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JRC Reference Report on Monitoring of Emissions to Air and Water from IED installations

Industrial Emissions Directive 2010/75/EU
(Integrated Pollution Prevention and Control)

JOINT RESEARCH CENTRE
Directorate Growth and Innovation
Circular Economy and Industrial Leadership Unit
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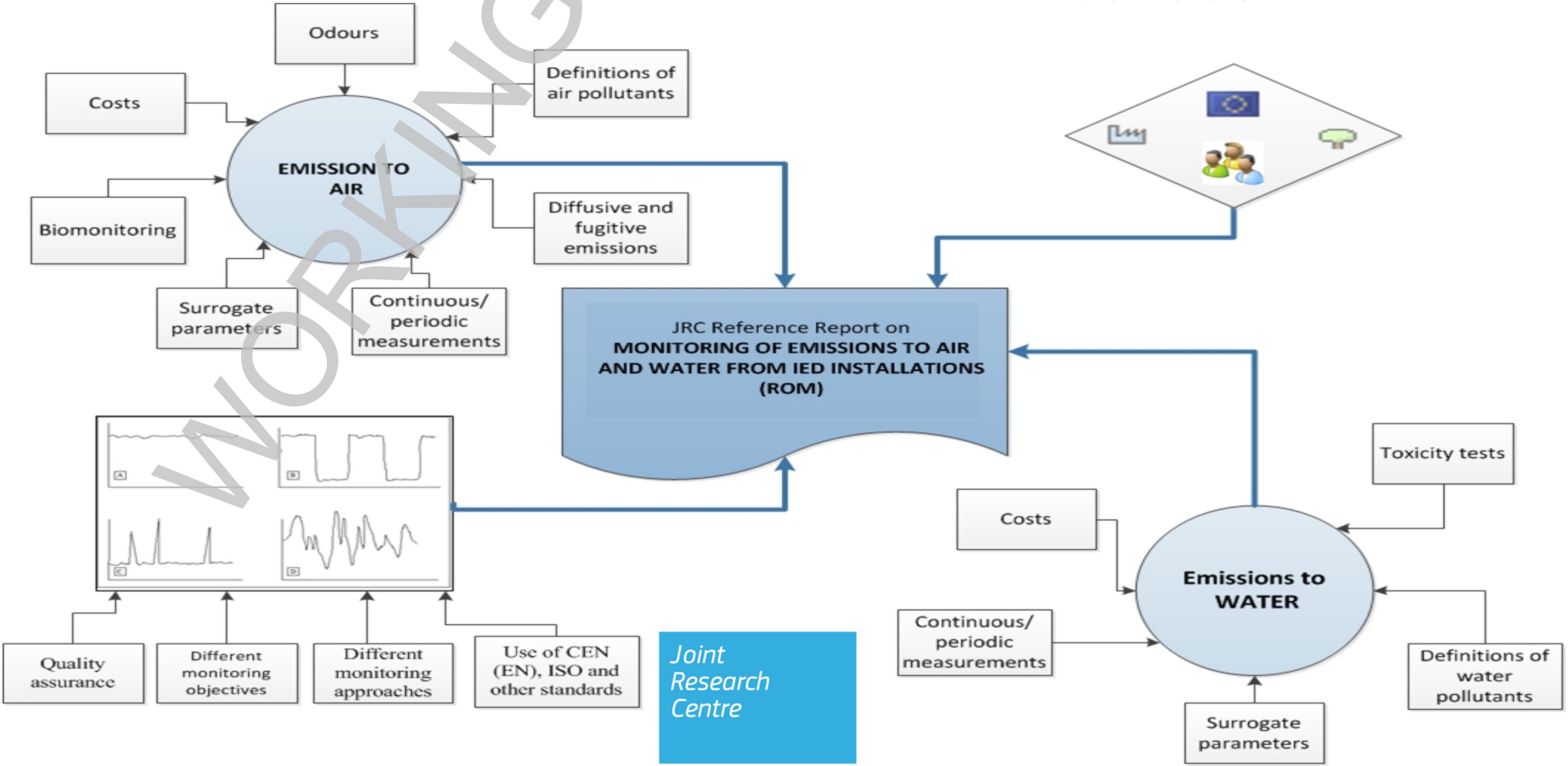

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This document is one from the series of documents listed below (at the time of writing, the following documents have been drafted):

