements. Typically this should be carried out at intervals of seven days, unless the equipment can demonstrate stability over longer periods. The standard for calibration and quality assurance of CEMs, BS EN 14181 requires regular zero and span drift operations.

When checking the zero and span values of CEMs, the entire system is assessed to check the sampling system integrity. Other zero and span checks may also be carried out to check analyser drift, these checks may be done directly into the analyser.

Standard reference methods for periodic instrumental techniques provide information on zero and span operations. The span value may be set at a percentage of the instrument range or at the ELV. Also, when using instrumental techniques, the operator must zero and span the instruments to check they are working correctly and that they have not drifted during the monitoring period. The zero and span results should be reported with the measurement results. If the drift is greater than the allowable value permitted in the applicable standard method, the sampling should be repeated.

Gases used for calibration should be traceable to national standards. When carrying out multi-point calibrations, users should use gas dilution or blending systems that comply with the requirements of US EPA Method 205.

#### **4.8 Choice of monitoring technique and standard method**

##### **4.8.1 Fitness-for-purpose**

The following aspects of monitoring must be fit-for-purpose for the intended application:

- the monitoring approach
- the monitoring technique
- the monitoring method
- the monitoring equipment

The distinction between these aspects of monitoring is outlined in Box 4.1.

**Box 4.1 Monitoring terms used in this guidance**

**Monitoring approach** – whether monitoring is periodic or uses CEMs.

**Monitoring technique** – the analytical principle behind the monitoring, for example, infrared absorption, chemiluminescence, isokinetic sampling followed by gravimetry, sorbent tube followed by gas chromatography.

**Monitoring method** – the published or documented procedure for using the monitoring approach and technique, so that comparable results can be obtained when the monitoring is carried out at different times or by different organisations. Some standard monitoring methods specify the exact equipment that must be used, but many do not.

**Monitoring equipment** – the instruments and apparatus used for the measurement method and technique.

There is a wide choice of different sampling and analytical techniques, published methods and equipment that can be used to carry out stack-emissions measurements. This applies not only for different substances - in many cases it is possible to measure the same substance using completely different techniques, methods and equipment. It is important that each of these is chosen to be suitable for the application.

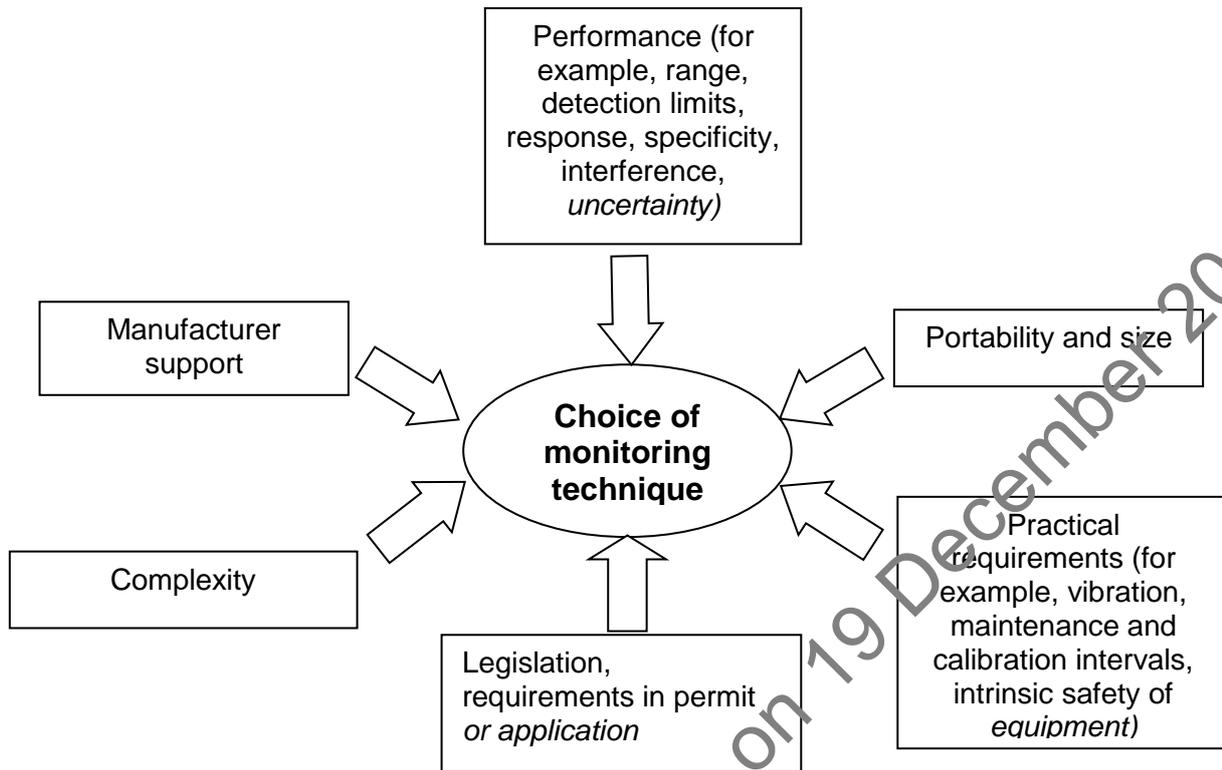
**4.8.2 Choice of monitoring technique**

This section is concerned with the general principles underlying selection of the measurement technique.

There are many techniques for measuring pollutant emissions. Each may have its own advantages or disadvantages in terms of performance and reliability. Terms used to characterise the performance of a method, such as range, response, drift, etc. are defined in MCERTS Performance Standards for Continuous Emission Monitoring Systems<sup>15</sup>.

Selecting a suitable monitoring technique requires careful consideration of these factors. The final choice of technique will also depend on the averaging period (discussed in Section 4.3.3) and some practical considerations, such as the portability of the equipment and its ease of operation. For periodic monitoring, the portability and size of equipment can limit the locations where they can be used. Also, most monitoring equipment requires an electrical supply at the monitoring point, although some battery-powered monitors do exist. These factors are summarised in Figure 4.2.

It is important to note that for demonstrating compliance with regulatory monitoring requirements, the standard method is likely to be specified in an operator's permit.

**Figure 4.2 Important considerations when choosing the monitoring technique**

#### 4.8.3 Selection of standard methods

Standards developed by different organisations vary in the degree of validation work carried out as part of their development. Standards developed and published by CEN are generally accepted as being most suitable and are referred to as reference methods (RM). However, other standards are still important, as there are substances that are not covered by CEN standards.

The choice of the method is often dictated by the requirements of a relevant EC directive, where, for example, the use of the relevant CEN standards is mandatory. If the standard is not dictated by mandatory requirements, then monitoring standards should be used in the following order of priority as given in the European IPPC Bureau's Reference Document on the General Principles of Monitoring:

- Comité Européen de Normalisation (CEN)
- International Standardisation Organisation (ISO)

An alternative method (AM) can be used provided the user can demonstrate equivalence to the RM by using EN 14793<sup>16</sup>. For example, CEN TS 17021<sup>17</sup> describes an AM for measuring SO<sub>2</sub>. The RM for measuring emissions of SO<sub>2</sub> is a manual method which employs wet chemistry. However, test laboratories may use an AM, as long as the test laboratory can demonstrate that the AM produces results of an equivalent quality to the RM.

AMs, such as CEN TS 17021, may be used for compliance assessment monitoring and calibration of CEMs for installations falling under EPR.

If the substance cannot be monitored using standards covered by the above, a method can be selected from the following:

- American Society for Testing and Materials (ASTM)
- British Standards Institution (BSI)\*\*
- United States Environmental Protection Agency (US EPA)
- Verein Deutscher Ingenieure (VDI)

If the substance cannot be monitored using standards covered by the above, then the following occupational methods may be adapted, following the requirements of ISO 17025, for stack emission monitoring:

- Method for the Determination of Hazardous Substances (MDHS) series published by the Health and Safety Executive (HSE)
- National Institute of Occupational Safety and Health (NIOSH)
- Occupational Safety and Health Administration (OSHA)

Under most circumstances, the methods detailed in Part 2 of this TGN should be used. However, it is important that the intended application of the method is taken into account. For example, a well validated method may be less suitable than another less rigorously validated method if the application is not one for which the method was developed.

A monitoring technique that is not covered by the above standards is the use of indicating detection tubes. These change colour due to a reaction with the tube contents and the substance being sampled. Detection tubes can be used for a wide variety of substances and may be useful if a process requires frequent (for example, hourly or daily) monitoring to ensure process requirements, such as the operation of an abatement system. However, the results obtained are semi-quantitative because a subjective decision is required to estimate changes in colour.

#### 4.9 Collection and reporting of data and process conditions

##### 4.9.1 Data collection

The means by which results are obtained from the monitoring equipment depends very much on the type of technique and equipment being used. Many manual monitoring techniques have an analytical end-method stage that is separate from the sampling stage. In such cases, supporting raw data will come from the on-site sampling. Site notes of relevant data, for example sample volumes, should be recorded on the appropriate forms on-site for inclusion in the raw-data section of the final results report. Data from the analysis stage will be provided later by a laboratory.

In contrast to most manual techniques, instrument-based methods usually provide real-time data, which must be recorded for immediate or later interpretation and reporting. This applies to CEMs and instruments used periodically. The data may be stored on site using a variety of systems, ranging from a simple chart recorder to automatic data loggers able to communicate with a remote central processing unit.

##### 4.9.2 Process conditions

The MCERTS performance standard for organisations specifies that, before an organisation carries out sampling at a site for the first time, a site review must be undertaken to ascertain the process conditions of the facility (for example, material balance, feedstock details, percentage load). This information should be collated to form part of the site-specific protocol, which details the process conditions under which sampling should occur. The

\*\* When a CEN method is published, BSI must adopt it and any equivalent BSI method must be withdrawn. ISO methods may also be adopted by BSI, although this is not a mandatory requirement.

process conditions during the sampling exercise must be recorded to ensure that they are the same as those specified in the site-specific protocol.

#### 4.10 Measurement uncertainty

##### 4.10.1 What is measurement uncertainty?

Measurement uncertainty quantifies the dispersion around the true value inherent in a measurement result. The uncertainty assigned to a result represents the range of values about the result in which the true value is expected to lie. It should be stressed that this true value is a conceptual term, which can never be exactly determined. All measurements have associated uncertainty; the goal is to quantify this uncertainty, so that the results can be properly interpreted. In the case of many stack measurements, it is also necessary to show that the measurement is fit for purpose, by demonstrating that the uncertainty of the measurements is within certain criteria. The statement of uncertainty includes a value for the level of confidence. This quantifies the probability that the true value lies within the region defined by the confidence interval. The measurement uncertainty defines the size of the region in which the true value is expected to lie, and the confidence interval defines how likely this is.

Consider the following measurement result with its associated uncertainty, NO<sub>2</sub> concentration =  $45 \pm 4 \text{ mg m}^{-3}$ .

The nature of the factors contributing to the uncertainty is such that it is not justifiable to say the concentration is certain to be in the range 41 to 49 mg m<sup>-3</sup>. However if the uncertainty of 4 mg m<sup>-3</sup> was calculated with a level of confidence of 95% then it can be assumed that 95 times out of 100 the result would be within those bounds. This enables regulatory bodies to interpret measurements and their uncertainties with respect to limit values and issues regarding demonstration of compliance.

There are other concepts which are important in understanding uncertainty. These include the concept of random and systematic sources of uncertainty:

- random sources of uncertainty are those which change between successive measurements in a random manner, over the period of measurements. The influence of random sources of uncertainty can be reduced by taking multiple measurements and averaging the results. The random component of a measurement uncertainty is sometimes referred to as the precision of the method used;
- systematic uncertainty sources are those that remain unchanged during the period of measurements. Increasing the number of measurements does not necessarily reduce the effects of these sources of uncertainty. The effect of systematic uncertainties on a measurement result is sometimes referred to as the 'bias' of the method used.

Another term that may be encountered, but is no longer commonly used, is 'accuracy'. The term was used in a number of early ISO standards as a measure of the agreement between a method and the assumed true value. Current ISO guidance suggests that accuracy is not a quantitative term.

The terms repeatability and reproducibility may also be encountered as properties of a measurement method. Repeatability refers to the random variations observed when an analyst in a single laboratory carries out a measurement. Reproducibility is the random variations seen between the results of different laboratories or analysts. These methods of

describing uncertainty do not apply to CEMs, though they may still be encountered in manual stack sampling methods.

#### 4.10.2 Procedure for the calculation of uncertainty

There are a number of sources of measurement uncertainty associated with any particular measurement, and the goal in calculating the uncertainty is to account for and quantify the effect of all significant sources. A generic approach to uncertainty calculation is described in the Guide to the Expression of Uncertainty in Measurement<sup>18</sup> (GUM). This document describes a procedure in which individual uncertainty sources are identified, quantified and combined to provide the measurement uncertainty. This philosophy has been adopted as the underpinning approach within the European and International standardisation bodies and will be used in standardised measurement methods. This approach is often described as a bottom-up approach. There is another technique for determining the uncertainty of a measurement, which is to repeat the measurement a number of times, compare with a SRM, and examine the spread of the results, known as a top-down approach. This has often been used to characterise measurement methods, by performing large-scale inter-laboratory studies to determine the repeatability and reproducibility of methods.

It is sometimes assumed that these two approaches are mutually exclusive. However, if the GUM approach is followed it is possible to include all significant component uncertainties. Additional uncertainty sources may be combined, for example those not covered in a method evaluation. The GUM approach should therefore be used as the most general method. The steps that should be taken are:

- review the measurement method and identify potential sources of uncertainty
- quantify the significant sources of uncertainty
- combine the uncertainty components and expand to give required level of confidence
- report the measurement uncertainty with the measurement result

#### 4.10.3 Determine potential sources of uncertainty

The first stage in determining the uncertainty of a measurement is to fully understand the method being followed to produce the final result. For example, is the measured quantity the concentration of the stack gas or a mass emission rate? It is important to consider all sources of uncertainty that may contribute to the final result, not just those which relate to the measurement of gas concentration.

All factors which may cause the result to be affected should be identified as potential sources of uncertainty. It should be noted however that process variability is not a contributing factor to measurement uncertainty.

Some sources of uncertainty may be controlled, or corrected for, as a part of the measurement procedure. For example, an instrument which is affected by changes in atmospheric pressure may be calibrated frequently enough that ambient pressure changes are accounted for. However, such sources must be included until they can be shown to be insignificant.

#### 4.10.4 Quantify the significant uncertainty sources

In many cases, what is known about the uncertainty source is the variation of an influence factor, for example the stack gas temperature or the range of an interferent gas in the stack. In these cases it is necessary to determine the sensitivity of the measurement to the influence and derive the sensitivity coefficient, usually by experiment. In stack emission

monitoring these can be obtained from MCERTS testing of CEMs or from data published in SRMs. The uncertainty contribution of such influences is then calculated from variation of the influence quantity multiplied by the sensitivity coefficient. It is generally assumed best practice, that where it is possible to correct for such an influence, for example by measuring temperature on-line, then the result should be corrected. In such cases there will still be a (smaller) uncertainty contribution due to measuring and applying the correction.

A review of the potential uncertainty sources should be carried out to identify any sources of uncertainty that are insignificant. These may be discounted from further evaluation. It is generally assumed that any uncertainty source which contributes less than 10% of the largest uncertainty source can be discounted.

Where a standard method provides information on the uncertainty of the results and is being followed exactly, then the uncertainties given in the standard may be quoted directly. In other cases additional sources of uncertainty, for example those due to flow measurements used to convert results to stack emission rates, or those due to variations from the method, must be determined in addition to the quoted uncertainty of the method.

In some cases the measuring instrument is calibrated against a SRM on site. The uncertainties due to the SRM and the calibration procedure should be used to determine the uncertainty of the results.

The individual uncertainties should be expressed as standard uncertainties or variances. The procedures used to do this are described in GUM. Guidance has also been published on estimation of uncertainty for analytical measurements in general<sup>19,20</sup> and for stack emission monitoring specifically<sup>21</sup>. The ISO standard ISO14956<sup>22</sup> provides a procedure for calculating the uncertainty of instrumental measurement methods based on performance characteristics. For CEMs these can be obtained from MCERTS testing.

Two terms are used in GUM to describe how uncertainty sources are evaluated, Type A and Type B. These terms are often wrongly thought of as the random and systematic terms respectively. This is not the case: GUM merely distinguishes between uncertainties which are derived from statistical analysis (the variance) of repeated measurements (Type A) and those derived by other means. In stack monitoring we do not always have repeated measurements and many sources of uncertainty are Type B. GUM describes how to calculate the standard uncertainties for both types. It should also be noted that there is no difference in the way the standard uncertainties derived from Type A and Type B terms are subsequently treated in the calculation of the combined measurement uncertainty.

#### 4.10.5 Calculating the measurement uncertainty

The standard uncertainties are combined as the root sum of squares to derive the combined standard uncertainty. All standard uncertainties are combined in the same way, whether they are due to uncertainty sources which are, Type A or Type B and random or systematic. Strictly speaking, if any sources of uncertainty are not independent - i.e. if the value of one uncertainty source is correlated to another - then additional terms should be included in the summation. GUM describes how such covariance terms should be derived. However, in practice such terms are usually not required. ISO 14956 provides a technique for accounting for correlation that may be expected between interfering gases present in the stack. The combined standard uncertainty is then multiplied by a coverage factor (generally known as  $k$ ) to provide the required level of confidence in the uncertainty estimation. A level of confidence of 95% is usually required, and in most cases a coverage factor of  $k = 2$  is used. GUM provides procedures to determine the value of  $k$ .