Reference Document on Best Available Techniques	**Code**
Ceramic Manufacturing Industry	CER
Common Waste Water and Waste Gas Treatment/Management Systems in the Chemical Sector	CWW
Emissions from Storage	EFS
Energy Efficiency	ENE
Ferrous Metals Processing Industry	FMP
Food, Drink and Milk Industries	FDM
Industrial Cooling Systems	ICS
Intensive Rearing of Poultry and Pigs	IRPP
Iron and Steel Production	IS
Large Combustion Plants	LCP
Large Volume Inorganic Chemicals – Ammonia, Acids and Fertilisers	LVIC-AAF
Large Volume Inorganic Chemicals – Solids and Others Industry	LVIC-S
Large Volume Organic Chemical Industry	LVOC
Management of Tailings and Waste-rock in Mining Activities	MTWR
Manufacture of Glass	GLS
Manufacture of Organic Fine Chemicals	OFC
Non-ferrous Metals Industries	NFM
Production of Cement, Lime and Magnesium Oxide	CLM
Production of Chlor-alkali	CAK
Production of Polymers	POL
Production of Pulp, Paper and Board	PP
Production of Speciality Inorganic Chemicals	SIC
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Reference Document	
Economics and Cross-media Effects	ECM
Monitoring of Emissions to Air and Water from IED installations	*ROM*

Electronic versions of draft and finalised documents are publicly available and can be downloaded from http://eippcb.jrc.ec.europa.eu/.

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The EIPPCB authors of the ROM were Mr Thomas Brinkmann, Mr Ralf Both and Ms Bianca-Maria Scalet.

This document was drafted by the EIPPCB on the basis of:

1. the reference document on the General Principles of Monitoring (MON REF [3, COM 2003], which this document replaces;
2. general available information on the monitoring of emissions;
3. the experiences derived from the exchange of information between stakeholders under Article 13 of the Industrial Emissions Directive (IED) [24, Directive 2010/75/EU 2010]; and
4. an exchange of information between an expert group on monitoring (MEG) which was set up for the purpose of drawing up this document.

The following members of the MEG played a particularly active role in the exchange of information:

- EU Member States: Austria, Belgium, Czech Republic, Denmark, Finland, France, Germany, Greece, Ireland, the Netherlands, Spain, Sweden and the United Kingdom;
- Industrial associations: British Glass, Cefic, CEMBUREAU, Cerame-Unie, CEWEP, CONCAWE, ESWET, EuLA, EURELECTRIC, EUROFER, Eurometaux, ECGA/EUROMINES;
- Non-governmental organisation promoting environmental protection: EEB.

Furthermore, the Technical Committees CEN/TC 230 'Water analysis' and CEN/TC 264 'Air quality' of the European Committee for Standardization actively participated in the working process and provided, among others, information to draft the Annexes on standards and methods for the measurement of emissions to air (A.1) and water (A.2), respectively.

The whole EIPPCB team contributed to the drafting and peer review of this document.

PREFACE

The European Commission decided in 2012 to develop a JRC Reference Report on Monitoring (ROM) under the Industrial Emissions Directive (IED) [24, Directive 2010/75/EU 2010]. The ROM is based on the revision of the reference document on the General Principles of Monitoring (MON REF [3, COM 2003]), which was adopted by the Commission in July 2003 under the IPPC Directive 96/61/EC (subsequently repealed and replaced by Directive 2008/1/EC).

The ROM replaces the MON REF, although it does not cover all of its topics, in particular compliance assessment.

The ROM summarises general and commonly available information collected by the European IPPC Bureau from various sources, such as international and national standards, as well as scientific publications. Some Member States also provided special contributions summarising their monitoring practices. All the information gathered, unless protected by copyright law, was made available to a Monitoring Expert Group (MEG), which carried out an exchange of views. All contributions are gratefully acknowledged.

The ROM does not interpret the IED [24, Directive 2010/75/EU 2010]. According to Article 16(1) of the IED, monitoring requirements in permits shall be based on the conclusions on monitoring as described in the BAT conclusions. In this framework, the ROM can act as a reference to enhance the consistent application of the BAT conclusions and the Directive by providing additional guidance on monitoring standards, strategies and practices.

This document aims to inform those involved in implementing the Directive about the general aspects of emission monitoring, and it also brings together information on monitoring that may be of use in the drawing up or review of BREFs and their BAT conclusions.

Since monitoring practices change over time, this document will be reviewed and updated as appropriate. All comments and suggestions should be made to the European IPPC Bureau at the following address:

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JRC Reference Report on Monitoring of emissions to air and water from IED installations

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1 INTRODUCTION

The monitoring of emissions to air and water represents an important element in preventing and reducing pollution from industrial installations and in ensuring a high level of protection of the environment taken as a whole. Therefore, the Industrial Emissions Directive (IED) [24, Directive 2010/75/EU 2010] addresses the monitoring of emissions in a number of instances, including the following:

- BAT conclusions contain the emission levels associated with the best available techniques (BAT) and the associated monitoring (IED Article 3(12)).
- The exchange of information on BAT for the drawing up and review of BREFs shall address the techniques used and the associated monitoring (IED Article 13(2)(b)).
- Permits shall contain suitable emission monitoring requirements (IED Article 14(1)(c) and (d)).
- Monitoring requirements in permits shall, where applicable, be based on the conclusions on monitoring as described in the BAT conclusions (IED Article 16(1)).
- The competent authority shall make publicly available the results of emission monitoring as required under the permit conditions and held by the competent authority (IED Article 24(3)(b)).

This JRC Reference Report on Monitoring (ROM) summarises information on the monitoring of emissions to air and water from IED installations, thereby providing practical guidance for the application of the BAT conclusions on monitoring in order to help competent authorities to define monitoring requirements in the permits of IED installations. Moreover, the information and recommendations provided by this document may help the Technical Working Groups (TWGs) to derive BAT conclusions during the drawing up and review of BREFs.

2 SCOPE

The aim of this JRC Reference Report on Monitoring (ROM) is twofold:

- to inform competent authorities and operators of the general aspects of the monitoring of emissions from installations under the scope of the IED;
- to bring together information on monitoring of emissions that may be of use to TWG members including the European IPPC Bureau when working on sectoral BREFs and their BAT conclusions.

In particular, this document covers topics which are related to the monitoring of emissions in connection with Articles 14(1)(c) and 16 of the IED.

This document addresses general principles and other relevant aspects concerning the monitoring of emissions and associated parameters that are the basis for deciding on the monitoring approach and frequency, as well as on the gathering, treatment and reporting of monitoring data. This document aims to promote the accuracy, reliability, representativeness and comparability of monitoring data from industrial installations.

This document covers the following topics:

- general aspects of monitoring such as:
    - monitoring objectives;
    - monitoring approaches including the choice of pollutants and parameters to monitor;
    - quality assurance, including personnel and laboratory qualifications, use of EN, ISO and other standards, as well as measurement uncertainty;
    - monitoring approaches for other than normal operating conditions;
- monitoring of emissions to air (including odours, diffuse and fugitive emissions, biomonitoring) and water (including toxicity tests), using continuous or periodic measurements, covering:
    - measurement planning;
    - monitoring frequency;
    - measurement, expression, and documentation of auxiliary parameters;
    - data treatment;
    - reporting;
    - costs of monitoring;
    - monitoring using indirect methods such as surrogate parameters, mass balances and Predictive Emission Monitoring Systems (PEMS).

The following topics are **not covered** by this document:

- Process monitoring: Monitoring of process parameters in order to confirm, using process control and optimisation techniques, that the plant performance is within the range considered appropriate for its correct operation. If required, this is covered by sectoral BREFs.
- Monitoring of waste, except waste water and waste gas.
- Detailed information on monitoring methods: Monitoring methods are described in EN standards developed by CEN, which is, according to Directive 98/34/EC, the European organisation for the planning, drafting and adoption of European Standards (together with CENELEC and ETSI) [25, EC 1998].
- Specific monitoring considerations for industrial sectors: Industry-specific aspects are covered by sectoral BREFs.
- Monitoring of greenhouse gases under the EU Emissions Trading System: This is covered by Commission Regulation (EU) No 601/2012 on the monitoring and reporting of greenhouse gas emissions pursuant to Directive 2003/87/EC of the European Parliament and of the Council [130, EU 2012].

- Reporting according to the European Pollutant Release and Transfer Register (E-PRTR): This is covered by the Guidance Document for the implementation of the European PRTR [131, COM 2006].
- Monitoring of the environmental quality, such as ambient air or surface water quality.
- Inspection of installations.
- Assessing compliance with emission limit values (ELVs).

3 GENERAL ASPECTS OF MONITORING

3.1 Definitions

Monitoring in this document means a systematic surveillance of the variations of a certain chemical or physical characteristic of an emission, discharge, consumption, etc. Monitoring is based on repeated measurements or observations, at an appropriate frequency in accordance with documented and agreed procedures, to obtain the intended information on emissions. This information may range from simple visual observations (e.g. visible emissions to air from doors, flanges or valves, or the alteration of the colour of a discharge) to precise numerical data (e.g. concentration or load of a pollutant).

Monitoring does not necessarily mean measurement even though the terms are often interchanged in common usage. In this document they have the following meanings:

- Measuring involves a set of operations to determine the value of a quantity, and therefore implies that an individual quantitative result is obtained.
- Monitoring can include the measurement of the value of a particular parameter and also the follow-up of variations in its value (so as to allow the true value of the parameter to be controlled within a required range). Occasionally, monitoring may refer to the simple surveillance of a qualitative parameter without numerical values, i.e. without measuring. Monitoring can also consist of a combination of measurements and calculations (see Section 3.3.3.3).