Some approaches to estimating uncertainty or components of uncertainty in practice are:

- repeat measurements using reference materials; this does not cover the effects of influences not present during these measurements (for example stack gas conditions, sampling losses) and these must be separately determined
- experimental work (for example, repeatability experiments, paired comparisons and ring tests)
- estimation based on previous results/data (for example, instrument manufacturers' specifications, calibration data, proficiency-testing schemes)

Where previous work, and in particular standard methods, are used to provide uncertainty estimates, care must be taken to be aware of what conditions the uncertainty estimate is appropriate for, and what aspects of the measurement are covered. For example, standard methods may quote "internal uncertainty" and "external uncertainty", which correspond to repeatability and reproducibility, respectively. These measures were determined under particular conditions, and may be applicable if similar conditions are present during subsequent measurements. If the method has been followed exactly then these values from the standard may be included in an uncertainty determination. It should be recognised, however, that these parameters do not necessarily include all the potential influence factors and other sources of uncertainty that may be present under stack conditions. It is therefore recommended that users carry out an uncertainty estimation for the specific measurement.

Further information on the calculation of measurement uncertainties, including an example calculation, is provided in Section 6 of this TGN.

#### 4.10.6 Non compliant sampling locations

In some circumstances, following the requirements of isokinetic methods (i.e. those which require sampling at multiple points in a stack) can be difficult due to a number of factors related to the sample location:

- limited access to the required number of sample lines
- limited access to sample points, which may restrict the number of points that can be used
- poor positioning of the sample plane, which may result in the flow criteria not being met

Unfortunately, it is not possible to quantify the effects of these factors on the uncertainty of the measurement and this means they cannot be taken into account when reporting the results (i.e. the reported uncertainty is based on the measurement method only and does not take account of the fact that the sampling location does not comply with the standard). The only practical option in these cases is to include qualifying remarks in the monitoring report, stating the deviations from the isokinetic method due to the non-compliant sampling location, and make clear in the report that the results were not produced in full compliance with the method.

#### 4.11 Quality assurance of CEMs

When selecting and installing CEMs, the operator must ensure that, wherever possible, the equipment is MCERTS certified at an appropriate range for their application.

Once a CEM has been installed, it must be checked for functionality and its performance verified. Typical performance checks include:

- leak test
- response time
- linearity
- interference, particularly any substances which could cause bias
- zero and span drift
- comparison with a reference method

European standard, EN14181, Stationary source emissions - Quality assurance of automated measuring systems, requires operators to check for functionality and verify performance of the CEMs. This standard consists of three quality assurance levels (QAL) and an annual surveillance check:

- QAL1: A procedure to demonstrate that the CEM is suitable for the intended purpose before installation, by meeting required performance standards and the uncertainty budgets specified in EU Directives.
- QAL2: quality assurance of installation: this includes a selection of performance tests, functionality checks and a comparison of the CEMs measurements against a reference method with a known uncertainty. The latter includes 15 or more repetitions of the reference method, in order to calculate a calibration function by linear regression. QAL2 therefore specifies a statistical technique to determine the total expanded uncertainty of the CEM. This should be used to determine compliance with the specified allowable uncertainty budget for a 95% confidence interval as specified in directives, such as the revised large combustion plant directive.
- QAL3: determination of a periodic zero, span drift and precision.
- AST: this is a simplified QAL2 check, using 5 or more repetitions of the reference tests to check the continuing validity of the calibration function.

EN 14181 was developed to implement requirements of applicable directives, such as WID and LCPD. Therefore, it is a mandatory requirement for waste incinerators and large combustion plants regulated by the IED. Further guidance is available in TGN M20.

#### 4.12 Quality assurance of predictive emissions monitoring systems

A predictive emissions monitoring system (PEMs) predicts real time emissions levels from a model based on previous stack emission results. This provides an alternative to carrying out ongoing stack emissions measurements.

PEMs use a model to correlate process parameters to stack emission results. A well developed model is based on being able to vary the process while recording process parameters and emissions results.

The reliability of PEMs is based on the assumptions made in developing the model remaining valid during the ongoing operation of the process.

PEMs need to be verified by parallel reference testing - the emissions must be measured using MCERTS accredited measurements over a range of load points. The procedure applied should follow similar general principles to those used during QAL2 of EN 14181. To date, the evidence from field experience is the use of PEMs can be a valid approach for predicting emissions of NO<sub>x</sub>, especially for smaller gas turbines, such as those below 20MW, although PEMs have been used successfully on larger gas turbines. The evidence

for other types of installations and determinands is limited. However, as stated above, PEMs on all installations need to be proven and validated.

#### **4.13 Reporting**

For periodic monitoring, reporting must be carried out in accordance with requirements detailed in the MCERTS performance standards for organisations undertaking stack-emission monitoring.

#### **4.14 Safety**

There are many hazards associated with carrying out stack emission monitoring on site. Some common hazards encountered during stack emission monitoring are described in TGN M1 and reference should be made to that document.

This document was withdrawn on 19 December 2019.

## 5. How to use the index of monitoring techniques and methods

### 5.1 Layout of the index of monitoring techniques and methods

The following index of monitoring techniques and methods has been structured to enable a user to determine an appropriate technique or monitoring method. It is split into three sections:

- Section 1: Continuous Emissions Monitoring systems (CEMs)
- Section 2: Periodic monitoring standards
- Section 3: Automatic batch samplers

Typically the user will be aware of what substance requires sampling, but will need guidance on the technique, equipment and method to use. Accordingly, the index is classified by substance in alphabetical order.

A number of abbreviations are used in the index. To assist the user, a list of abbreviations is provided in Section 6.

### 5.2 Information given in the index of techniques and monitoring methods

The index states for key substances (that is, those most routinely monitored for regulatory purposes) which methods are generally acceptable for regulatory monitoring. Where a CEN or ISO method is unavailable, a national method, if available, has been included. The national method selected is one that is commonly used in the UK.

Some comment is made on the applications and limitations of each method. Where information is available, the performance characteristics of the methods have been provided.

It is important for the user to be aware that, historically, performance characteristics have been quoted in published methods in various ways (for example, accuracy, precision, repeatability, reproducibility, uncertainty, error and the like). Many of these are not comparable with each other and are not necessarily compatible with current definitions. Therefore, such performance characteristics should be accepted with caution for all but the most recent, validated, standard methods. Also, uncertainty estimates quoted here are for guidance only – monitoring organisations must produce their own uncertainty estimate for the method under the particular conditions of test.

### 5.3 Method implementation documents

Standards may contain various options and approaches, as well as potential ambiguities. Method implementation documents (MIDs) have been produced for several standards to ensure they are applied consistently. If a MID has been produced it is included in the index alongside the relevant standard.

### 5.4 Use of MCERTS certified instruments

The MCERTS performance standards for CEMs apply the requirements of BS EN 15267-3<sup>23</sup>. When selecting a CEM, operators must, wherever possible, choose an MCERTS certified instrument with an appropriate certified range and scope of application.

If a certified CEM is unavailable for the substance to be monitored, or for the scope of application required, then the decision on the appropriate instrument is currently left to the user's judgement.

Some MCERTS certified CEMs are classed as transportable instruments. These are designed to perform to the same high standard as CEMs and hence are used for manual stack emission monitoring activities, such as compliance monitoring and calibrating CEMs. The extensive testing under MCERTS provides evidence that the instrument complies with the relevant European monitoring standards. Therefore, an MCERTS certified transportable instrument with an appropriate certified range will meet the minimum performance standards specified by the relevant European monitoring standard. This also applies even if the instrument has a different measurement technique to the standard reference method, as it can be used as an alternative method to the standard reference method.

BS EN 15267-4<sup>24</sup> is a European standard that specifies the performance criteria and test procedures for performance testing of transportable automated measuring systems used for periodic manual measurements. EN 15267-4 will supersede the requirements for transportable systems, currently described in Annex F of MCERTS for CEMs.

The MCERTS performance standards for portable monitoring systems contains the performance requirements for portable emission monitoring systems. These instruments are lightweight, battery powered instruments, which are used to make measurements in a wide variety of applications, such as for example fugitive emissions and gaseous releases from landfill bore-holes. For stack emission monitoring they may be used for indicative purposes.

### 5.5 Overarching standards

The index of techniques and monitoring methods contains substance specific standards for periodic stack emissions monitoring. Besides these substances specific standards contained in the index there are also overarching standards for periodic and continuous monitoring that are not listed in the index.

European standard, EN15259<sup>25</sup>, is an overarching standard that is to be used in conjunction with periodic substance specific reference methods. It provides generic principles on the following:

- a) locating suitable measurement sites and sections
- b) planning and reporting of stack emission measurements
- c) taking representative samples of stack emissions

European standard, EN 14181, is an overarching standard for continuous stack emissions monitoring. It was developed for LCP and waste incineration installations that fall under the remit of IED. EN 14181 is not substance specific but may be supplemented by substance specific standards, such as BS EN 13284-2 for measuring particulate matter.

## Index of monitoring methods and techniques

### Section 1: Continuous Emissions Monitoring systems (CEMs)

Table S1.1 CEMs

Substance	Type of CEMs	Monitoring technique	Further information
Aldehydes	In situ	DOAS	A system can be set up to measure acetaldehyde, propionaldehyde and formaldehyde. Typical range up to 1,000 mg m <sup>-3</sup> . Typical LOD approx. 1 mg m <sup>-3</sup> .
	Extractive	FTIR	
Amines and amides	Extractive	Continuous ion-mobility spectrometer	Able to separate and analyse specific amines. LOD down as far as 5 ppb. Not in widespread use in UK.
		FTIR	Able to separate and analyse specific amines.
Ammonia	In situ	NDIR	Applicable to gas-phase NH <sub>3</sub> . Typical range 0-100 ppm. Typical LOD 0.25-1 ppm.
		DOAS	Applicable to gas-phase NH <sub>3</sub> . Typical range up to 1,000 mg m <sup>-3</sup> . Typical LOD <0.5 mg m <sup>-3</sup>
		IMS	Applicable to gas-phase NH <sub>3</sub> .
		TDL	Applicable to gas-phase NH <sub>3</sub> .
	Extractive	NDIR	Applicable to gas-phase NH <sub>3</sub> . Main interference from NO <sub>x</sub> , amines and amides. Typical range up to 100 ppm. Typical LOD 0.25-1 ppm.
		FTIR	Applicable to gas-phase NH <sub>3</sub> . Reduced interference compared to NDIR. Typical range up to 500 mg m <sup>-3</sup> .
		NDUV	Applicable to gas-phase NH <sub>3</sub> . Main interference is SO <sub>2</sub> . Typical range up to 1,000 ppm. Typical LOD 0.25-1 ppm.
		Chemiluminescence with catalytic reduction	Gives simultaneous readout of NO <sub>x</sub> and NH <sub>3</sub> by cycling between converted and unconverted signal. Typical range up to 100 ppm. Typical LOD 1 ppm.
		Continuous-flow analysers using electrochemical detection	Suitable only for steady emissions with no transient peaks. Slow response (typically 5 minutes). Typical uncertainty ±5% claimed.
Carbon dioxide	In situ	NDIR	CO is a positive cross interferent. Methane also interferes.
		DOAS	Simultaneous monitoring of CO <sub>2</sub> along with many other pollutants. Range up to 100%, LOD approx. 0.1% by volume.
	Extractive	NDIR	Interference from CO, water, methane and ethane.
		FTIR	Simultaneous monitoring of CO <sub>2</sub> along with many other pollutants. Faster response than NDIR. Typical range 0 to 35%.

Table S1.1 CEMs (continued)

Substance	Type of CEMs	Monitoring technique	Further information
<b>Carbon monoxide</b>	In situ	NDIR	Measurement of CO and CO <sub>2</sub> . CO <sub>2</sub> are positive cross interferents. Methane also interferes, primarily with CO <sub>2</sub> . LOD <3 mg m <sup>-3</sup>
		DOAS	Measurement of CO and CO <sub>2</sub> . Typical range up to 10,000 mg m <sup>-3</sup>
	Extractive	NDIR	Interference from water, methane and ethane
		Electrochemical cell	Requires appropriate conditioning and purging with clean air for sensor recovery
		FTIR	Measurement of CO and CO <sub>2</sub> . Wide range (typically up to 10,000 mg m <sup>-3</sup> ); short response times; low LODs. Reduced interferences compared to NDIR
<b>Carbon disulphide</b>	See hydrogen sulphide		
<b>Carbonyl sulphide</b>	See hydrogen sulphide		
<b>Carboxylic acids</b>	In situ	DOAS	System can be set up to measure formic, acetic, benzoic acids. Typical range up to 1,000 mg m <sup>-3</sup> . Typical LOD 1 mg m <sup>-3</sup>
	Extractive	FTIR	Used to measure carboxylic acids, such as methanoic acid (formic), ethanoic acid (acetic), propanoic acid (propionic) acrylic acid (prop-2-enoic)
<b>Cresols</b>	See phenols		
<b>Di-isocyanates</b>	See isocyanates		
<b>Gas velocity<sup>1</sup></b>	In situ	Dynamic pressure technique	Measures gas velocity. Uses probe with series of openings and pressure-sensing device
		Ultrasonic sensors and receivers	Gas velocity related to speed of pulsed sound waves. Interference from vibrations and turbulence
		Balance technique	Measure gas velocity. Force exerted by flow on probe element measured by strain gauge
		Tribo-electric	Measures gas velocity. Good agreement with Pitot tube demonstrated in combustion plants. Interference from moisture delete
		Thermal mass	Gas velocity related to energy required to keep a probe at temperature (wind chill effect). Good for low velocities. Limited temperature range

<sup>1</sup>BS EN 16911-2 is for the automatic determination of velocity and volume flow rates in ducts.

Table S1.1 CEMs (continued)

Substance	Type of CEMs	Monitoring technique	Further information
<b>Halogens and halides (excluding methods specific to monitoring HCl and HF)</b>	In situ	DOAS	Can measure gas-phase Cl <sub>2</sub> , HBr. Does not measure halide salts. For Cl <sub>2</sub> range 0-1,000 mg m <sup>-3</sup> , LOD 10 mg m <sup>-3</sup> .
	Extractive	NDIR	Does not measure halide salts or halogens. Interference from particulates, H <sub>2</sub> O, CO <sub>2</sub> and any other IR-absorbing components.
		FTIR	Reduced interference compared to NDIR and faster response. Measures gas phase only, not halide salts or halogens.
		IMS	Can measure gas-phase Cl <sub>2</sub> and HBr. Suitable for ppb levels.
		TDL	
		Continuous-flow analysers, based on IC, ISE etc	Instruments available for measuring gas-phase HBr and HI. Measures halides absorbed into collection solution. Interference from particulates, CO <sub>2</sub> , SO <sub>2</sub> , SO <sub>3</sub> , NO <sub>2</sub> and NH <sub>3</sub> . Require consumable reagents.
<b>Hydrogen chloride</b>	In situ	DOAS	Measures HCl, specifically, rather than total chlorides. Simultaneous monitoring of HCl along with many other pollutants. Measures gas-phase HCl only. Range up to 5000 mg m <sup>-3</sup> , LOD <1 mg m <sup>-3</sup> . Not suitable for the measurement of chlorides.
		TDL	
		NDIR	
	Extractive	NDIR	Measures HCl, specifically, rather than total chlorides. Measures gas phase HCl only. Interference from particulates, H <sub>2</sub> O, CO, CO <sub>2</sub> and any other IR-absorbing components.
		FTIR	Measures HCl, specifically, rather than total chlorides. Simultaneous monitoring of HCl along with many other pollutants. Faster response and fewer interferences than NDIR. Typical range up to 1000 mg m <sup>-3</sup> . Measures gas phase HCl only.
		Ion mobility spectrometry	LOD down to ppb levels
		Continuous-flow analysers, based on IC, ISE etc	Simultaneous monitoring of chloride expressed as HCl along with many other halides. Measures gas phase only. Not specific to HCl (also responds to chlorides). Interference from particulates, H <sub>2</sub> O, CO <sub>2</sub> , Cl <sub>2</sub> , SO <sub>2</sub> , SO <sub>3</sub> , NO <sub>2</sub> and NH <sub>3</sub> . Slow response time, require consumable reagents.

Table S1.1 CEMs (continued)

Substance	Type of CEMs	Monitoring technique	Further information
<b>Hydrogen cyanide</b>	Extractive	Continuous flow with ISE	Will measure total CN <sup>-</sup> species reaching the instrument. Typical analytical precision $\pm 4\%$ .
		Continuous-flow IC analyser	Will measure total CN <sup>-</sup> species reaching the instrument. Excellent detection limits and specificity. If monitoring HCN alone, it is essential that sample is filtered to remove CN <sup>-</sup> salts.
		Electrochemical cell	Low maintenance. Can also be mounted in situ. Limited cell life. Typical range 0-50 mg m <sup>-3</sup> . Strong interference from H <sub>2</sub> S and other sulphur species.
		FTIR	Applicable to gas-phase HCN. Simultaneous monitoring of several pollutants.
<b>Hydrogen fluoride</b>	In situ	DOAS	Can measure gas-phase HF. Does not measure fluoride salts. For HF, range is 0-1,000 mg m <sup>-3</sup> , LOD 0.2 mg m <sup>-3</sup> .
	Extractive	NDIR	Can measure gas-phase HF. Does not measure fluoride salts. Interference from particulates, H <sub>2</sub> O, CO <sub>2</sub> and any other IR-absorbing components.
		FTIR	Applicable to gas-phase HF. Reduced interference compared to NDIR and faster response. Does not measure fluoride salts.
		IMS	Can measure gas-phase HF. Suitable for ppb levels.
		TDL	Can measure gas-phase HF.
		Continuous-flow analysers, based on IC, ISE etc	Instruments available for measuring gas-phase HF. Measures halides absorbed into collection solution. Interference from particulates, CO <sub>2</sub> , SO <sub>2</sub> , SO <sub>3</sub> , NO <sub>2</sub> and NH <sub>3</sub> . Require consumable reagents.
<b>Hydrogen sulphide, total reduced sulphur (TRS) compounds, carbon disulphide, carbonyl sulphide</b>	In situ	DOAS	Can measure H <sub>2</sub> S, carbonyl sulphide (COS), carbon disulphide (CS <sub>2</sub> ) and methyl mercaptan. Typical range (CS <sub>2</sub> ) up to 1,000 mg m <sup>-3</sup> . LOD 10 mg m <sup>-3</sup> .
	Extractive	UV fluorescence analyser with scrubber and catalyst	Can measure H <sub>2</sub> S. Scrubber removes SO <sub>x</sub> , catalyst converts H <sub>2</sub> S passing through scrubber to SO <sub>2</sub> , which is detected. Typical LOD 0.5 ppb.
		FPD analyser with scrubber and catalyst	Can measure TRS. Need two instruments or two switching channels to give difference of total S by FPD and total reduced sulphur less SO <sub>x</sub> using FPD with scrubber.
		Electrochemical cell	Can measure H <sub>2</sub> S. Can also be mounted in the gas stream for an in-situ CEMs measurement. Typical range 0-500 ppm. Interference from HCN. Requires appropriate conditioning and purging with clean air for sensor recovery.
		Continuously sampling chromatographic S gas analyser	Able to separate and analyse H <sub>2</sub> S, SO <sub>2</sub> and organic sulphides. Typical LOD 2 ppb.