3.2 Possible objectives of monitoring

The objectives of monitoring are many and diverse. For example, monitoring can be applied to:

- assess compliance with permit requirements;
- find the optimal balance between process yield, energy efficiency, resource input and emission levels;
- analyse the causes of certain types of emission behaviour (e.g. to detect reasons for variations in emissions under normal operating conditions or other than normal operating conditions);
- predict the emission behaviour of an installation, e.g. after operational conversions, operational breakdowns or an increase in capacity;
- check the performance of abatement systems;
- determine the relative contribution of different sources to the overall emissions;
- provide measurements for safety checks;
- report emissions for specific inventories (e.g. local, national and international, such as the E-PRTR);
- provide data for assessing environmental impacts (e.g. for input to models, pollutant load maps, assessment of complaints);
- set or levy environmental charges and/or taxes.

Operators and competent authorities should have a clear understanding of the objectives of monitoring before monitoring begins. The objectives and the monitoring system should also be clear for any third party involved, including contractors, e.g. accredited testing laboratories, and other possible users of the monitoring data (e.g. land-use planners, public interest groups and central government). The objectives should be clearly stated and be taken into account in the monitoring plan and in the reporting of the monitoring results (see Sections 4.3 and 5.3).

A clearly defined monitoring objective, an appropriate monitoring plan based on standardised methods (e.g. EN standards) and a quality assurance system, e.g. in accordance with EN ISO/IEC 17025:2005 [1, CEN 2005], help to ensure reliable, representative and comparable monitoring data.

Such monitoring information may then be used in the drawing up and review of BREFs, and in particular in defining BAT and BAT-associated performance levels (BAT-AEPLs) including emission levels associated with the BAT (BAT-AELs). In order to adequately assess the performance of techniques, a great amount of data, gathered over a long time period (e.g. one or more years) is generally required, so as to ensure that the data collected are representative.

3.3 General approaches to decide on an appropriate monitoring regime

3.3.1 Overview

In principle there are various approaches that can be taken to monitor a specific parameter, although some may not be appropriate for particular applications. In general, the approaches can be classified into two main groups: direct measurements (see Section 3.3.3.2) and indirect methods (see Section 3.3.3.3).

When choosing one or a combination of these approaches for monitoring, a balance is sought between the availability of the method, the reliability, representativeness and comparability of the results, the level of confidence, the costs and the environmental benefits.

The selection of the parameter(s) to be monitored depends on the processes, the raw materials, fuel and other substances used, the key environmental issues and the techniques used to prevent or reduce emissions. It is efficient if the parameter chosen to be monitored also serves to control the operation of the plant. The frequency at which a given parameter is monitored varies widely depending on the needs, the risks to the environment and the monitoring approach taken [139, Saarinen 1999].

Emission monitoring should provide adequate information on their variations in time. For this purpose, not only are the specific pollutants monitored, but also other parameters that may serve to qualify the emissions such as reference conditions (e.g. temperature, pressure; see Sections 4.3.2.5 and 4.3.3.11), air and water flow, raw material input, and production load. Usually, the number of parameters to be monitored exceeds the number indicated in a permit or in the BAT conclusions for a given industrial sector. All parameters necessary to describe emissions and the related circumstances should be mentioned in the measurement or sampling plan and should be part of the measurement report.

To decide on an appropriate monitoring regime, a risk-based approach may be applied as described in the following section, especially in cases where the monitoring regime is not already defined in existing laws or regulations.

3.3.2 Risk-based approach

It is best practice to assess the overall risk posed by the (potential) emissions from an installation to the environment and to match the frequency and scope of the monitoring regime to this risk. These aspects of the monitoring programme may be determined by considering and combining several individual risk factors. These may be assessed, for example, as trivial, significant or critical. Monitoring requirements may then be judged to range from minimal for trivial cases to comprehensive for critical cases. Examples of the risk factors to be considered include the following [2, IMPEL 2001]:

- the size and type of the installation, which may determine its environmental impact;
- the complexity of sources (number and diversity, source characteristics (e.g. area sources, channelled emissions, peak emissions));
- the complexity of the process, which may increase the number of potential malfunctions;
- the frequency of process switching, particularly at multi-purpose chemical plants;
- possible hazards posed by the type and amount of input feedstock and fuel materials;
- possible environmental and human health effects resulting from emissions, taking into account the pollutant types and their rates of release, and including the potential failure of abatement equipment;
- the stability of the emission;
- the proximity of the emission source to sensitive environmental receptors;

- the presence of natural hazards, such as geological, hydrological, meteorological or marine factors;
- past performance of the installation and its management;
- the degree of public concern, particularly with regard to contentious installations.