Table S1.1 CEMs (continued)

Substance	Type of CEMs	Monitoring technique	Further information
<b>Isocyanates</b>	Extractive	Continuous ion-mobility spectrometer	Able to separate and analyse specific di-isocyanates. LOD down as far as 5 ppb.
<b>Mercaptans (thiols)</b>	In situ	DOAS	Can measure mercaptans simultaneously with other pollutants. Typical range up to 1,000 mg m <sup>-3</sup> , LOD 1 mg m <sup>-3</sup> .
	Extractive	Continuously sampling chromatographic S gas analyser	Able to separate and analyse mercaptans, H <sub>2</sub> S, SO <sub>2</sub> and organic sulphides. LOD down to 2 ppb.
<b>Metals<sup>1</sup></b>	In situ	DOAS	Will measure many other pollutants simultaneously. For mercury vapour only. Range up to 1000 µg m <sup>-3</sup> , LOD <3 µg m <sup>-3</sup> .
	Extractive	Thermocatalytic reduction then UV absorption	Good LOD (<1 µg m <sup>-3</sup> ). For mercury vapour only. Range up to 1000 µg m <sup>-3</sup> .
		AFS	For total mercury. BS ISO 6978 Part 2 is for mercury in gaseous matrices. Specifically natural gas and stack gas.
<b>Moisture</b>	See water vapour		
<b>Nitrogen monoxide and nitrogen dioxide</b>	In situ	NDUV	Measurement of NO and NO <sub>2</sub> . The principal interference is from SO <sub>2</sub> .
		DOAS	Measurement of NO, NO <sub>2</sub> . Typical range up to 2,000 mg m <sup>-3</sup> , LOD <1 mg m <sup>-3</sup> .
		NDIR	Measurement of NO and NO <sub>2</sub> . Wide range (typical NO to 5,000 mg m <sup>-3</sup> , NO <sub>2</sub> to 5,000 mg m <sup>-3</sup> ); Main interference from particulates and H <sub>2</sub> O, which can be reduced by precise selection of wavelength. Not suitable for high-moisture gases.
	Extractive	NDUV	As above for in-situ CEMs.
		NDIR	As above for in-situ CEMs. Main interference from particulates and H <sub>2</sub> O, which can be removed by conditioning.
		Chemiluminescence	Measurement of NO and NO <sub>2</sub> . Very low LOD (typically 0.1 ppm); wide range (typically 0-10,000 ppm); short response (a few seconds). The principal interference is from CO <sub>2</sub> , H <sub>2</sub> O and NH <sub>3</sub> .
		Electrochemical	Measurement of NO and NO <sub>2</sub> typically up to 3,000 ppm and 500 ppm, respectively. Requires appropriate conditioning and purging with clean air for sensor recovery.
		NDIR	Measurement of N <sub>2</sub> O. Steps required to reduce potential interference effects of CO, CO <sub>2</sub> and moisture.
FTIR	Simultaneous monitoring with many other pollutants. Faster response and less interference than NDIR. Measurement of NO, NO <sub>2</sub> and N <sub>2</sub> O.		

<sup>1</sup>BS EN 14884 is for calibration of mercury CEMs. It is used in conjunction with BS EN 14181 and is applicable to installations under IED.

Table S1.1 CEMs (continued)

Substance	Type of CEMs	Monitoring technique	Further information
<b>Nitrous oxide (Dinitrogen monoxide)</b>	Extractive	NDIR	Measurement of N <sub>2</sub> O. Steps required to reduce potential interference effects of CO, CO <sub>2</sub> and moisture.
		FTIR	Simultaneous monitoring with many other pollutants. Faster response and less interference than NDIR.
<b>Oxygen</b>	In situ	Zirconium oxide film	Main interferences: hydrocarbons, CO.
	Extractive	Paramagnetic	Range 0-100% with typical resolution of 0.1%. Interference from high concentrations of NO <sub>2</sub> , NO and certain hydrocarbons.
		Electrochemical cell	Electrochemical cell can also be mounted in the gas stream for an in-situ CEMs measurement. Interference from SO <sub>2</sub> , NO <sub>x</sub> and acid gases. Requires appropriate conditioning and purging with clean air for sensor recovery.
		TDL	
<b>PAHs</b>	Extractive	Continuous, automatic isokinetic batch sampler	Integrated samples obtained over averaging periods ranging from 1 h to 30 days. Though sample is obtained continuously, results are not instantaneous: the filter and PUF cartridge are sent off for analysis.

Table S1.1 CEMs (continued)

Substance	Type of CEMs	Monitoring technique	Further information
Particulate matter <sup>1,2</sup>	In situ	Opacity meter or transmissometer	Opacity or smoke density measurements. Laser opacimeters have LOD down to 1 mg m <sup>-3</sup> . Does not measure mass of particulates directly. Concentration calibration factor dependent on particle size, composition, shape, colour and refractive index. Gives a measure of particulate concentration after calibration with gravimetric SRM. Typical range about 10 to 2000 mg m <sup>-3</sup> , not suitable for low concentration emissions.
		Tribo-electric probe	Can be used simply as an alarm indicator or as quantitative monitor. Claimed to be suitable for low particulate concentrations (LOD less than 1 mg m <sup>-3</sup> ). Tribo-electric response dependent on particle size, composition and moisture. Gives a measure of particulate concentration after calibration against SRM.
		Light scattering	Reported to be suitable for low particulate concentrations (LOD down to 1 mg m <sup>-3</sup> ). Gives a measure of particulate concentration, but only after calibration with SRM.
	Extractive	Beta-attenuation	Can be calibrated to give particulate concentration in mgm <sup>-3</sup> directly. Gives successive average readings over set sampling periods. Absorption coefficient is independent of particulate composition. Typical range about 2 to 2,000 mg m <sup>-3</sup> depending on sampling rate, frequency and integrating time.
		Extractive light-scattering	Suitable for low particulate concentrations. Extractive part of the system may retain particulates. Manufacturer's data: range 0-1000 mg m <sup>-3</sup> ; LOD 0.02 mg m <sup>-3</sup> ; reproducibility 0.5% FSD.

<sup>1</sup>BS EN 13284-2 is for calibration of particulate CEMs. It should be used in conjunction with BS EN 14181. It is applicable to large combustion plant and waste incineration installations under the IED. For other processes the ongoing quality assurance should follow the principles of EN 14181 (i.e. QAL2/AST and QAL3) but a reduced number of parallel measurements may be acceptable. The table below summarises this:

Spread of data (Spread > 15% of ELV)	Medium to high level cluster (emissions higher than 30% of daily average ELV)	Low-level cluster (emissions not more than 30% of daily average ELV; linear regression produces R <sup>2</sup> <0.9)
<ul style="list-style-type: none"> <li>Functional tests annually: linearity, response time, system integrity</li> <li>Verify CEMs read zero at zero emissions</li> <li>9+ SRM repetitions over 2+ days</li> <li>Calibration function plus statistical tests</li> </ul>	<ul style="list-style-type: none"> <li>Functional tests annually: linearity, response time, system integrity</li> <li>Verify CEMs read zero at zero emissions</li> <li>5 SRM repetitions over 1 day</li> <li>Average of SRM and CEM data to derive a calibration factor</li> </ul>	<ul style="list-style-type: none"> <li>Functional tests annually: linearity, response time, system integrity</li> <li>Verify CEMs read zero at zero emissions</li> <li>3 SRM repetitions over 1 day</li> <li>Calibrate with surrogates if possible; if not, then set the CEMs gain-factor to respond to process changes.</li> </ul>

<sup>2</sup>BS EN 15859 is for the certification of CEMs used to ensure that particulate abatement is working satisfactorily. It uses the term filter dust monitor to describe CEMs that can be calibrated in mass concentration units (e.g. mg/m<sup>3</sup>) and used for particulate arrestment control purposes. It also includes dust leakage monitors, which indicate a potential problem with a particulate arrestment plant by monitoring a change in the emissions levels or a change in the magnitude of the particulate pulses created by the cleaning process.

Table S1.1 CEMs (continued)

Substance	Type of CEMs	Monitoring technique	Further information
Particulate matter size fractionation	In situ	Light scattering	Light scattering systems can be configured to classify particulate numbers into size ranges. Gives a measure of particulate concentration, but after calibration with the SRM.
	Extractive	Photometric analyser	Low range. Suitable for low-range, large, wet processes. Range 0 – 40 mg m <sup>-3</sup> .
PCBs	Extractive	Continuous, automatic isokinetic batch sampler	Installed on some processes in Europe. Integrated samples obtained over averaging periods ranging from 1h to 30 days. Samples at multiple points along one sample line. Though sample is obtained continuously, results are not instantaneous: the filter and absorption media need to be sent off for analysis.
Phenols and cresols	In situ	DOAS	System can be used to measure phenol. Typical range up to 1,000 mg m <sup>-3</sup> . Typical LOD 1 mg m <sup>-3</sup> .
	Extractive	None in common use for phenols and cresols specifically	

Table S1.1 CEMs (continued)

Substance	Type of CEMs	Monitoring technique	Further information
<b>Sulphur dioxide</b>	In situ	NDUV	Low limit of detection. Wide linear response range. Short response times. Monitoring by NDUV is the most commonly encountered CEMs technique. The principal interference is from H <sub>2</sub> O and NO <sub>2</sub> .
		DOAS	Simultaneous monitoring of SO <sub>2</sub> along with many other pollutants. SO <sub>2</sub> range up to 2000 mg m <sup>-3</sup> , LOD <1 mg m <sup>-3</sup> .
		NDIR	Low limit of detection. Wide linear response range. Short response times. Common interference from particulates, H <sub>2</sub> O, CO, CO <sub>2</sub> , NO, NO <sub>2</sub> , SO <sub>3</sub> , unsaturated hydrocarbons, aromatic amines and nitro-compounds. Not suitable for ducts with high moisture content.
	Extractive	UV-fluorescence and UV-absorption	Particulates and H <sub>2</sub> O can be removed by conditioning, leaving NO <sub>2</sub> as the principal interferent.
		IR-absorption	Particulates and H <sub>2</sub> O can be removed by conditioning, leaving as the principal interferents CO, CO <sub>2</sub> , NO, NO <sub>2</sub> , SO <sub>3</sub> , unsaturated hydrocarbons, aromatic amines and nitro-compounds.
		Electrochemical	Typical range up to 5000 ppm. Can also be installed in situ in duct. Requires periodic purging with pure air for the sensor to recover. Removal of particulates and moisture is necessary to stop the condensation and dissociation of salts.
		FTIR	Simultaneous monitoring of many pollutants. Faster response and fewer interferences than NDIR.
<b>Sulphur trioxide and total sulphur</b>	Extractive	UV-fluorescence and UV-absorption	Measurement of SO <sub>2</sub> and other sulphur species using catalytic converters. Particulates and H <sub>2</sub> O can be removed by conditioning, leaving NO <sub>2</sub> as the principal interferent.
		Flame photometric	Measurement of total sulphur. Non-selective: measures total sulphur species and not specific to SO <sub>2</sub> . Main interferents H <sub>2</sub> O and SO <sub>3</sub> .
		Conductivity	Not in common use in the field. Non-selective. Interference from other sulphur species and any other ionic species.
		FTIR	Simultaneous monitoring of many pollutants.
<b>Thiols</b>	See mercaptans		
<b>Total cyanide</b>	See hydrogen cyanide		
<b>Total reduced sulphur</b>	See hydrogen sulphide		
<b>Total sulphur</b>	See sulphur trioxide		

Table S1.1 CEMs (continued)

Substance	Type of CEMs	Monitoring technique	Further information
<b>VOCs (total)</b>	Extractive	FID (low range)	Validated on waste incinerators. High specificity to VOCs. Developed for incinerators. Different response factor for each VOC species. Suitable for low ranges of VOC concentrations (0-20 mg m <sup>-3</sup> ). Interference from oxygen (reduced by mixed H <sub>2</sub> /He fuel).
		FID (high range)	Extensively validated for solvent processes. High specificity to VOCs. Different response factor for each VOC species. Suitable for VOC concentrations up to 500 mg m <sup>-3</sup> .
<b>VOCs (speciated)</b>	In situ	DOAS	Can measure certain specific organic compounds, e.g. benzene, toluene and xylene. Benzene typical range 0-1,000 mg m <sup>-3</sup> , LOD 1 mg m <sup>-3</sup> ; toluene typical range up to 1,000 mg m <sup>-3</sup> , LOD 0.5 mg m <sup>-3</sup> ; xylene typical range up to 1,000 mg m <sup>-3</sup> , LOD 1 mg m <sup>-3</sup> .
	Extractive	Continuously-cycling GC with appropriate detector (FID, ECD)	Can measure virtually any individual organic compounds, many simultaneously. Not truly continuous, but successive measurements in cycles of about 30 minutes. LOD typically 1 ppm.
		FTIR	Can measure many individual organic compounds simultaneously, with better specificity. LOD (at ppb level) and better response than NDIR.
		NDIR	Can measure many individual organic compounds, but only one at a time. Instrument must be set up specifically for the determinand of interest. Interferences from H <sub>2</sub> O and other species with overlapping spectra.
<b>Water vapour (moisture)</b>	In situ	NDIR	In widespread use. Interference from other IR absorbing species, e.g. CO, CO <sub>2</sub> hydrocarbons.
		DOAS	Simultaneous monitoring of H <sub>2</sub> O and other pollutants. Typical range 0-30%, LOD approx. 0.1% volume.
	Extractive	NDIR	Interference from CO, CO <sub>2</sub> , hydrocarbons.
		FTIR	Simultaneous monitoring of H <sub>2</sub> O and other species. Faster response than NDIR. Typical range 0 to 35%.
		Paramagnetic analysers	Range 0-100%, typical resolution 0.1%. H <sub>2</sub> O calculated from the difference between two analysers, one measuring O <sub>2</sub> wet and other dry. Not a direct measurement of moisture. Interferences from high concentration of NO <sub>2</sub> , NO and hydrocarbons.

**Section 2: Periodic monitoring standards****Table S2.1. Aldehydes**

Type of monitoring	Monitoring technique	Monitoring standard	Further information
Manual	None in common use for aldehydes specifically	Sampling BS CEN/TS 13649, analysis to NIOSH 2016 or NIOSH 2539 for aldehyde <sup>1</sup> screening	Moisture may restrict the use of a sorbent tube method. Under these circumstances it may be possible to adapt an impinger method.
	Isokinetic <sup>2</sup> extraction and impingement into water. Analysis by spectrophotometric determination of pararosaniline derivative	US EPA Method 316	Method specific to formaldehyde. Intended for the mineral fibres industry. Range 11.3 ppb to 23,000 ppm on a 0.85 m <sup>3</sup> sample. Interference from other aldehydes, sulphites and cyanides. Samples must be maintained / transported below 8°C.
Instrumental	Extractive sampling and portable FTIR analyser	TGN M22	

<sup>1</sup>US EPA Method 316 is the preferred method for measuring formaldehyde. However, for practical reasons (e.g. on very small ducts), it may be acceptable to measure formaldehyde using a method based on BS CEN/TS 13649. The reasons for using an alternative method must be explained in the SSP.

<sup>2</sup>Formaldehyde entrains in moisture droplets, so should be sampled isokinetically when in-stack moisture levels are above saturation for a given temperature. It is not necessary to sample isokinetically if the stack gas does not contain droplets.

Table S2.2 Amines and amides

Type of monitoring	Monitoring technique	Monitoring standard	Further information
Manual	Non-isokinetic sampling <sup>1</sup> and collection on silica gel tubes. Analysis by GC	Sampling BS CEN/TS 13649, NIOSH 2002 and NIOSH 2010 for analysis	Measures aromatic and aliphatic amines. For a 0.003 to 0.030 m <sup>3</sup> sample: range up to 60 mg m <sup>-3</sup> ; LOD 0.5 mg m <sup>-3</sup> . Stack gas must be dried before reaching the silica gel tubes
	FTIR analyser	TGN M22	Able to separate and analyse specific amines.

<sup>1</sup>Where both vapour-phase and particulate-phase/aerosol amines are to be measured, isokinetic sampling will be required following the main principles of, BS EN 13284-1.

Table S2.3. Ammonia

Type of monitoring	Monitoring technique	Monitoring standard	Further information
Manual	Non-isokinetic and isokinetic sampling and impingement into dilute H <sub>2</sub> SO <sub>4</sub> . Analysis by IC <sup>1</sup> .	Procedural requirements of BS EN 14791 for sampling	Will measure total NH <sub>3</sub> and NH <sub>4</sub> <sup>+</sup> species reaching the impinger. Interference from NH <sub>4</sub> <sup>+</sup> salts. Typical measurement uncertainty ±30%. Stainless steel is not a suitable probe material as it may result in losses of NH <sub>3</sub> .
Instrumental	Extractive sampling and FTIR analyser	TGN M22	Applicable to gas-phase NH <sub>3</sub> . Reduced interference compared to NDIR. Typical range up to 500 mg m <sup>-3</sup> .