An example of how some of these risk factors can be classified into different risk levels is given in Table 3.1. Individual risk factors are classified into two groups representing the probability of an event and its impact.

Table 3.1: Example of risk factors influencing the likelihood of exceeding the ELV and the consequences of exceeding the ELV in the case of emissions to water

Risk factor	Risk level		
	Low	**Medium**	**High**
Risk factors influencing the likelihood of exceeding the ELV			
Number of individual sources contributing to the emission	Single	Several (2 to 5)	Numerous (> 5)
Stability of operating conditions	Stable	Occasionally unstable	Unstable
Buffer capacity of effluent treatment	Sufficient to cope with upsets	Limited	None
Treatment capacity of the source for excess emissions	Able to cope with peaks (by stoichiometric reaction, oversize, spare treatment)	Limited capabilities	No capabilities
Potential for mechanical failure due to corrosion	No or limited corrosion	Normal corrosion, covered by design	Corrosion conditions still present
Flexibility in product output	Single dedicated production unit	Limited number of product grades	Many product grades, multi-purpose plant
Inventory of hazardous substances	Not present or production-dependent	Significant (compared to ELV)	Large inventory
Maximum possible emission load (i.e. concentration × flow rate)	Significantly below the ELV	Around the ELV	Significantly above the ELV
Risk factors influencing the consequences of exceeding the ELV			
Duration of potential failure	Short (< 1 hour)	Medium (1 hour to 1 day)	Long (> 1 day)
Acute effect of the substance(s)	No	Potential	Likely
Location of the installation	Industrial area	Safe distance between industrial and residential areas	Residential area nearby
Dilution ratio in the receiving water body	High (e.g. above 1 000)	Normal	Low (e.g. less than 10)

Source: [3, COM 2003]

Any risk evaluation should take local conditions into consideration, including risk factors that may not be reflected in Table 3.1. The final assessment of likelihood or consequences should be based on the combination of all factors, not on a single one, taking into account the specific legal requirements of the Member State or the region.

The results of the assessments of these factors can then be combined and represented in a simple diagram plotting the likelihood of exceeding the ELV against the consequences of exceeding that ELV (Figure 3.1). The combinations of these factors can be decided on a case-by-case basis and in such a way that more weight may be given to the most relevant factors. The location of the result on the risk-based grid, as shown in Figure 3.1, determines the appropriate monitoring regime conditions for routine process operation [3, COM 2003].

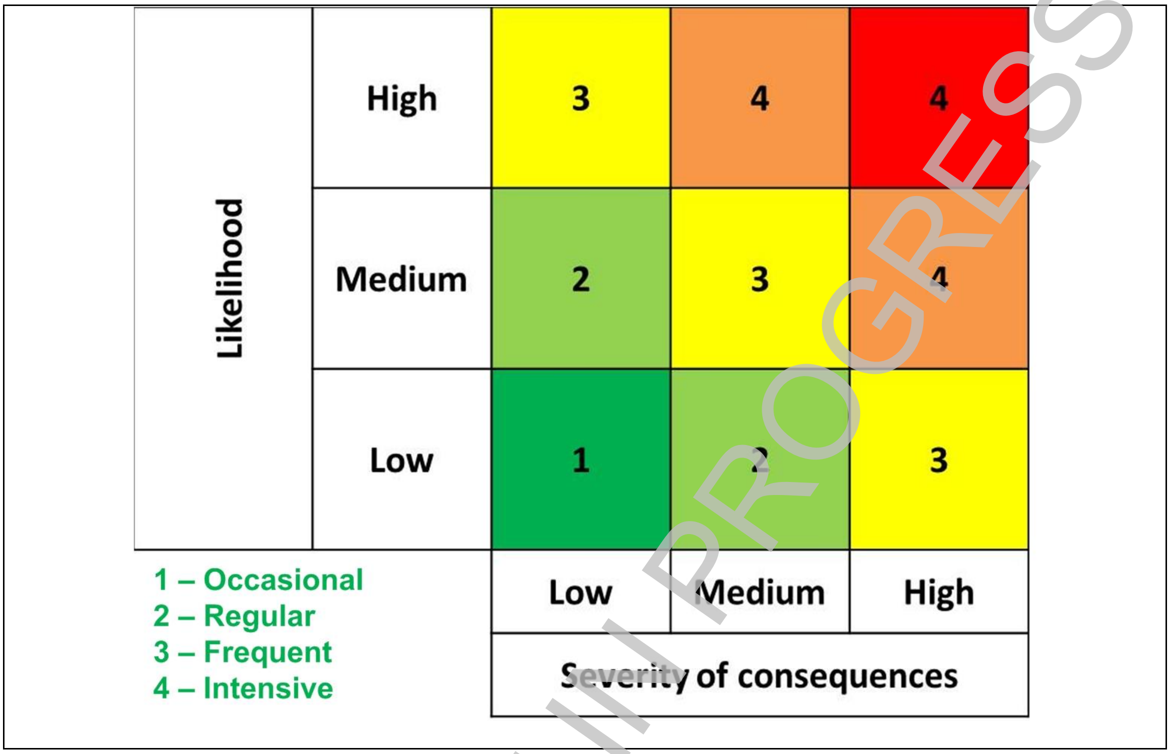


Figure 3.1: **Monitoring regime depending on the risk of exceeding the ELV**

The corresponding monitoring regimes for this water-related example based on 24-hour flow-proportional composite samples or spot samples, as relevant (see Section 5.3.5), are [3, COM 2003]:

1. **Occasional** - four times per year up to once per month.
2. **Regular (to frequent)** - once per month up to once per week and/or spot samples in special cases.
3. **(Regular to) Frequent** - once per week up to once per day and/or spot samples in special cases.
4. **Intensive** - once per day or continuous or high frequency (3 to 24 spot samples per day, where appropriate).

In case of emissions to air, the approach given in Table 3.1 needs to be adapted by taking into account typical factors such as the capacity and functioning of the abatement system, the possibility of diffuse emissions, or the risk of accidents causing unexpected emissions. The corresponding monitoring regimes for emissions to air have to be adapted as well, and could be differentiated as follows:

1. **Occasional** - periodic measurements once every three years up to once per year, possibly accompanied by indicative monitoring between measurements.
2. **Regular (to frequent)** - periodic measurements once per year up to twice per year, possibly accompanied by indicative monitoring between measurements.
3. **(Regular to) Frequent** - continuous or periodic measurements (several times per year).
4. **Intensive** - continuous measurements, when AMS are available.

Section 4.3 describes in detail continuous and periodic measurements of emissions to air and associated indicative monitoring.

An example of an existing risk-based approach can be found in the Netherlands Emissions Guidelines for Air [4, NL 2012]. It is based on the increase in emissions upon failure of an emission abatement technique or process-integrated measure and is expressed as a failure emission. The harmfulness of an emission that occurs additionally when an emission abatement technique or process-integrated technique fails is expressed as a mass flow check value. This value is based on a classification system and varies for different substances according to their environmental harmfulness. By dividing the failure emission by the mass flow check value, a failure factor F is determined. The failure factor F is an indicator of the stringency of the failure of the emission abatement technique, and so, by calculating the failure factor F, the monitoring regime and its stringency can be determined. Different monitoring regimes of increasing stringency can be applied, including the following:

- emission-relevant parameters, which are measurable quantities directly or indirectly related to the emissions to be assessed;
- periodic measurements; and
- continuous measurements.

3.3.3 Direct measurements and indirect methods

3.3.3.1 Overview

Several approaches can be taken to monitor a specific parameter, including [2, IMPEL 2001]:

- direct measurements (see Section 3.3.3.2);
  - continuous measurements (see Section 3.3.3.2.1.1);
  - periodic measurements (see Section 3.3.3.2.1.2);
  - campaign measurements (see Section 3.3.3.2.2);
- indirect methods (see Section 3.3.3.3):
  - surrogate parameters (see Section 3.3.3.3.1);
  - mass balances (see Section 3.3.3.3.2);
  - emission factors (see Section 3.3.3.3.3);
  - other calculations (see Section 3.3.3.3.4).

In principle, direct measurements (specific quantitative determination of the emitted compounds) are preferred, usually because they are more straightforward, but they are not necessarily always more accurate. However, in cases where direct measurements are complex, costly and/or impractical, other methods could be more appropriate. For instance, when the use of surrogate parameters provides an equally good assessment of the actual emission compared to a direct measurement, these methods may be preferred for their simplicity and economy. In each situation, the necessity for, and the added value of, direct measurements should be weighed against the possibility of simpler verification using surrogate parameters or other methods (such as mass balances).

When methods other than direct measurements are used, the relationship between the method used and the parameter of interest should be established, demonstrated and well documented on a regular basis.

In many cases, the IED and national regulations impose requirements on the monitoring approach to be used for a particular installation, e.g. the compulsory use of relevant standards or the requirement for continuous measurements. Moreover, provisions on monitoring are generally a part of the BAT conclusions, which according to Article 14(3) of the IED shall be the reference for setting permit conditions.

When deciding on the monitoring approach, the following considerations are important:

- Fitness for purpose, i.e. is the method suitable to achieve the objectives (see Section 3.2)?

- Legal requirements, i.e. is the method in line with EU or national legislation?
- Facilities and expertise, i.e. are the facilities and expertise available for applying the method adequately, e.g. qualified laboratory with suitable technical equipment and experienced staff (see Section 3.4.2)?