<sup>1</sup> Ammonia may be analysed using IC

Table S2.4. Arsine

Type of monitoring	Monitoring technique	Monitoring standard	Further information
Manual	Extractive sampling onto sorbent, solvent extraction and analysis by AA with a graphite furnace.	Procedural requirements of BS CEN/TS 13649 for sampling and NIOSH 6001 for analysis.	The NIOSH method uses the same sorbent tube material as CEN/TS 13649 (a solid sorbent tube made of coconut shell charcoal). The working range is 0.001 to 0.2 mg/m <sup>3</sup> for a 10-L air sample. Other arsenic compounds (gases or aerosols) may be collected on the sampler and would be erroneously reported as arsine. A cellulose ester filter in front of the charcoal tube may be used to remove aerosols.

Benzene (see VOCs)

Table S2.5. Bioaerosols

Type of monitoring	Monitoring technique	Monitoring standard	Further information
Manual	Isokinetic sampling and impingement into saline solution. Analysis by serial dilution and cultivation onto agar plates followed by counting of visually recognisable colonies following cultivation.	VDI 4257 Blatt 2	<p>The method was validated on a dry process (intensive pig farm)<sup>1</sup>. An additional impinger may be added for processes with elevated moisture levels. If necessary the impinger and rinse solution can be filtered before analysis, so that the limit of detection is reduced. The standard defines several field blank pass criteria. A field blank is satisfactory if the agar plate value is not greater than 3 CFU/plate count.</p> <p>The culture and enumeration of samples must be carried out in accordance with Environment Agency TGN M9<sup>2</sup>.</p> <p>VDI 4257 part 2 assessed measurement uncertainty in terms of relative standard deviation based on 20 duplicate measurements. It states an uncertainty of 30% for bacteria and 23% for fungi. As a guideline these uncertainty values can be applied as follows:</p> <ul style="list-style-type: none"> <li>- 30% for total bacteria onto half strength nutrient agar</li> <li>- 23% for <i>Aspergillus fumigatus</i> cultured onto malt extract agar.</li> </ul>

<sup>1</sup> In the UK the method has been trialled on a mechanical and biological treatment plant for municipal and garden waste.

<sup>2</sup> EA TGN M9: Monitoring bioaerosols from regulated facilities is available from [www.mcerts.net](http://www.mcerts.net).

Table S2.6. Biomass (biogenic) and fossil derived carbon dioxide (ratio)

Type of monitoring	Monitoring technique	Monitoring standard	Further information
Manual method	Absorption of CO <sub>2</sub> in liquid and solid alkaline media or collection of gas in gas bags, canisters or gas bottles. Analysis by accelerator mass spectrometry, beta-ionization or liquid scintillation.	EN ISO 13833	Method for the determination of the ratio of biomass and fossil derived CO <sub>2</sub> in the CO <sub>2</sub> from stack gases. The method is based on measurement of radiocarbon ( <sup>14</sup> C isotope). The lower limit of application is a biogenic to total CO <sub>2</sub> fraction of 0.02. The working range is a biogenic to total CO <sub>2</sub> fraction of 0.02 to 1.0.
Instrumental method	Uses a mathematical model based on stack gas and fuel composition.	ISO 18466	Method for the determination of the biogenic fraction in CO <sub>2</sub> in stack gas. The method is used when: <ul style="list-style-type: none"> <li>- the elementary composition of moisture, ash free biomass and fossil matter in fuel used is known</li> <li>- online stack gas composition measurements (O<sub>2</sub> and CO<sub>2</sub>) are available at a high accuracy</li> </ul> Online modelling of the biomass fossil ratio enables the biomass ratio to be controlled and reported. The generated model data can be verified using radiocarbon ( <sup>14</sup> C) determined biomass fuel ratio. The results are complementary to the results obtained with ISO 13833.

Table S2.7. Carbon dioxide

Type of monitoring	Monitoring technique	Monitoring standard	Further information
Instrumental	NDIR analyser	ISO 12039 <sup>1</sup>	Interference from CO, water, methane and ethane.
	FTIR analyser	ISO 12039 / TGN M22	Simultaneous monitoring of CO <sub>2</sub> along with many other pollutants. Faster response than NDIR. Typical range 0 to 35%.

<sup>1</sup> ISO 12039 is a performance standard for automated emission- monitoring equipment. When the standard is applied to periodic stack-emission monitoring equipment, it should be supplemented by a set of work instructions addressing the sampling and quality control procedures.

Table S2.8. Carbon monoxide

Type of monitoring	Monitoring technique	Monitoring standard	Further information
Instrumental	Extractive sampling and NDIR analyser	BS EN 15058	Validated on waste incineration, co-incineration and large combustion installations. Range 0 to 400 mg m <sup>-3</sup> for LCP and 0 to 740 mg m <sup>-3</sup> waste incinerators. Overall uncertainty should be less than ± 6% of the daily ELV. Possible interference from water vapour, carbon dioxide, nitrous oxides and hydrocarbons.
	Extractive sampling and electrochemical cell	AM for BS EN 15058 <sup>1</sup>	
	Extractive sampling and FTIR analyser	AM for BS EN 15058 <sup>1</sup> /TGN M22	Measurement of CO and CO <sub>2</sub> . Low LODs; wide range (typically up to 10,000 mg m <sup>-3</sup> ); short response times. Reduced interferences compared to NDIR

<sup>1</sup> BS EN 15058 is a reference method based on using a NDIR analyser. An AM may be used provided the user can demonstrate equivalence to EN 14793 - "Intralaboratory procedure for an alternative method compared to a reference method", to the satisfaction of UKAS and the regulator. Further information is available in the MCERTS performance standard for organisations.

Table S2.9. Carbon disulphide

Type of monitoring	Monitoring technique	Monitoring standard	Further information
Manual	Non-isokinetic sampling and collection on charcoal sorbent tube. Analysis by GC	Procedural requirements of BS CEN/TS 13649 for sampling, NIOSH 1600 for analysis	Method for CS <sub>2</sub> . A drying tube is required as water vapour may cause interference
Instrumental	Portable GC with appropriate detector (GC-FID, GC-PID, GC-ECD)	US EPA Method 15	Method for carbon disulphide (CS <sub>2</sub> ). Range 0-1,000 ppm, LOD 0.5 ppm. CO, CO <sub>2</sub> and water vapour interfere.

Table S2.10. Carbonyl sulphide

Type of monitoring	Monitoring technique	Monitoring standard	Further information
Instrumental	Portable GC with appropriate detector (GC-FID, GC-PID, GC-ECD)	US EPA Method 15	Method for carbonyl sulphide (COS). Range 0-1,000 ppm, LOD 0.5 ppm. CO, CO <sub>2</sub> and water vapour interfere.
	Extractive sampling and FTIR analyser.	TGN M22	

Table S2.11. Carboxylic acids

Type of monitoring	Monitoring technique	Monitoring standard	Further information
Manual	Extractive sampling onto carbon sorbent. Solvent desorption by formic acid, analysis by GC-FID	Sampling BS CEN/TS 13649, NIOSH 1603 for analysis	Method for acetic acid only. For other carboxylic acids, use appropriate occupational hygiene or HSE methods. Typical LOD 5 mg m <sup>-3</sup> . Typical range up to 100 mg m <sup>-3</sup> . Precision of analysis ±6%.
Instrumental	Extractive sampling and FTIR analyser	TGN M22	Used to measure carboxylic acids, such as methanoic acid (formic), ethanoic acid (acetic), propanoic acid (propionic) acrylic acid (prop-2-enoic).

**Chromium (VI)** (see metals)

**Cresols** (see phenols)

**Diisocyanates** (see isocyanates)

Table S2.12. Dioxins and furans

Type of monitoring	Monitoring technique	Monitoring standard	Further information
Manual	Isokinetic sampling , extraction, then GC-MS analysis	BS EN 1948: Parts 1,2 and 3 <sup>1</sup> and MID	A standard reference method validated on waste incinerators. Validated at concentrations around 0.1 ng m <sup>-3</sup> in total particulate concentration range 1-15mg m <sup>-3</sup> . The scope states that it can be applied more widely, with practical experience showing that it can be used on a wide range of processes and stack gas conditions.

<sup>1</sup>The Standard is in three parts covering sampling, extraction and quantification.

**Formaldehyde** (see aldehydes)

**Flow** (see Gas Velocity)

Table S2.13. Gas velocity

Type of monitoring	Monitoring technique	Monitoring standard	Further information
Manual	Several different techniques with different applications are specified.	BS EN 16911-1 and MID <sup>1,2</sup>	<p><b>Velocity measurement at point:</b> differential pressure devices and vane anemometer.</p> <p><b>Determination of swirl:</b> differential pressure devices able to determine flow direction (S-type, 2D or 3D Pitot tube).</p> <p><b>Periodic measurement of average velocity in a duct:</b> grid of point velocity measurements, tracer dilution technique, tracer transit time technique, calculation approach based on energy consumption.</p> <p><b>Calibration of AMS for average velocity or volume:</b> grid of point velocity measurements, tracer dilution technique, tracer transit time technique.</p>

<sup>1</sup>The MID for EN 16911-1 provides information on the application of EN 16911-1 to flow measurements used for isokinetic sampling and for calculating mass emissions from manual monitoring.

<sup>2</sup>PD CEN TR 17078 – Guidance on the application of EN 16911-1. This technical report provides guidance on applying the standard to a range of applications with different uncertainty requirements (i.e. calibration of CEMs and emissions trading).

**Table S2.14. Halogens and halides (excluding methods specific to monitoring HCl and HF<sup>1</sup>)**

Type of monitoring	Monitoring technique	Monitoring standard	Further information
Manual	Non-isokinetic or isokinetic sampling and impingement. Analysis by ion chromatography	US EPA Method 26 (non-isokinetic) and 26A (isokinetic)	Method 26 for gas-phase halides only; method 26A for both aerosol and gas-phase halides. Also suitable for halogens with H <sub>2</sub> SO <sub>4</sub> scrubber to remove halides. LOD 0.1 ppm. Potential cross-interference from carbonates, which may be present in equilibrium with dissolved carbon dioxide. The methods may be used for HBr, Cl <sub>2</sub> and Br <sub>2</sub> .
	FTIR	TGN M22	Reduced interference compared to NDIR and faster response. Measures gas phase halides only, not halide salts. Does not measure halogens.
	MS	None published	Can measure gas-phase Cl <sub>2</sub> , Br <sub>2</sub> . Fast response and wide analysis range. Measures gas phase only, not halide salts.

<sup>1</sup>For methods specific to the monitoring of HCl and HF, refer to tables for HCl and HF.

**Heavy metals** (see metals)

**Hexavalent chromium** (see metals)

**Table S2.15. Homogeneity test**

Type of monitoring	Monitoring technique	Monitoring standard	Further information
Instrumental	Measurement of gas concentrations using a grid measurement approach	BS EN 15259 (section 8.3) and MID	A homogeneity test is used to determine if a stack gas pollutant concentration is sufficiently homogenous at the sample plane location to enable it to be sampled from a single point. It usually requires the use of two instrumental analysers, which record gas concentration changes across the sample plane and over the time of the homogeneity test. Statistical analysis is used to show if the gas can be considered homogenous or in-homogenous. If the gas is in-homogenous an alternative location or a grid measurement approach should be used. This approach is also used to determine the location of CEMs.

Table S2.16. Hydrogen chloride<sup>1</sup>

Type of monitoring	Monitoring technique	Monitoring standard	Further information
Manual	Isokinetic / non-isokinetic sampling and impingement. Analysis by titration, spectrometry or IC	BS EN 1911	Measures total gaseous chlorides, reported as HCl. Typical range 0-1000 mg m <sup>-3</sup> (can be varied with volume). "External uncertainty" (reproducibility) at 5 mg m <sup>-3</sup> approx. ±30%.
Instrumental	Extractive sampling and NDIR analyser	AM for BS EN 1911 / CEN/TS 16429 <sup>2</sup>	Measures HCl, specifically, rather than total chlorides. Measures gas phase HCl only. Interference from particulates, H <sub>2</sub> O, CO, CO <sub>2</sub> and any other IR-absorbing components.
	Extractive sampling and FTIR analyser	AM for BS EN 1911 / TGN M22 <sup>3</sup>	Measures HCl, specifically, rather than total chlorides. Simultaneous monitoring of HCl along with many other pollutants. Faster response and fewer interferences than NDIR. Typical range up to 1000 mg m <sup>-3</sup> . Measures gas phase HCl only.

<sup>1</sup> For halogens and halides, excluding HCl and HF, see table for halogens and halides

<sup>2</sup> CEN TS 16429 is a technical specification that provides an instrumental method for the measurement of HCl using an infra red technique. It may be used as an AM provided the user can demonstrate equivalence to EN 14793 - "Intralaboratory procedure for an alternative method compared to a reference method", to the satisfaction of UKAS and the regulator. Further information is available in the MCERTS performance standard for organisations.

<sup>3</sup>TGN M22 is available from [www.mcerts.net](http://www.mcerts.net).

Table S2.17. Hydrogen cyanide<sup>1</sup>

Type of monitoring	Monitoring technique	Monitoring standard	Further information
Manual	Isokinetic sampling <sup>2</sup> and impingement. Analysis by ion chromatography	US EPA OTM29 <sup>3,4</sup>	<p>Will measure total CN<sup>-</sup> species reaching the impinger. A filter is used to remove particulate cyanide. High concentrations of acidic gases, including CO<sub>2</sub>, may lower the pH of the sodium hydroxide impinger solution. It is crucial that the pH of the impingers are maintained at 12 throughout the sampling, as such they should be measured at the end of the test. Modifications for sampling highly acidic stack gases are given in the method. Lead acetate solution may be used to remove sulphide interferences. Oxidizing agents (which may decompose cyanides in the impinger solutions) may be removed during sample recovery by adding ascorbic acid.</p> <p>The method specifies a 6.0N NaOH reagent solution. It gives a warning about safety issues using a solution of this strength. It also states that it may become difficult to analyse because of its viscosity. Due to this, it is acceptable to use a weaker NaOH solution, provided the pH of the impingers are checked at the end of the test to ensure the required pH has been maintained. An impinger efficiency test (&lt;5% HCN in the last impinger) is also a useful quality assurance check.</p> <p>The following changes to the method are acceptable<sup>5</sup>:</p> <ul style="list-style-type: none"> <li>- it is not necessary to carry out a field blank spike</li> <li>- it is not necessary to measure CO<sub>2</sub> concentration of the stack gas for non-combustion processes</li> <li>- a titanium probe and filter holder may be used instead of glass.</li> </ul>
Instrumental	FTIR	TGN M22	Applicable to gas-phase HCN.

<sup>1</sup>US EPA OTM29 may be used to obtain an estimate of particulate cyanide by recovering and analyzing the particulates on the filter. To extend OTM29 in this manner, detailed instructions for sample digestion, analysis, and interpretation of results must be added to the method.

<sup>2</sup>Sampling is conducted isokinetically because of the significant solubility of HCN in water droplets, such as after with wet scrubber systems. If it is proved that droplets are not present in the stack then non-isokinetic sampling may be carried out.

<sup>3</sup>This test method is an update of CTM33. It was updated to address issues related to maintaining a pH of  $\geq 12$  in the sodium hydroxide (NaOH) impingers during the test. Other modifications improve the recovery, analytical, and quality assurance procedures.

<sup>4</sup>Validation showed that the capture of HCN in impingers is strongly affected if the pH of the NaOH impinger solutions is reduced by acidic stack gases, including CO<sub>2</sub>.

<sup>5</sup>The method specifies several requirements that are required by US EPA methods but are not required by European or ISO methods.

Table S2.18. Hydrogen fluoride<sup>1</sup>

Type of monitoring	Monitoring technique	Monitoring standard	Further information
Periodic manual techniques	Isokinetic or non-isokinetic sampling and impingement. Analysis by ion selective electrode <sup>2</sup>	BS ISO 15713 and MID	Applicable to all stacks with fluoride concentrations below 200 mg m <sup>-3</sup> but may be applied to higher concentrations if the absorption efficiency of the bubblers is checked. The detection limit of the test estimated as 0.1 mg m <sup>-3</sup> based on sample volume of 0.1 mg m <sup>-3</sup> . Used to measure gas phase only. Isokinetic sampling required if droplets present. The method does not measure fluorocarbons or fluoride salts. The amount of fluoride is expressed as hydrogen fluoride.
Periodic instrumental techniques <sup>3</sup>	Extractive sampling and NDIR analyser	None published	Can measure gas-phase HF. Does not measure fluoride salts. Interference from particulates, H <sub>2</sub> O, CO <sub>2</sub> and any other IR-absorbing components.
	Extractive sampling and FTIR analyser	TGN M22	Applicable to gas phase HF. Reduced interference compared to NDIR and faster response. Measures gas phase only, does not measure fluoride salts.

<sup>1</sup> See Table 10 for halogens and halides excluding HF and HCl

<sup>2</sup> Ion chromatography may be used in conjunction with BS ISO 15713

<sup>3</sup> Instrumental techniques are normally not appropriate for routine stack emissions measurement of HF because it is technically challenging to generate certified HF reference material for checking a portable emissions monitoring system's integrity.