In some cases, a certain monitoring approach may not be available for the parameter of interest. The choice depends on several factors, including the nature and quantity of the emission, the likelihood and consequences of exceeding the ELV (as explained in Section 3.3.2), the required accuracy, costs, simplicity, rapidity, and reliability.

3.3.3.2 Direct measurements

3.3.3.2.1 Regular measurements

3.3.3.2.1.1 Continuous measurements

Two types of continuous measurement techniques are generally considered (for more details see Sections 4.3.2 and 5.3.4) [3, COM 2003]:

- Fixed *in situ* (or in-line) continuous reading instruments. These instruments do not need to withdraw any sample to analyse it and are usually approved for specific applications. There are two possible designs: The measuring cell is either placed in the duct, pipe or stream itself or the transmitter and the receiver are placed outside the stack opposite each other. Regular maintenance and calibration of these instruments is essential.
- Fixed on-line (or extractive) continuous reading instruments. These instruments continuously extract samples from the stream along a sampling line and transport them to an on-line measurement station, where the samples are analysed continuously. The measurement station may be far away from the stream, and therefore care is taken so that the sample integrity is maintained along the sampling line. This type of equipment often requires pretreatment of the sample.

3.3.3.2.1.2 Periodic measurements

The following types of periodic measurement techniques are generally considered (for more details see Section 4.3.3 and 5.3.5) [3, COM 2003]:

- Portable instruments used for series of measurements. These instruments are carried to and set up at the measurement site. Normally a probe is introduced at an appropriate measurement port to measure *in situ* or to sample the stream and analyse it on-line. These instruments are appropriate for checking emission concentrations and also for calibrating other monitoring equipment.
- Laboratory analysis of samples taken by fixed on-line samplers. These samplers withdraw the sample continuously and collect it in a container. From this container, a portion is then analysed in the laboratory, giving an average concentration over the total volume accumulated in the container. The amount of sample withdrawn can be proportional to time or to flow and has to be sufficient for the applied measurement technique.
- Laboratory analysis of spot samples. A spot sample is a sample taken from the sampling point at a certain time over a certain time period. The sample is then analysed in the laboratory, providing an average over the sampling period, which is representative of the time at which the sample was taken. The amount of sample taken has to be sufficient for the applied measurement technique.

3.3.3.2.1.3 Continuous versus periodic measurements

Continuous measurement techniques have an advantage over periodic measurement techniques as they provide a larger amount of data that can facilitate statistical analysis and can highlight periods of different operating conditions. Continuous measurement techniques, though, may also have some drawbacks, e.g. they need to be calibrated regularly with periodic standard reference methods. Advantages and disadvantages of continuous and periodic measurements are covered in more detail in Sections 4.3 and 5.3, together with recommendations on their uses.

3.3.3.2.2 Campaign measurements

One special type of measurements are campaign measurements, which are carried out in response to a need or an interest in obtaining more comprehensive information than that generally provided by routine monitoring, which is mainly performed for compliance assessment. Campaign measurements usually involve relatively detailed and sometimes extensive and expensive measurements which are usually not justified to be carried out on a regular basis [2, IMPEL 2001].

Situations in which campaign measurements might be carried out include the following [2, IMPEL 2001], [3, COM 2003]:

- a new measurement technique is to be introduced and needs to be validated;
- a fluctuating parameter is to be investigated in order to identify the root causes of the fluctuation or to assess opportunities to reduce the range of the fluctuations;
- a surrogate parameter is to be defined and correlated with process parameters or other emission values;
- the actual compounds/substances of an emission are to be determined or evaluated in addition to the regular measurement of a sum parameter;
- the ecological impact of an emission is to be assessed by ecotoxicological analyses;
- volatile organic compounds are to be determined for odour;
- measurement uncertainties are to be evaluated;
- a new process is to be started without previous knowledge of emission patterns;
- a preliminary study is necessary to design or improve techniques for the prevention or abatement of emissions (treatment systems);
- the total emissions (of a substance) from several sources (types and characteristics) need to be determined;
- the relative emission contribution of a pollution source to the total emissions needs to be identified (graduation emission sources);
- a cause-effect relationship is to be investigated.

3.3.3.3 Indirect methods

3.3.3.3.1 Surrogate parameters

Surrogate parameters are measurable or calculable quantities which can be closely related, directly or indirectly, to conventional direct measurements of pollutants, and which may therefore be monitored and used instead of the direct pollutant values for some practical purposes [2, IMPEL 2001]. The use of surrogate parameters either individually or in combination, or also in combination with direct measurements, may provide a sufficiently reliable picture of the nature and quantity of the emission [3, COM 2003].