Table S2.19. Hydrogen sulphide

Type of monitoring	Monitoring technique	Monitoring standard	Further information
Manual	Non-isokinetic sampling. Impingement in cadmium sulphate. Analysed idiometrically.	US EPA Method 11	Method for H <sub>2</sub> S. Compounds that reduce iodine or oxidize the iodide ion will interfere if collected in the impingers. The method involves using hazardous materials and potentially hazardous operations. Zinc acetate is commonly used in the UK in place of cadmium sulphate. Range 8 mg/m <sup>3</sup> – 740 mg/m <sup>3</sup> . An impinger containing H <sub>2</sub> O <sub>2</sub> is used to remove SO <sub>2</sub> . This impinger may be omitted from the sample train, if no SO <sub>2</sub> is present in the stack gas.
	Non-isokinetic sampling and collection on charcoal tube.	Procedural requirements of BS CEN/TS 13649 for sampling, NIOSH 6013 for analysis	Method for H <sub>2</sub> S. SO <sub>2</sub> is a positive interferent, so the method is not suitable for some combustion processes. Useful for odour work because of lower LOD than US EPA Method 11. NIOSH 6013 states LOD for 20 litre sample is 0.9 mg/m <sup>3</sup> .
	Portable GC with detector (GC-FID, GC-PID, GC-ECD)	US EPA Method 15	Method for H <sub>2</sub> S. Range 0-1,000 ppm, LOD 0.5 ppm. CO, CO <sub>2</sub> and water vapour interfere.

Table S2.20. Isocyanates

Type of monitoring	Monitoring technique	Monitoring standard	Further information
Manual	Isokinetic sampling onto a filter coated with 1-(2-pyridyl) piperazine. Analysis by HPLC	US EPA CTM 36 (sampling), CTM 36 A (analysis) <sup>1,2</sup>	Standard refers to TDI, MDI, HDI and IPDI (but may also be used for other isocyanates). 1-2-PP may suffer from impurities that cause interference. Alcohols interfere. A titanium probe and filter holder may be used instead of glass <sup>3</sup> . An out of stack filter may be used.
Instrumental	Continuously sampling ion-mobility spectrometer	None published	Able to separate and analyse specific di-isocyanates. LOD down as far as 5 ppb.

<sup>1</sup>US EPA CTM 36 has been validated using US EPA Method 301.

<sup>2</sup>US EPA Method 207 may also be used. It requires the use of an impinger train and is generally more complex than US EPA CTM 36.

<sup>3</sup>The use of titanium for sample trains is not specified in US EPA methods. However, it is acceptable in CEN and ISO monitoring standards.

**Mercury** (see metals)

**Table S2.21 Mass emissions and emission factors**

Type of monitoring	Monitoring technique	Monitoring standard	Further information
Manual / instrumental	Describes measurement procedures to determine mass emissions and emission factors.	BS EN ISO 11771	Emission factors can be used to calculate and report mass emissions. These mass emissions can be used for emission trading, pollution inventory reporting and air quality modelling.

**Table S2.22. Mercaptans (thiols)**

Type of monitoring	Monitoring technique	Monitoring standard	Further information
Manual	Extractive sampling onto a desorption tube with a molecular sieve or a dual bed sorbent ATD tube with an inert coating designed for sulphur compounds, including mercaptans. Analysis by GC-FPD or GC-MS.	BS CEN/TS 13649 for sampling. None published for analysis	
	Extractive sampling onto a mercuric acetate treated filter, analysis by GC-FPD or GC-MS	None published, NIOSH 2542 for analysis	
Instrumental	Continuously sampling chromatographic S gas analyser	None published	Able to separate and analyse mercaptans, H <sub>2</sub> S, SO <sub>2</sub> and organic sulphides. LOD down to 2 ppb.

Table S2.23. Metals

Type of monitoring	Monitoring technique	Monitoring standard	Further information
Manual	Isokinetic sampling and impingement. Analysis by CVAAS, ICPMS or AFS.	BS EN 13211 (see MID for BS EN 14385 <sup>1</sup> )	Method for the determination of Hg and its compounds in all phases. The method was validated on the incineration of waste at a concentration range 0.001 to 0.5 mg m <sup>-3</sup> of Hg.
	Isokinetic sampling and impingement. Analysis by ICPMS, ICP-OES or AAS.	BS EN 14385 and MID <sup>1</sup>	Method for the determination of total emissions of As, Cd, Cr, Co, Cu, Mn, Ni, Pb, Sb, Ti, V and other metals as specified in MID 14385 <sup>2</sup> .
	Isokinetic sampling and impingement. Analysis by IC.	US EPA Method 0061	This method provides procedures for the determination of hexavalent chromium <sup>3</sup> emissions from hazardous waste incinerators, municipal waste incinerators and sewage sludge incinerators. The lower limit of the detection range can be extended to 16 ng/m <sup>3</sup> with a 3 m <sup>3</sup> gas sample (0.1 ppb in solution). The standard refers to US EPA M7199 for additional requirements on sample transport, storage, preparation and analysis. Samples are transported and stored at <5°C. Other analysis methods may be used, such as colorimetry, provided the impinger reagent specified in the method is used.

<sup>1</sup> A MID has been produced that provides an option for measuring mercury with other metals.

<sup>2</sup> The scope of the standard can be extended to cover other metals. (see MID).

<sup>3</sup> Hexavalent chromium in fine particulate matter (i.e. PM<sub>10</sub> fraction) can be determined by using BS EN ISO 23210 (see table on particulate matter size fractionation). The PM<sub>10</sub> fraction collected can be analysed for hexavalent chromium using standard analysis techniques for metals in solids.

Table S2.24. Methane

Type of monitoring	Monitoring technique	Monitoring standard	Further information
Manual	Extraction into a gas sampling bag or canister. Analysis by GC-FID.	BS EN 25139	Validated up to 1500 mg/m <sup>3</sup> . Validated on a gas engine at a waste water purification plant.
Instrumental	Extractive sampling and FID analyser	BS EN 25140	Validated on a gas engine at a waste water purification plant. A catalytic converter is used to oxidise all organic compounds in the extracted gas, with the exception of methane.
	Extractive sampling and FTIR analyser.	TGN M22	Simultaneous monitoring with many other pollutants.

Table S2.25. Methanol

Type of monitoring	Monitoring technique	Monitoring standard	Further information
Manual	Extractive sampling onto sorbent and analysis by GC.	Sampling BS CEN/TS 13649, analysis NIOSH 2000 or OSHA 91	NIOSH 2000 uses a silica gel tube. OSHA 91 specifies an adsorb carbon tube.
Instrumental	Extractive sampling and FTIR analyser.	TGN M22	

**Moisture** (see water vapour)

Table S2.26. Nitric acid vapour

Type of monitoring	Monitoring technique	Monitoring standard	Further information
Manual	Non-isokinetic sampling into impingers containing alkaline potassium permanganate. Analysis by IC	USEPA M7d	Measures NO, NO <sub>2</sub> and nitric acid vapour. To be used for processes, which may emit nitric acid vapour emissions, such as the surface treatment of metals.
Instrumental	Extractive sampling and FTIR analyser	TGN M22	Measures nitric acid vapour specifically, rather than total oxides of nitrogen. Simultaneous monitoring with many other pollutants.

Table S2.27. Nitrogen monoxide and nitrogen dioxide

Type of Monitoring	Monitoring technique	Monitoring standard	Further information
Instrumental	Extractive sampling and chemiluminescence <sup>1, 2</sup> analyser	BS EN 14792	Validated on waste incineration, co-incineration and large combustion installations. Range 0 to 1300 mg m <sup>-3</sup> for LCP and 0 to 400 mg m <sup>-3</sup> for waste incinerators. Overall uncertainty should be less than ± 10% of the daily ELV.
	Extractive sampling and NDUV analyser	AM for BS EN 14792 <sup>2</sup>	Measurement of NO and NO <sub>2</sub> . The principal interference is from SO <sub>2</sub>
	Extractive sampling and NDIR analyser		Measurement of NO and NO <sub>2</sub> . Wide range (typical NO to 5,000 mg m <sup>-3</sup> , NO <sub>2</sub> to 5,000 mg m <sup>-3</sup> ). Main interference from particulates and H <sub>2</sub> O, which can be reduced by precise selection of wavelength. Not suitable for high-moisture gases. Main interference from particulates and H <sub>2</sub> O, which can be removed by conditioning.
	Extractive sampling and electrochemical analyser		Measurement of NO and NO <sub>2</sub> typically up to 3,000 ppm and 500 ppm, respectively.
	Extractive sampling and FTIR analyser	AM for BS EN 14792 <sup>1</sup> / TGN M22	Simultaneous monitoring with many other pollutants. Faster response and subject to less interference than NDIR. Measurement of NO and NO <sub>2</sub> .

<sup>1</sup>For processes that have a significant amount of NO<sub>2</sub>, it may be advisable to use a different analytical technique to chemiluminescence, due to the greater relative importance of the NO<sub>2</sub> and the potential difficulty in maintaining the 95% NO<sub>2</sub> to NO converter efficiency. Examples include the production of dye-stuffs in the chemical industry or the brightening of aluminium components in acid baths.

<sup>2</sup> The determination of the NO<sub>2</sub> / NO converter efficiency should be carried out by an organisation that has MCERTS accreditation for EN 14792. If an analyser is only used for monitoring processes that have less than 10% NO<sub>2</sub> / NO<sub>x</sub> ratio, the NO<sub>2</sub> / NO converter efficiency is demonstrated at least every year. If an analyser is used on processes with over 10% NO<sub>2</sub> / NO<sub>x</sub> ratio, the determination of the NO<sub>2</sub> / NO converter efficiency is carried out at a frequency established by the monitoring organisation. The frequency is based on the length of time the analyser is used on processes with over 10% NO<sub>2</sub> / NO<sub>x</sub> ratio, the concentration of NO<sub>2</sub> encountered and the expected life span of the converter material. If the NO<sub>2</sub> converter fails to meet the conversion efficiency, then all the monitoring work carried out on processes with over 10% NO<sub>2</sub>, since the last successful determination of the converter efficiency is out of compliance with EN 14792. If an analyser is used on processes with over 10% NO<sub>2</sub> / NO<sub>x</sub> ratio, the NO<sub>2</sub> / NO converter efficiency must also be determined before the material in the converter is replaced. If it fails to meet the 95% converter efficiency, then all the monitoring work carried out on processes with over 10% NO<sub>2</sub>, since the last successful determination of the NO<sub>2</sub> / NO converter efficiency, is out of compliance with EN 14792. The converter efficiency may be checked using a cylinder of NO<sub>2</sub>, as soon as practicable after the converter efficiency has been proven as acceptable. This cylinder may then be used to provide checks of the converter between carrying out gas phase titration checks.

<sup>3</sup> BS EN 14792 is a reference method based on chemiluminescence. An AM may be used provided the user can demonstrate equivalence to EN 14793 - "Intralaboratory procedure for an alternative method compared to a reference method", to the satisfaction of UKAS and the regulator. Further information is available in the MCERTS performance standard for organisations.

Table S2.28. Nitrous oxide (Dinitrogen monoxide)

Type of monitoring	Monitoring technique	Monitoring standard	Further information
Instrumental	Extractive sampling and NDIR analyser	BS EN ISO 21258	Validated on a sewage sludge incinerator with N <sub>2</sub> O concentrations up to 200 mg/m <sup>3</sup> . Interference from CO and CO <sub>2</sub> (CO <sub>2</sub> may need to be measured alongside N <sub>2</sub> O, so that it can be compensated for). Water vapour must be removed.
	Extractive sampling and FTIR analyser	AM for BS EN ISO 21258 / TGN M22	Simultaneous monitoring with many other pollutants.

Table S2.29. Odour

Type of monitoring	Monitoring technique	Monitoring standard	Further information
Manual	Extractive sampling into inert containers. Assessment by olfactometry using an odour panel.	BS EN 13725 and MID	The unit of measurement is the European odour unit per cubic metre (ouE/m <sup>3</sup> ). Method may be used to measure the emission rate of odorous emissions from stacks.

Table S2.30. Oil mist

Type of monitoring	Monitoring technique	Monitoring standard	Further information
Manual	Isokinetic sampling, extraction into cyclohexane, then gravimetric analysis.	BS EN 13284-1 with analysis based on MDHS 84.	This technique measures fume and condensed vapours, not volatiles. Sticky particulates can foul sampling equipment leading to low recoveries unless precautions are taken (e.g. use of an in-stack filter). No published standard covering entire technique, hence no overall technique performance has been calculated. MDHS 84 only includes analysis of oil mist collected on a filter. In order to comply with EN 13284-1, it is necessary to analyse oil mist collected on the equipment upstream of the filter. The sample train may be set up with an out of stack filter at ambient temperature. This indicative method can be used to identify if oil mist is contributing to a visible plume.

Table S2.31. Oxygen

Type of monitoring	Monitoring technique	Monitoring standard	Further information
Instrumental	Paramagnetic analyser	BS EN 14789	Validated on waste incineration, co-incineration and large combustion installations. Range 5 to 25% O <sub>2</sub> . Overall uncertainty should be less than $\pm 6\%$ of the measured concentration.
	Zirconium cells	AM for BS EN 14789 <sup>1</sup>	Interference from CO and hydrocarbons if their concentrations are in the same order as oxygen. Intended for use in the range of up to 25% volume fraction.
	Electrochemical cell	AM for BS EN 14789 <sup>1</sup>	As above for CEMs.

<sup>1</sup> BS EN 14789 is a reference method based on using a paramagnetic analyser. An AM may be used provided the user can demonstrate equivalence to EN 14793 - "Intralaboratory procedure for an alternative method compared to a reference method", to the satisfaction of UKAS and the regulator. Further information is available in the MCERTS performance standard for organisations.

Table S2.32. PAHs

Type of monitoring	Monitoring technique	Monitoring standard	Further information
Manual	Isokinetic sampling, extraction, then HPLC or GC-MS analysis	BS ISO 11338-1,2.	Range of PAHs <sup>1</sup> measured dependent on spectrometer settings. A sample volume of 6 m <sup>3</sup> , enables method detection limits in the range of 0.1 $\mu\text{g}/\text{m}^3$ to 1 $\mu\text{g}/\text{m}^3$ . Uncertainty $\pm 25\%$ . PAH samples may be transported at below 25°C before storage in cold conditions <sup>2</sup> .

<sup>1</sup>The regulatory authorities specify the set of PAH compounds that should be measured. This set may vary depending on the process or purpose of the measurement. The monitoring organisation should ensure that the analytical laboratory analyses the PAH compounds specified.

<sup>2</sup>This requirement is taken from VDI 3874:2006, which states that samples are transported light-protected and at ambient temperature.

Table S2.33. Particulate matter

Type of monitoring	Monitoring technique	Monitoring standard	Further information
Manual	Isokinetic sampling followed by weighing	BS EN 13284-1 and MID	Reference method for concentrations below to 50 mg m <sup>-3</sup> . However the scope states that it can be used for higher concentrations. Primarily developed for waste incinerators, however the scope also states that it can be applied more widely. Reproducibility (worst quoted) ±5.7 mg m <sup>-3</sup> at 6.4 mg m <sup>-3</sup> and 30 min sample. Validated at concentrations around 5 mg m <sup>-3</sup> and 30-minute sampling duration. The overall uncertainty of the method complies with the uncertainty of ±30% required by IED.

Table S2.34. Particulate matter (condensable)

Type of monitoring	Monitoring technique	Monitoring standard	Further information
Manual	Dilution sampling technique	BS ISO 25597 <sup>1</sup>	The dilution sampling technique measures condensable, secondary particulate matter that is similar in character to ambient particulate matter <sup>2</sup> .

<sup>1</sup>ISO 25597 uses a cyclone and isokinetic sampling to measure PM<sub>10</sub> and PM<sub>2.5</sub>. It includes a dilution sampling technique to measure condensable particulates. Under MCERTS accreditation and the hierarchy of standards PM<sub>10</sub> and PM<sub>2.5</sub> must be measured using European standard EN ISO 23210.

<sup>2</sup>The regulation of particulate emissions in England is based on primary particulates. It does not normally take account of secondary particulates that may form once the stack gas enters ambient air.

**Table S2.35. Particulate matter size fractionation<sup>1</sup>**

Type of monitoring	Monitoring technique	Monitoring standard	Further information
Manual	Impaction based on a round nozzle two stage impactor	BS EN ISO 23210	Allows simultaneous measurement of <PM <sub>10</sub> to >PM <sub>2.5</sub> concentrations and <PM <sub>2.5</sub> concentrations using a cascade impactor. The standard does not measure the contribution of stack gas emissions to the formation of secondary particulate matter in ambient air. It was primarily developed for measurements of mass concentrations below 40 mg/m <sup>3</sup> at STP <sup>2</sup> . However, it states that it is applicable for particulate concentrations between 1 – 50 mg/m <sup>3</sup> . The standard also specifies limitations on stack gas temperature, pressure and humidity. It is suitable for combustion sources, cement and steel processes. It cannot be used to measure stack gases that are saturated with water vapour. It is not applicable to stack gases where the majority of particulates are greater than PM <sub>10</sub> . It cannot be used for the measurement of total mass concentration of particulates. The velocity and temperature profile of the sample plane is used to determine a single representative sample point.

<sup>1</sup>EA TGN M15 provides guidance on size fractionation measurements. It also provides further information on the use of BS EN ISO 23210. TGN M15 is available from [www.mcerts.net](http://www.mcerts.net).

<sup>2</sup>For stack gas emissions with particulate concentrations above 50 mg/m<sup>3</sup> the following are available:

- BS ISO 25597: Test method for determining PM<sub>2.5</sub> and PM<sub>10</sub> mass in stack gases using cyclone samplers and sample dilution.
- BS ISO 13271: Determination of PM<sub>10</sub> / PM<sub>2.5</sub> mass concentration in the gas - Measurement at higher concentrations by use of virtual impactors.

**Table S2.36. PCBs (dioxin like)**

Type of monitoring	Monitoring technique	Monitoring standard	Further information
Manual	Isokinetic sampling, extraction, then GC-MS analysis	BS EN 1948-4	The scope of the method includes dioxin like PCBs. Requires liaison with analytical laboratory to determine capture medium and analytical LOD. Validated at concentrations around 0.1 ng m <sup>-3</sup> in total particulate concentration range 1-15 mg m <sup>-3</sup> .

**Table S2.37. Phenols and cresols**

Type of monitoring	Monitoring technique	Monitoring standard	Further information
Manual	Extractive sampling onto XAD-7 sorbent resin <sup>1</sup> . Methanol desorption and analysis by HPLC-UV detection	Sampling BS CEN/TS 13649, OSHA 32 or NIOSH 2546 for analysis	OSHA 32: method for phenol and cresols (ortho-, meta- and para-). Typical LOD 0.05 mg m <sup>-3</sup> , target concentration 20 mg m <sup>-3</sup> .  NIOSH 2546: method for phenol and cresols. Typical LOD 1 mg m <sup>-3</sup> . Range up to 60 mg m <sup>-3</sup> for a 0.020 m <sup>3</sup> sample.

<sup>1</sup>Phenols and cresols entrain in moisture droplets, so should be sampled isokinetically, when in-stack moisture levels are above saturation for a given temperature.

**Table S2.38. Phosphorous and its inorganic compounds**

Type of monitoring	Monitoring technique	Monitoring standard	Further information
Manual	Non-isokinetic extraction and impingement. Analysis by visible spectrophotometry	Procedural requirements of BS EN14791, NIOSH 6402 for analysis.	For gas phase only. Method specific to phosphorous trichloride (PCl <sub>3</sub> ). Validated analysis method. Typical LOD 1 mg m <sup>-3</sup> . Range 1-80 mg m <sup>-3</sup> on a 100 litre sample.
	Non-isokinetic extraction and adsorption onto mercuric cyanide-treated silica gel tubes. Analysis by colorimetry	Procedural requirements of BS CEN/TS 13649, NIOSH 6002 for analysis. OSHA 10180 may also be used for analysis	For gas phase only. Method specific to phosphine (PH <sub>3</sub> ). Validated analysis method. Typical LOD 0.01 mg m <sup>-3</sup> . Range 0.02 – 0.9 mg m <sup>-3</sup> on a 16 litre sample. Interferents include phosphorous chlorides and organic phosphorous compounds.
	Isokinetic extraction and impingement. Analysis by AAS or ICP	BS EN14885 (see metal)	Method for total phosphorous in all phases. Limited validation of sampling and analysis. Typical LOD 0.03 mg m <sup>-3</sup> . No speciation of phosphorous compounds possible.

**Table S2.39. Quality assurance of CEMs (EN 14181 – QAL2 & AST)<sup>1</sup>**

Type of monitoring	Monitoring standard	Further information
Manual / instrumental	BS EN 14181	A quality assurance standard for the calibration of CEMs. Mandatory requirement for LCP and waste incinerators regulated under IED. Much of the standard is applicable to manual stack emissions monitoring organisations (i.e. auditing functional tests, carrying out parallel reference measurements, determining a calibration function and carrying out a variability test).

<sup>1</sup>EA TGN M20 provides further guidance on the quality assurance of CEMs. TGN M20 is available from [www.mcerts.net](http://www.mcerts.net).

**Table S2.40. Selenium**

Type of monitoring	Monitoring technique	Monitoring standard	Further information
Manual	Isokinetic sampling and impingement. Analysis by ICP-OES, ICP-MS, GFAAS, HG-AAS, HG-AFS, HG-ICP-OES or HG-ICP-MS.	BS ISO 17211	Method for determination of Se in particulate and gaseous phase.

Table S2.41. Siloxanes<sup>1</sup>

Type of Monitoring	Monitoring technique	Monitoring standard	Further information
Manual	VOC sampling techniques with GC MS analysis	BS CEN/TS 13649 or procedural requirements of BS EN 14791.	<p>The following techniques / capture medium have been used to measure siloxanes:</p> <ul style="list-style-type: none"> <li>- methanol (impinger method)</li> <li>- charcoal (sorbent tube method)</li> <li>- canister method</li> <li>- evacuated bag method</li> </ul> <p>Their main use has been to measure untreated gas, such as raw landfill gas before it enters a gas engine.</p>
Instrumental	Extractive sampling and FTIR analyser.	TGN M22	Simultaneous monitoring of many pollutants.

<sup>1</sup>When gas containing siloxanes passes through a combustion process (e.g. gas engine or a flare stack), the siloxanes are primarily converted to silicon dioxide (SiO<sub>2</sub>). Silicon dioxide emissions are measured using particulate sampling techniques (i.e. EN 13284-1).

**Speciated VOCs** – see VOCs (speciated)

Table S2.42. Sulphur dioxide

Type of Monitoring	Monitoring technique	Monitoring standard	Further information
Manual	Non isokinetic / isokinetic extraction and impingement into hydrogen peroxide solution. Analysis by IC or Thorin method.	BS EN 14791	Validated on waste incineration, co-incineration and large combustion installations. Range 0.5 to 2000 mg m <sup>-3</sup> . Overall uncertainty should be less than ± 20% of the daily ELV.
Instrumental	Extractive sampling and UV-fluorescence analyser.	CEN TS 17021 <sup>1</sup> / TGN M21 <sup>2</sup> (AM for BS EN 14791) /	CEN TS 17021 is based on the use of instrumental techniques. It specifies performance criteria for instrumental systems, rather than the specific type of instrument.
	Extractive sampling and UV-absorption analyser.		
	Extractive sampling and NDIR-absorption analyser <sup>3</sup> .		
	Extractive sampling and electrochemical analyser.		
	Extractive sampling and FTIR analyser.	TGN M22 <sup>4</sup>	Simultaneous monitoring of many pollutants.

<sup>1</sup> CEN TS 17021 is a technical specification that provides an instrumental method for the measurement of sulphur dioxide, using various techniques. It may be used as an AM provided the user can demonstrate equivalence to EN 14793 - "Intralaboratory procedure for an alternative method compared to a reference method", to the satisfaction of UKAS and the regulator. Further information is available in the MCERTS performance standard for organisations.

<sup>2</sup> TGN M21 is available from [www.mcerts.net](http://www.mcerts.net). TGN M21 may be used under MCERTS accreditation until 31 December 2018. After this date it will be replaced by CEN TS 17021.

<sup>3</sup> Some NDIR analysers may suffer from interference from methane. This may be an issue when measuring emissions from landfill gas engines and biowaste plants because of the concentration of methane present in the stack gas emissions. Appropriate provisions should be made to quantify the interference. In instrument type-testing (e.g. MCERTS), the overall specification is that interference collectively must not have an effect greater than 4% of the certification range at either the zero or span point. Therefore, monitoring organisations should refer to the MCERTS certificate to find the interference effects of methane. The potential interference effect for any concentration of methane on sulphur dioxide is calculated as follows:

$$(\text{expected methane concentration} / 50 \text{ mg/m}^3) \times \text{interference effect}$$

If the new interference value exceeds 4% of the certification range, then the monitoring organisation must test the interference effect using methane. If the result using methane shows that the actual interference effect is more than 4%, another technique must be used.

<sup>4</sup> TGN M22 is available from [www.mcerts.net](http://www.mcerts.net).

**Table S2.43. Sulphuric acid including sulphuric acid mist and sulphur trioxide**

Type of monitoring	Monitoring technique	Monitoring standard	Further information
Manual	Isokinetic extraction and impingement with propan-2-ol. Analysis by barium-thorin titration method or IC.	US EPA method 8	Measures H <sub>2</sub> SO <sub>4</sub> , including H <sub>2</sub> SO <sub>4</sub> mist and SO <sub>3</sub> . H <sub>2</sub> SO <sub>4</sub> and SO <sub>3</sub> cannot be measured separately therefore a combined result is obtained. The barium-thorin titration method should not be used if fluorides, free ammonia or dimethyl amine are present in the process.

**Table S2.44. Tar and bitumen fume**

Type of monitoring	Monitoring technique	Monitoring standard	Further information
Manual	Isokinetic sampling, extraction into cyclohexane, then gravimetric analysis <sup>1</sup> .	BS EN 13284-1 with analysis based on MDHS 84.	This technique measures fume and condensed vapours, not volatiles though a condensation/resin trap can be used if the latter is required. Sticky particulates can foul sampling equipment leading to low recoveries unless precautions are taken (e.g. use of an instack filter). No published standard covering entire technique, hence no overall performance has been calculated. MDHS 68 quotes LOD of 0.15mg m <sup>-3</sup> for 0.8m <sup>3</sup> sample.

<sup>1</sup>Measured as total particulate first. Tar or bitumen determined as the weight loss after the filters are treated with cyclohexane.

**Temperature** (see gas velocity)

**Thiols** (see mercaptans)

**Total cyanide** (hydrogen cyanide)

**Total organic carbon** (see VOCs total)

**Table S2.45. Total reduced sulphur compounds (TRS)**

Type of monitoring	Monitoring technique	Monitoring standard	Further information
Manual	Non-isokinetic sampling. Combustion of S in sample to SO <sub>2</sub> , analysis by barium-thorin titration	US EPA Method 15A (combustion air added) or 16A (no combustion air added)	Method for TRS species. No speciation possible. Complexity of method restricts its use on site. Not in common field use in UK. Typical LOD 0.1 ppm (for 0.360 m <sup>3</sup> sample).
	Sampling through tube furnace and combustion of S in sample to SO <sub>2</sub> , analysis by FPD	US EPA Method 16B	Method for TRS species. No speciation possible. Requires sufficient oxygen in sample gas stream to fully combust sulphur species. Range 0-1,000 ppm. CO and CO <sub>2</sub> interfere. Not in common use in UK.

**Total sulphur** (see sulphur trioxide)

**Total VOCs** (see VOCs total)

**Trace metals** (see metals)

Table S2.46. VOCs (specified)

Type of monitoring	Monitoring technique	Monitoring standard	Further information
Manual	Extractive sampling onto sorbent, solvent extraction and analysis by GC with appropriate detector	BS CEN/TS 13649 <sup>1</sup>	<p>Developed for solvent processes. Applicable to a wide range of aliphatic and aromatic VOCs (refer to standard). Useful in areas where intrinsically safe equipment must be used. Only VOCs that adsorb onto activated charcoal may be sampled. Suitable for range 0.5-2,000 mg m<sup>-3</sup>. Can be sampled directly or using dilution to avoid condensation. The method may be used to quantitatively measure total VOCs provided the VOCs adsorb onto activated charcoal and have been identified before sampling. If the stack gas contains an unknown mixture of VOCs this method cannot be used to give a total VOC measurement.</p> <p>When different absorption medium are used, such as ATD, it is acceptable to use thermal desorption in conjunction with BS CEN/TS 13649. In all cases, there must be evidence to show that the proposed desorption and analytical techniques are valid.</p> <p>Sample tubes (charcoal and ATD) are stored and transported below 25°C in an airtight VOC free container, without exposure to direct sunlight. Samples may be stored under these conditions for a prolonged time period (for samples that are to be stored for over 7 days before analysis, it is <b>not</b> necessary to store them at &lt;4°C).</p>
Instrumental	Extractive sampling and portable GC with appropriate detector (GC-FID, GC-PID, GC-ECD)	US EPA Method 18	Specifies several sampling options. The option using a portable GC to take real time results is the applicable periodic instrumental technique. Can measure virtually any individual organic compounds, many simultaneously. Not truly continuous, but successive measurements in cycles of about 30 minutes. LOD typically 1 ppm.
	Extractive sampling and portable FTIR analyser	TGN M22	Can measure many individual organic compounds simultaneously.

<sup>1</sup>In the absence of a national or international standard method for stack monitoring covering the organic compound of interest, it is recommended that BS CEN/TS 13649 is modified, taking into account the analytical requirements (e.g. sorbent, extraction method, column and detector) of occupational hygiene standard methods published by NIOSH and OSHA.

Table S2.47. VOCs (total)<sup>1</sup>

Type of monitoring	Monitoring technique	Monitoring standard	Further information
Instrumental	Extractive sampling and FID analyser	BS EN 12619 <sup>2</sup>	<p>Validated on waste incinerators and solvent processes. High specificity to VOCs. Developed for incinerators and solvent processes. Different response factor for each VOC species. Suitable for low ranges of VOC concentrations (0-20 mg m<sup>-3</sup>) and for ranges up to 1000 mg m<sup>-3</sup> (this range can be extended by carrying out a lack of fit test using gases with higher concentrations). Interference from O<sub>2</sub> is reduced by using a mixed H<sub>2</sub>/He fuel.</p> <p>The sampling system is heated, with the exception of the probe, which may be unheated, provided it is fully inserted into the stack.</p> <p>Requires interference from O<sub>2</sub> to be checked at 10% and 20%. This applies to combustion processes, especially when calibrating a CEM for EN 14181 purposes. If the FID does not meet the performance criteria at these concentrations, gases with a oxygen concentration similar to stack gas should be used for the zero and span checks at combustion processes, with emissions typically around 10% oxygen (e.g. W/ plants).</p>
	Extractive sampling and NDIR analyser	BS EN ISO 13199	<p>Based on the use of an NDIR analyser equipped with a catalytic converter for oxidation of TVOCs to CO<sub>2</sub>. Unlike FID techniques this approach does not have a flame or hydrogen fuel, so can be used in applications where it is necessary to use intrinsically safe equipment.</p> <p>As the VOCs are oxidised to CO<sub>2</sub>, they all have the same response factor.</p> <p>The technique does not have cross interference from O<sub>2</sub>.</p> <p>The method is suitable for non-combustion processes. It cannot be used to measure emissions from combustion processes.</p> <p>The method was validated on painting and printing processes, where VOC concentrations were from 70 to 600 mg/m<sup>3</sup>.</p>

<sup>1</sup>VOCs (total) are also referred to by different acronyms, such as total VOCs, TVOCs, TOCs or VOCs.

<sup>2</sup>BS EN 12619:1999 and BS EN 13526:2002 were revised in 2013 to produce a single standard for measuring VOCs (total). The combined standard was given the number BS EN 12619:2013. BS EN 13526:2002 was withdrawn in July 2013. Industrial operators with EN 13526:2002 specified in their Permits are able to use BS EN 12619:2013 instead, as this supersedes EN 13526:2002.

Table S2.48. Water vapour (moisture)

Type of monitoring	Monitoring technique	Monitoring standard	Further information
Manual	Gravimetric (impingers)	BS EN 14790	The method is incorporated into several other periodic manual methods, therefore allowing moisture to be measured as part of another sampling method. Validated on waste incineration, co-incineration and large combustion installations. Requires a balance to be taken on site. Range 4 to 40% relative humidity. Overall uncertainty should be less than $\pm 20\%$ of the measured concentration. Not applicable for saturated conditions.
Instrumental	Paramagnetic and zirconium analysers	AM for BS EN 14790 <sup>1</sup>	Range 0-100%, typical resolution 0.1%. H <sub>2</sub> O calculated from the difference between two analysers, one measuring O <sub>2</sub> wet (zirconium) and other dry (paramagnetic). Not a direct measurement of moisture. Interferences from high concentration of NO <sub>2</sub> , NO and hydrocarbons.
	NDIR analyser	AM for BS EN 14790 <sup>1</sup>	Interference from CO, CO <sub>2</sub> , hydrocarbons.
	FTIR analyser	AM for BS EN 14790 <sup>1</sup> / TGN M22	Simultaneous monitoring of H <sub>2</sub> O and other species. Faster response than NDIR. Typical range 0 to 35%.

<sup>1</sup> An AM may be used provided the user can demonstrate equivalence to EN 14793 - "Intralaboratory procedure for an alternative method compared to a reference method", to the satisfaction of UKAS and the regulator. Further information is available in the MCERTS performance standard for organisations.

### Section 3: Automatic batch samplers

**Table S3.1. Dioxins, furans and dioxin like PCBs**

Monitoring Technique	Monitoring standard	Further information
Isokinetic sampling, extraction, then GC-MS analysis	BS CEN/TS 1948-5	Integrated samples obtained over averaging periods typically ranging from 14 to 28 days. Sampling methods described in EN 1948-1 have been modified for long term sampling requirements (filter / condenser, dilution and cooled probe method). Although sample is obtained continuously, results are not instantaneous, as the filter and absorption media are taken to an analytical laboratory for analysis.

**Table S3.2. Mercury**

Monitoring Technique	Monitoring standard	Further information
Sampling with in stack paired sorbent media traps. Analysis by extractive or thermal analytical technique, such as UV AA and UV AF cold vapour analysers	US EPA M30B / Performance specification 12B	Measures total vapour phase mercury emissions from coal-fired combustion sources. This method is designed to measure the mass concentration of total vapour phase mercury in flue gas, including elemental mercury ( $\text{Hg}^0$ ) and oxidized forms of mercury ( $\text{Hg}^{+2}$ ), in micrograms per dry standard cubic meter ( $\mu\text{g}/\text{m}^3$ ). The method is only intended for use when particulate concentrations are low (e.g. sampling after abatement systems) because it does not measure particulate bound mercury. Although a sample is obtained continuously, results are not instantaneous, as the sorbent media traps are taken to an analytical laboratory for analysis.

## 6. Calculation of measurement uncertainties in stack emissions monitoring\*

### 6.1 Introduction

The following documents on uncertainty are relevant to stack emissions monitoring:

- ENV 13005:1999 – Guide to the expression of uncertainty in measurement (GUM)
- BS EN ISO 14956:2002 Air quality – Evaluation of the suitability of a measurement by comparison with a required measurement uncertainty.
- BS EN ISO 20988: 2007 Air quality – Guidelines for estimating measurement uncertainty

European stack emissions monitoring standards also give extensive guidance on uncertainty.

It is a regulatory requirement that stack emissions measurements must be accompanied by an estimate of the overall measurement uncertainty. These uncertainties are included in European Standard Reference Methods (SRM) for stack emissions monitoring.

The overall measurement uncertainties incorporate all possible significant sources of variation in the measurement method. They are expanded uncertainties with 95% confidence limits. In other words if measurements are made with techniques, which are fully compliant with the SRM, 95 times out of a hundred the true value will lie within the limits quoted.

The general approach to uncertainty estimation is to:

- Specify what is being measured and the parameters which affect it
- Identify potential sources of uncertainty for each parameter
- Quantify the component standard uncertainties  $u_c$  (by measurement or estimation)
- Determine the combined standard uncertainty of the measured value using the accepted rules
- Determine the expanded uncertainty enabling the final answer to be expressed as:

$$\text{Value} = X \pm U_c$$

Where  $U_c$  is the overall uncertainty conventionally expressed at a confidence level of 95%.

A summary of the terminology is given at the end of these notes for reference.

### 6.2 Approach to determining uncertainty

#### 6.2.1 Problem specification

The first step is to specify what is being measured and to identify all the parameters which affect it.

Manual methods, whether for gases or particles, are based on simple mathematical equations (the analytical function or measurement equation) relating the input quantities to the concentration of the determinand in the gas phase. At its simplest this is:

$$\text{Concentration} = \text{Mass of determinand collected} / \text{Volume of gas sampled}$$

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\* This Annex is based on material provided by Dr Andrew Clarke, University of Leeds.

For particles this involves the weight of particles collected both on the filter and in the probe washings. For gases collected in liquid solution it involves:

$$\text{Mass of determinand collected} = \text{Solution concentration} \times \text{Volume of solution}$$

Each of these input quantities have associated uncertainties, for example:

- Uncertainty of weighing particles
- Uncertainty of chemical analysis of solution
- Uncertainty of measurement of sample gas volume or liquid solution volume
- Efficiency of sampling bottles in collecting the determinand

The sample gas volume in turn depends on the temperature and pressure at the gas meter. These temperature and pressure measurements also have associated uncertainty. Finally, there may be corrections for water vapour and oxygen level before a result is reported at reference conditions, so the uncertainty of the water vapour and oxygen concentration must be included.

The mathematical relationships also tell us by how much a particular input quantity affects the measured concentration. This is sometimes called the sensitivity coefficient - the deviation of the result of measurement divided by the deviation of an input quantity causing the change, if all other influence quantities are kept constant. Mathematically, the sensitivity coefficient is determined by partial differentiation of the equation with respect to the relevant input quantity. That is why the detailed formal descriptions of uncertainty estimation contain many partial derivatives. The important thing to remember is that

$$\text{Uncertainty in measured value} = \text{Sensitivity coefficient} \times \text{Uncertainty in input quantity}$$

For instrumental gas analysers there is no measurement equation, since the analyser is calibrated using a gas of known concentration and a specified uncertainty. We do not need to deal with uncertainties associated with every component of an instrumental analyser since most of them are covered by the calibration process. There are still many sources of uncertainty which need to be quantified but, generally, the effect on the concentration is not determined by simple mathematical equations. The sensitivity coefficients have to be determined experimentally. This is primarily undertaken by the instrument manufacturer in demonstrating the performance characteristics of the instrument prior to first use. Satisfactory performance characteristics are required for MCERTS certification or meeting the QAL1 requirements of EN 14181.

### 6.2.2 Identify possible sources of uncertainty for each parameter

For all extractive methods of gas or particle analysis there is the possibility of leakage of the sample handling line and losses to the walls of the sampling system. Those must be quantified. For manual methods some indications of the possible sources of uncertainty have been given above. For fuller details refer to EN 1911:2010 for manual measurement of HCl, as a typical manual gas sampling example. For instrumental methods, the following is a typical list of sources of uncertainty:

- Lack of fit (linearity)
- Zero drift
- Span drift
- Sensitivity to sample volume flow
- Sensitivity to atmospheric pressure

- Sensitivity to ambient temperature
- Sensitivity to electrical voltage
- Interferences from other gaseous components present in the flue gas
- Repeatability standard deviation in laboratory at span level
- Calibration gas

The repeatability standard deviation (or detection limit) at zero is not included because the uncertainty for this is assessed by the repeatability standard deviation at span level (including both would be double counting).

### 6.2.3 Quantify the component standard uncertainties

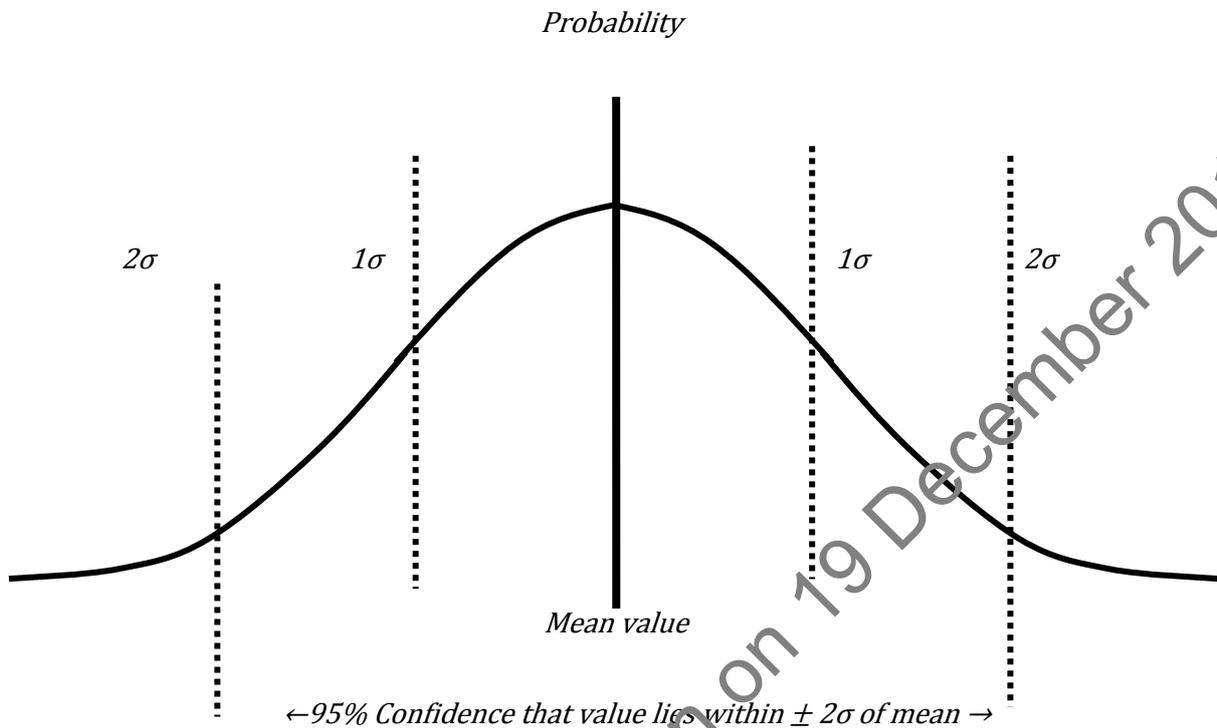
In dealing with the quantification of the uncertainties we have to explain the statistical basis on which this whole exercise is founded.

There are different types of component uncertainty:

Type A component uncertainties – those which are obtained from experimental data and can thus lead directly to a standard deviation. An example of a type A uncertainty is the repeatability at span for a gas analyser or the standard deviation of a set of readings of pressure at a gas meter taken during a run which show small random variations rather than significant overall drift.

This is the standard uncertainty  $u$ , for that component input or influence quantity determined by repeat measurement. Assuming an approximately normal distribution of points around the mean then, with 95% confidence, any measurement will lie within  $\pm 2$  times the standard deviation  $\sigma$  of the mean (see Figure 6.1). The standard uncertainty is identical to the standard deviation.

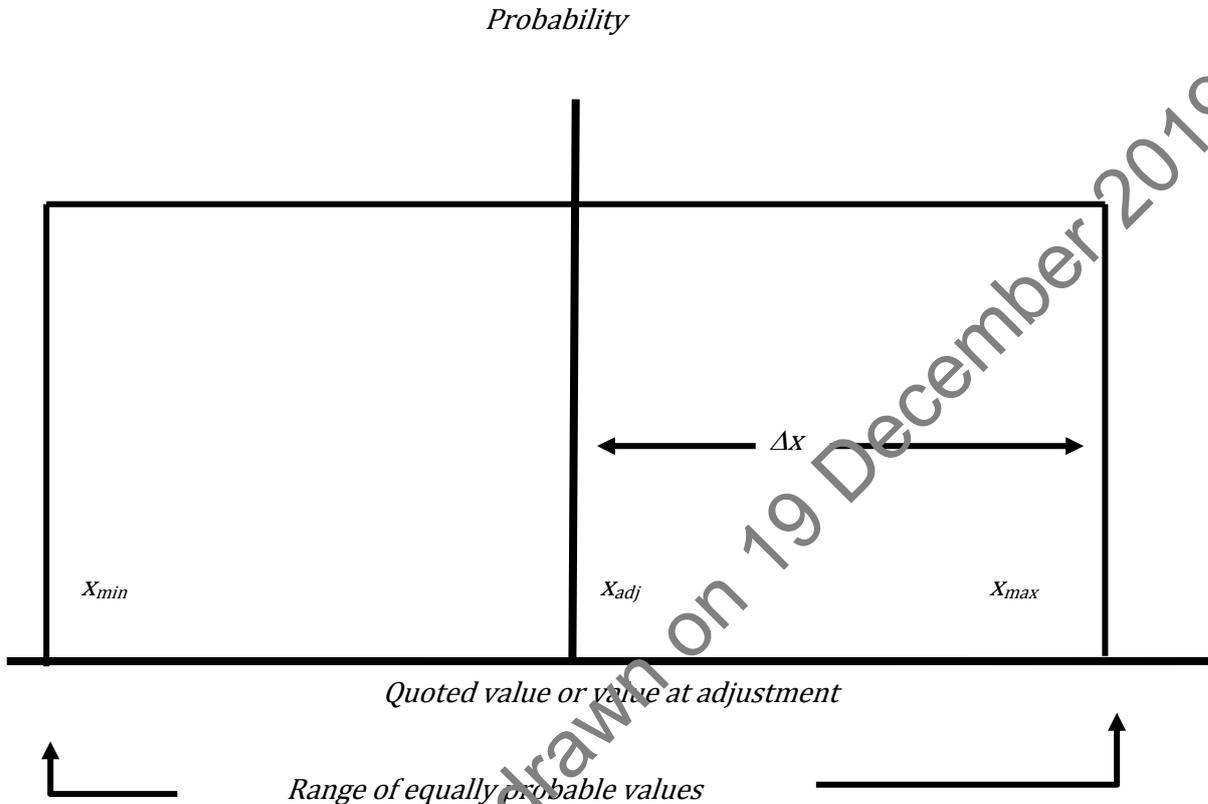
Figure 6.1: Probability distribution A



The factor of 2 (more precisely 1.96) is sometimes called the coverage factor  $k$ . When quoting uncertainty values, we must be very clear whether we are giving the standard uncertainty ( $u = 1$  standard deviation) or the expanded uncertainty ( $U = ku$ ) for a particular degree of confidence such as 95% when  $k=2$ .

Type B uncertainties - for some parameters that influence the output of an instrument there may be a range of values during a measurement series or estimates of the maximum possible variation but the probability distribution is presumed to be rectangular (not the normal error curve). In other words, there is an equal probability of any value within the specified range (see Figure 6.2).

Figure 6.2: Probability distribution B



Examples might be:

- The tolerance of a physical dimension for example (e.g. nozzle size)
- The ambient temperature range during the period of measurement
- The variation of electrical voltage during the measurement

Often the majority of the component uncertainties will be of this type. These ranges have to be converted to a standard uncertainty. Suppose the value of a parameter influencing the measurement during adjustment of an instrument is  $x_{adj}$  and during the measurements the values of the parameter range from  $x_{min}$  to  $x_{max}$ . If  $x_{adj}$  is halfway between  $x_{min}$  and  $x_{max}$  then defining:

$$\Delta X = (x_{adj} - x_{min}) = (x_{max} - x_{adj})$$

$$u_x = \Delta X / (\sqrt{3})$$

If  $x_{adj}$  is close to one end of the range i.e. near to either  $x_{min}$  or  $x_{max}$  then:

$$u_x = (x_{max} - x_{min}) / (\sqrt{3})$$

If the value of  $x_{adj}$  is offset from the centre of the range, then it is necessary to use the more complex general expression:

$$u_x^2 = [ (x_{\max} - x_{\text{adj}})^2 + (x_{\min} - x_{\text{adj}})(x_{\max} - x_{\text{adj}}) + (x_{\max} - x_{\text{adj}})^2 ] / 3$$

In order to relate the standard uncertainty of the input quantity to the uncertainty of the measured concentration we need to bring in the sensitivity coefficient.

#### Examples

a) Component standard uncertainty due to atmospheric pressure variation:

Emission Limit Value = 75 mg/m<sup>3</sup>

Sensitivity of concentration to atmospheric pressure at ELV = 0.8%/kPa

Variation during measurements = 99 - 100 kPa (i.e. 99.5±0.5)

Standard Uncertainty in concentration units = (0.8/100) x 75 x 0.5 / √3 = 0.17mg/m<sup>3</sup>

The sensitivity is converted to concentration units by multiplying by the ELV. This is multiplied by the maximum pressure deviation from the average value and converted to a standard uncertainty by dividing by the square root of 3.

b) Component standard uncertainty due to calibration gas

Assume the calibration gas has the same concentration as the ELV of 75mg/m<sup>3</sup> and has a specified uncertainty of 2%. This is a type B uncertainty in that the true concentration could be anywhere between 73.5 and 76.5mg/m<sup>3</sup>.

Standard uncertainty = (2/100) x 75/ √3 = 0.87mg/m<sup>3</sup>

In this case there is no sensitivity coefficient involved – an error in the calibration gas affects the reported measured concentration directly and proportionately (formally the sensitivity coefficient is 1.0).

Having identified all possible sources of uncertainty and quantified them we have completed our uncertainty budget for the problem. We now have to put the results together.

### 6.2. Determine the combined standard uncertainty and expanded uncertainty

There are simple rules for combining standard uncertainties based on the mathematics of the normal curve of error. If we have a series of component uncertainties  $u_1, u_2, u_3, \dots$  the combined uncertainty  $u_c$  is obtained from the sum of squares of the component uncertainties:

$$u_c^2 = u_1^2 + u_2^2 + u_3^2 + \text{etc}$$

Some of the component standard uncertainties will be determined experimentally and applied directly in the summation. The same applies to the calibration gas (example b above). Some will be in the form of the product of a sensitivity coefficient  $S$  and the uncertainty of an input quantity. For example, if there is uncertainty due to ambient temperature  $u = S_T u(T)$ , where  $u(T)$  is the standard uncertainty of the temperature.

For manual methods the dependence on temperature, pressure and volume is defined by the analytical function and the sensitivities are mathematically defined by partial differentiation of the equations. In this document the use of partial differentiation is avoided but fortunately the results for most cases are simple. Suppose a measurement  $X$  depends on three input quantities  $a$ ,  $b$  and  $d$ , each of which has associated uncertainty  $u_a$ ,  $u_b$  and  $u_d$ . Then if  $X$  is obtained by addition or subtraction absolute values of component uncertainties are combined as follows:

$$X = a + b + d$$

$$u_x^2 = u_a^2 + u_b^2 + u_d^2$$

If  $X$  is obtained by multiplication or division, relative or percentage values of component uncertainties are combined:

$$X = \frac{a \times b}{d}$$

$$\frac{u_x^2}{X^2} = \frac{u_a^2}{a^2} + \frac{u_b^2}{b^2} + \frac{u_d^2}{d^2}$$

As can be seen, the sensitivity for  $a$  is  $X/a$ , for  $b$  is  $X/b$  etc.

These relationships are used in section 4 below.

For minor component uncertainties, when one component uncertainty is greater by a large factor than the others, the smaller ones can be ignored. A factor of four is generally sufficient.

By combining all the component standard uncertainties we obtain the combined uncertainty  $u_c$  for the measurement. It is then a simple step to multiply by the coverage factor  $k$  to obtain the expanded uncertainty, which for clarity is always written as an upper case quantity:

$$U_c = k u_c \quad \text{with } k = 2 \text{ for 95\% confidence}$$

Often  $U_c$  will be calculated in concentration units and then expressed as a percentage by dividing by the ELV since that is the form which the standard reference methods require.

Alternatively the whole calculation may be done in percentages of the ELV.

### 6.3 Uncertainty calculations for manual sampling

This section illustrates how the uncertainty is calculated for manual sampling but only covers the uncertainties associated with the input quantities, i.e. quantities that are related by equations to the final concentration.

The concentration of pollutant  $C_x$  is given by the ratio of the sampled mass of  $Q_x$  and the sampled gas volume corrected to standard conditions  $V_{std}$ :

$$C_x = Q_x / V_{std} \quad \text{eq. 1}$$

$$V_{std} = V_{T,p} \times \frac{T_{std}}{T} \times \frac{p}{p_{std}} \quad \text{eq. 2}$$

$T$  and  $p$  are the actual temperature and absolute pressure at the gas meter and  $V_{T,p}$  is the actual measured volume. Normally, a pressure relative to atmospheric pressure is measured by manometer and  $p$  is then estimated by  $p = p_{rel} + p_{atm}$ .

$T_{std} = 273.1\text{K}$ ,  $p_{std} = 101.3\text{KPa}$  and both are assumed to have negligible uncertainty.  $p_{rel}$ ,  $p_{atm}$  and  $V_{T,p}$  have uncertainties due to calibration of measuring instruments, repeatability of the readings, the resolution or readability of the device and possible drift.

In addition our final reported concentration may need to be corrected to a particular reference oxygen concentration  $O_{2\text{ref}}$ :

$$C_{x,O2ref} = C_x \times \frac{(21 - O_{2ref})}{(21 - O_{2meas})} \quad \text{eq.3}$$

$O_{2meas}$  also has an associated uncertainty.

Assuming that we can calculate the component standard uncertainties relating to each of the 6 input quantities:  $u(Q_x)$ ,  $u(V_{T,p})$ ,  $u(p_{rel})$ ,  $u(p_{atm})$ ,  $u(T)$  and  $u(O_{2meas})$  then we calculate the standard uncertainty of  $C_x$  by summing the squares of the component uncertainties multiplied in each case by the sensitivity coefficients. Using the principle that when dealing with products or quotients we sum the fractional (or percentage) quantities and when dealing with addition we sum the absolute quantities, then from equations 1 and 2:

$$\frac{u^2(C_x)}{C_x^2} = \frac{u^2(Q_x)}{Q_x^2} + \frac{u^2(V_{T,p})}{V_{T,p}^2} + \frac{u^2(T)}{T^2} + \frac{u^2(p_{rel})}{(p_{rel} + p_{atm})^2} + \frac{u^2(p_{atm})}{(p_{rel} + p_{atm})^2} \quad \text{eq.4}$$

(This is the same as writing  $u^2(C_x)$  as the sum of terms with sensitivities  $C_x/Q_x$ ,  $C_x/V_{T,p}$ ,  $C_x/T$ , etc).

The addition of the uncertainty due to the oxygen uncertainty in the correction factor gives:

$$\frac{u^2(C_{x,O2ref})}{C_{x,O2ref}^2} = \frac{u^2(C_x)}{C_x^2} + \frac{u^2(O_{2meas})}{(21 - O_{2meas})^2} \quad \text{eq.5}$$

We can now apply these to the most common sampling situations.

For particle sampling the collected mass  $Q_x$  is obtained from weighing the filter before and after sampling and weighing the residue from the probe washings. Four balance readings are involved with uncertainties associated with the calibration of the balance, repeatability of the reading and drift.

For speciated volatile organic compounds by adsorption tube,  $Q_x$  for any species will involve uncertainties in the efficiency of sample recovery from the tube, whether by solvent extraction or thermal desorption. Added to that is the uncertainty of the analysis which is usually performed by gas chromatography.

For wet chemical absorption  $Q_x$  is obtained from the volume of the solution plus washings and the concentration of the analyte determined in the laboratory (e.g. chloride by ion chromatography). There are uncertainties associated with the liquid volume and the analytical result. For a detailed discussion see the hydrogen chloride standard BS EN 1911 (2010).

#### 6.4 Uncertainty calculations for instrumental gas analysis

This example for  $SO_2$  by infra-red analyser is taken from the Annex to EA TGN M21 (2008).

First we gather together the site specific information and then results of laboratory and field testing, which define the performance characteristics of the instrument. Then we are in a position to draw up our uncertainty budget by estimating the component uncertainties. These are combined to give the total combined uncertainty and then expanded using the usual coverage factor to give the overall uncertainty at 95% confidence.

The site specific conditions are given in Table 6.1.

**Table 6.1: Example of site specific conditions**

Specific conditions	Value
Type of process	Incineration
Daily average emission limit value	75 mg.m <sup>-3</sup>
MCERTS certification range of the monitoring system	0 to 75 mg.m <sup>-3</sup>
Measurement range of the monitoring system	0 to 300 mg.m <sup>-3</sup>
Measurement technique	Infrared analyser with a sample drier
Atmospheric pressure variation	99-100 kPa
Sample pressure variation	100 ±5 kPa
Fluctuations of temperature compared to calibration temperature (298°C)	278 to 318 °C
Voltage variation	93V to 121V, 110V nominal voltage

The calculations are undertaken in this example at the daily ELV, which is also the MCERTS certification range. This is because of the context of TGN M21, which is to demonstrate that a particular instrument meets the criteria for equivalence with the European (manual) standard reference method (i.e. BS EN 14791).

The performance characteristics are shown in Table 6.2.

**Table 6.2: Example performance characteristics**

Performance characteristics	Performance criteria (percentage of the certification range)	Results laboratory and field tests (percentage of the certification range)
Response time	≤180s	120s
Lack of fit	≤±2%	±0.7%
Zero drift	≤±2%/24h	±0.01%/24h
Span drift	≤±2%/24h	±1%/24h
Sensitivity of the sample volume flow or of the sample pressure	≤±1%	±0.02%/kPa
Sensitivity to atmospheric pressure	≤±3%	±0.3%/kPa
Sensitivity of the ambient temperature	≤±3%/10K	±1%/10K
Sensitivity of electric voltage at span level	≤±2%/10V	±0.6%/10V
Interferents	≤±4%	≤±1.4%
Losses and leaks in the sample line	≤±5%	±1.2%
Standard deviation of repeatability in laboratory at zero	≤±0.2%	±0.15%
Standard deviation of repeatability in laboratory at span level	≤±2%	±0.8%
Uncertainty of calibration gas	≤±2%	±2%

This Table contains the information needed to calculate the standard component uncertainties using the relationships defined earlier. These calculations are shown in Table 6.3, which is based on Table A3 in TGN M21, with the omission of the repeatability standard deviation at zero. Note that all the component calculations involve the root 3 factor except the repeatability terms, which are already statistically defined.

The combined uncertainty  $u_c$  is obtained as the square root of the sum of the squares of all the component uncertainty  $u$  values in the right hand column, from which:

$$u_c = 1.75 \text{ mg.m}^{-3}$$

The overall uncertainty  $U_c = 2 u_c = \pm 3.5 \text{ mgm}^{-3}$

This corresponds to ±4.7% of the ELV of 75mgm<sup>-3</sup>

Table 6.3: Results of uncertainty calculations

Performance characteristic	Standard Uncertainty	Value of standard uncertainty, mg/m <sup>3</sup>
Lack of fit	$u_{fit}$	$\frac{(0.7/100) \times 75}{\sqrt{3}} = 0.30$
Zero drift	$u_{0,dr}$	$\frac{(0.01/100) \times 75}{\sqrt{3}} = 0.004$
Span drift	$u_{s,dr}$	$\frac{(1/100) \times 75}{\sqrt{3}} = 0.43$
Sensitivity to interference	$u_i$	$\frac{(1.4/100) \times 75}{\sqrt{3}} = 0.61$
Sensitivity to the sample volume flow or to the sample pressure	$u_{spress}$	$\frac{(0.02/100) \times 75 \times 5}{\sqrt{3}} = 0.04$
Sensitivity to atmospheric pressure	$u_{apress}$	$\frac{(0.8/100) \times 75 \times (1/2)}{\sqrt{3}} = 0.17$
Sensitivity to ambient temperature	$u_{temp}$	$\frac{(1/100)}{10} \times 75 \times \sqrt{\frac{(318 - 298)^2 + (278 - 298)(318 - 298) + (278 - 298)^2}{3}} = 0.83$
Sensitivity to electrical voltage	$u_{volt}$	$\frac{(0.6/100)}{10} \times 75 \times \sqrt{\frac{(121 - 110)^2 + (93.5 - 110)(121 - 110) + (93.5 - 110)^2}{3}} = 0.34$
Repeatability in lab at span level	$u_{s,r}$	$(0.8/100) \times 75 = 0.6$
Losses and leaks in the sample line	$u_l$	$\frac{(1.2/100) \times 75}{\sqrt{3}} = 0.52$
Uncertainty of calibration gas	$u_{cal}$	$\frac{(2/100) \times 75}{\sqrt{3}} = 0.87$

## 6.5 Glossary of Terms and Definitions used in Section 6

### Uncertainty

Parameter associated with the result of a measurement that characterises the dispersion of the values that could reasonably be attributed to the measurand.

### Uncertainty budget

Calculation table combining all the sources of uncertainty according to ENV 13005 in order to calculate the overall uncertainty of the method at a specified value.

**Standard uncertainty, u**

Uncertainty of the result of a measurement expressed as a standard deviation, u

**Combined uncertainty, u<sub>c</sub>**

Standard uncertainty u<sub>c</sub> attached to the measurement result calculated by combination of several standard uncertainties according to GUM.

**Expanded uncertainty, U**

Quantity defining a level of confidence about the result of a measurement that may be expected to encompass a specific fraction of the distribution of values that could reasonably be attributed to a measurand.

$$U = k \cdot u$$

The expanded uncertainty is generally calculated with a coverage factor of k=2, and with a level of confidence of 95 %.

**Sensitivity coefficient**

Deviation of the result of measurement divided by the deviation of an influence quantity causing the change, if all other influence quantities are kept constant

This document was withdrawn on 19 December 2019.

## 7. Applying measurement uncertainties to periodic monitoring

The following measurement uncertainties are the **maximum** uncertainties the Environment Agency use to assess compliance of periodic measurement results against emission limit values specified in Permits.

**Table 7.1 Maximum measurement uncertainties (MU) for periodic monitoring**

Species	% uncertainty	MU source
PM	±15	Measurement uncertainty half the value given in directives for continuous emissions monitoring systems.
TOC	±15	
HCl	±30	BS EN 1911
CO	±6	BS EN 15058
NO <sub>x</sub>	±10	BS EN 14792
SO <sub>2</sub>	±20	BS EN 14791
HF	±30	Given the same uncertainty as HCl due to similar reactive nature and measurement technique
NH <sub>3</sub>	±30	
Cd & Tl	±15	Value based on a review of uncertainties applied by monitoring organisations
Hg	±15	
Other metals	±15	
Dioxins and furans / PCBs	±30	BS EN 1948
Speciated VOCs	±25	Value based on information in CEN/TS 13649 and a review of uncertainties applied by monitoring organisations
Generic wet chemistry methods (not listed above)	±25	Value based on uncertainties applied by monitoring organisations
Generic sorbent tube methods (not listed above)	±25	Value same as speciated VOCs, as the analysis and sampling, using occupational hygiene methods, is very similar
Generic analyser methods (not listed above)	±25	Value based on uncertainties applied by monitoring organisations
O <sub>2</sub>	±0.5	BS EN 14789. The standard states ±6%. It was developed for reference conditions of 11%, which gives an absolute value of approximately 0.5%.
H <sub>2</sub> O	±20	BS EN 14790

Normally we will use the uncertainty values reported by the organisation that carried out the measurement. However, if these are above the maximum values given below, we will use the maximum values. When uncertainties are above the maximum values, we will investigate why.

The values in Table 7.1 are applicable to the measurement uncertainties for results that are at or above the ELV.

If a reported result is above the ELV, we will assess the result for compliance by taking account of its measurement uncertainty. This is achieved by subtracting the measurement uncertainty from the measured value (see Box 7.1).

If after completing the assessment the result is still above the ELV, it is likely to be considered a breach of the ELV. However, if after completing the assessment the result is below the ELV, it is likely to be considered an approach to limit.

If the original reported result is below the ELV, the compliance assessment shown in Box 7.1 does not need to be carried out.

Please note the above provides general guidance on our approach to assessing compliance. Other factors may also be considered by us when assessing results for compliance (see Box 7.2).

#### **Box 7.1: Assessing compliance with the ELV**

1. Determine the measurement uncertainty:

$$\text{measurement uncertainty} = (\text{measured value} \times \% \text{ uncertainty}) / 100$$

Note: the measured value is already corrected to the permit reporting conditions.

2. Adjust the measured result by subtracting the measurement uncertainty:

$$\text{Adjusted value} = \text{measured value} - \text{measurement uncertainty}$$

3. Compare the adjusted data versus the appropriate emission limit value to assess compliance.

Example calculation:

Based on a measured value for particulates of 11 mg/m<sup>3</sup> (STP) a measurement uncertainty of 15% and an ELV of 10mg/m<sup>3</sup>.

Following the procedure above:

1.  $(11 \times 15) / 100 = 1.65 \text{ mg/m}^3$  measurement uncertainty
2.  $11 - 1.65 = 9.35 \text{ mg/m}^3$  adjusted value
3. Adjusted value is less than the ELV, therefore the measured value should be classified as an approach to limit rather than a breach.

Note: the measurement uncertainty is the expanded uncertainty at a 95% confidence interval.

**Box 7.2 Note on oxygen measurement uncertainty**

The overall uncertainty of a measurement for combustion processes that requires oxygen correction must include the uncertainty of the pollutant being measured, plus the uncertainty of the oxygen measurement and the uncertainty of the correction to a fixed oxygen reference value. Further information is provided below:

$$1) \text{ Oxygen correction factor} = \frac{21 - O_2\% \text{ reference}}{21 - O_2\% \text{ measured}}$$

$$2) \text{ Uncertainty of oxygen correction} =$$

$$\left( \frac{21 - O_2\% \text{ reference}}{21 - O_2\% \text{ measured} * 21 - O_2\% \text{ measured}} \right) * \text{uncertainty of } O_2 \text{ measurement}$$

$$3) \text{ Uncertainty of oxygen factor (\%)} =$$

$$(\text{Uncertainty of } O_2 \text{ correction} / \text{Oxygen correction factor}) * 100$$

$$4) \text{ Overall measurement uncertainty (mu) (\%)} =$$

$$\sqrt{\mu \text{ of the determinand}^2 + \mu \text{ of the oxygen correction factor}^2}$$

Example calculation based on a:

- Reference oxygen of 11%
- Measured oxygen of 13%
- Measurement uncertainty of oxygen measurement of 0.5% (absolute value – see Table 7.1))
- Measurement uncertainty of pollutant measured (e.g. particulates) of 15%

$$\text{Oxygen correction factor} = (21 - 11) / (21 - 13)$$

$$= 1.25$$

Measurement uncertainty of oxygen correction =

$$\left( \frac{21 - 11}{21 - 13 * 21 - 13} \right) * 0.5$$

$$= 0.0781$$

$$\text{Overall measurement uncertainty for the oxygen correction (\%)} = (0.0781 / 1.25) * 100$$

$$= 6.25\%$$

$$\text{Overall uncertainty for the measurement} = \sqrt{15^2 + 6.25^2}$$

$$= 16.25\%$$

Note1 : the measurement uncertainties in this example are the expanded uncertainties at a 95% confidence interval.

Note 2: the reported measurement uncertainty should be below the overall uncertainty (i.e. the uncertainty given in Table 7.1 plus the additional uncertainty from the oxygen correction).

## 8. List of abbreviations

List of abbreviations	
AAS	Atomic absorption spectroscopy
AFNOR	Association Francaise de Normalisation
AMS	Automated measuring system
AFS	Atomic Fluorescence Spectrometry
AM	Alternative method
AST	Annual surveillance test
ASTM	American Society for the Testing of Materials
BS	British Standard
BSI	British Standards Institute
CEMs	Continuous emission monitoring system
CEN	Comité Européen de Normalisation
COSHH	Control of Substances Hazardous to Health
CVAAS	Cold vapour atomic absorption spectrometry
DIN	Deutsches Institut für Normung
DIS	Draft International Standard
DMPDA	Dimethyl phenylenediamine
DOAS	Differential optical absorption spectroscopy
EC	European Commission
ECD	Electron capture detection
EDAX	Energy dispersive analysis by X-rays
ELV	Emission limit value
EN	European Standard
EU	European Union
FDIS	Final draft international standard
FID	Flame-ionisation detector
FPD	Flame-photometric detector
FSD	Full-scale deflection
FTIR	Fourier transform infrared spectrometry
GC	Gas chromatography
GC-FPD	Gas chromatography-flame photometric detection
GC-MS	Gas chromatography – mass spectrometry
HPLC	High-performance liquid chromatography
HSE	Health and Safety Executive
IC	Ion chromatography

<b>List of abbreviations (continued)</b>	
ICP	Inductively coupled plasma (spectroscopy)
IED	Industrial Emissions Directive
IMS	Ion mobility spectrometry
IPPC	Integrated Pollution Prevention and Control
IR	Infrared
ISC	Intersociety Committee
ISE	Ion-selective electrode
ISO	International Standards Organisation
LAAPC	Local Authority Air Pollution Control
LAQM	Local Air Quality Management
LOD	Limit of detection
MCERTS	The Environment Agency Monitoring Certification Scheme
MDHS	Method for the Determination of Hazardous Substances
MID	Method Implementation Document
MMMF	Man-made mineral fibres
MS	Mass spectrometry
MSW	Municipal solid waste
NDIR	Non-dispersive infrared spectrometry
NDUV	Non-dispersive ultraviolet spectrometry
NIOSH	National Institute of Occupational Safety and Health
NMVOCs	Non-methane volatile organic compounds
OES	Optical emission spectroscopy
OMA	Operator monitoring assessment
OSHA	Occupational Safety and Health Administration
OU	Odour units
PAHs	Polynuclear aromatic hydrocarbons
PCBs	Polychlorinated biphenyls
PID	Photo-ionisation detector
PM	Particulate matter
PM <sub>10</sub> , PM <sub>2.5</sub>	Particle fraction with diameter less than 10 µm or 2.5 µm
PPC Regulations	Pollution Prevention and Control Regulations
prEN	Draft European Standard
PUF	Polyurethane foam
QA	Quality assurance
QC	Quality control
Rsd	Relative standard deviation

<b>List of abbreviations (continued)</b>	
SCD	Sulphur chemiluminescence detector
SD	Standard deviation
SEM	Scanning electron microscopy
SRM	Standard reference method
SSP	Site-specific protocol
TD	Thermal Desorption
TDL	Tuneable diode laser
TEOM	Tapered element oscillating microbalance
TPM	Total particulate matter
TRS	Total reduced sulphur
UKAS	United Kingdom Accreditation Service
US EPA	United States Environmental Protection Agency
US EPA CT	United States Environmental Protection Agency Conditional Test
UV	Ultraviolet
VDI	Verein Deutscher Ingenieure (German national standards body)
VOC	Volatile organic compound
WID	Waste incineration directive
XAD/XAD-2	Trade name for a polystyrene adsorbent resin

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