The surrogate parameter is normally an easily and reliably measured or calculated parameter that may indicate various aspects of the process, such as throughput, energy consumption, temperatures, volumes of residue (water, air, solid waste) or emission concentrations (e.g. total volatile organic carbon (TVOC) as a surrogate parameter for organic solvents). The surrogate parameter may provide an indication of whether another parameter is within a desired range provided that the surrogate parameter is maintained within a certain range [3, COM 2003]. In specific cases, it may be possible to achieve more reliable results if the surrogate parameter is combined with direct measurements.

Whenever a surrogate parameter is proposed to determine the value of another parameter of interest, the relationship between the surrogate parameter and the parameter of interest needs to be clearly identified, demonstrated and documented (e.g. via campaign measurements as described in Section 3.3.3.2.2). In addition, traceability of the parameter's evaluation on the basis of the surrogate parameter is needed [3, COM 2003].

A surrogate parameter is only likely to be useful for monitoring purposes if [2, IMPEL 2001], [3, COM 2003]:

- it is closely and consistently related to the pollutant to be measured;
- it is more economical or easier to monitor than to carry out direct measurements, or if it can provide more frequent information;
- it is capable of being related to specified limits;
- the operating conditions when surrogate parameters are monitored match the conditions when direct measurements are required;
- its use is generally supported and approved by sufficient data; this implies that any extra uncertainty due to the surrogate parameter is insignificant for regulatory decisions;
- it is properly described, including regular evaluation and follow-up.

Key **advantages** of the use of surrogate parameters may include the following [2, IMPEL 2001], [3, COM 2003]:

- ease and reliability of measurements or calculations;
- reduced costs;
- higher monitoring frequency for the same or lower costs;
- higher number of measurement/sampling points for the same or lower costs;
- in certain cases, higher accuracy compared to direct measurements;
- possibility to detect other than normal operating conditions, e.g. combustion temperature changes to alert of a potential increase in dioxin emissions;
- less disruption to the process operation compared to direct measurements;
- more versatile usability, e.g. a temperature measurement may be useful to assess several issues such as energy efficiency, pollutant emissions, process operation and control of raw material;
- recovery of corrupted emission monitoring data.

Key **disadvantages** of the use of surrogate parameters may include the following [2, IMPEL 2001], [3, COM 2003]:

- calibration potentially more demanding than for direct measurements;
- restriction to a relative rather than an absolute value;
- validity potentially restricted to a certain range of operating conditions;
- potentially lower public confidence compared to direct measurements;
- in certain cases, lower accuracy compared to direct measurements;
- potential unsuitability for legal purposes.

Different categories of surrogate parameters may be distinguished on the basis of the strength of the relationship between the emission parameter of interest and the surrogate parameter (see Sections 4.4 and 5.4) [3, COM 2003]:

- Quantitative surrogate parameters give a reliable quantitative picture of the emission and can substitute direct measurements.

- Qualitative surrogate parameters give reliable qualitative information on the composition of the emission.
- Indicative surrogate parameters give information about the operation of an installation or process and therefore give an indicative impression of the emission.

The border between these different categories is to a certain extent ambiguous.

Surrogate parameters may be monitored periodically or continuously.

Examples for the different categories of surrogate parameters are given in Sections 4.4.1 and 5.4.1. Biological test methods are special surrogate parameters. They include biomonitoring to determine the effects of airborne pollutants on organisms including the impact caused by industrial activities (see Section 4.7) and toxicity tests to assess the possible hazardous character of waste water (see Section 5.5).

3.3.3.3.2 Mass balances

Mass balances can be used for an estimation of the emissions to the environment from an installation, process or piece of equipment. The procedure normally accounts for inputs, accumulations, outputs and the generation or destruction of the substance of interest, and the difference is accounted for as a release to the environment [141, Environment Australia 1999].

The use of mass balances has the greatest potential when:

- emissions are of the same order of magnitude as inputs or outputs;
- the amounts of the substance (input, output, transfer, accumulation) can be readily quantified over a defined period of time.

When part of the input is transformed (e.g. the feedstock in a chemical process) or when the emission results from a transformation process, the mass balance method may be more difficult to apply; in these cases, a balance by chemical elements is needed instead [141, Environment Australia 1999].

If mass balances are to be used as monitoring associated to a BAT-AEPL or associated to an ELV in a permit, sufficient data should be available that show the applicability of the proposed mass balance.

The following simple equation can be applied when estimating emissions by a mass balance [3, COM 2003]:

Total mass into process = accumulations + total mass out of process + uncertainties

Applying this equation to the context of an installation, process or piece of equipment, this equation could be rewritten as follows [3, COM 2003]:

Inputs = products + transfers + accumulations + emissions + uncertainties

where

Inputs = all incoming material used in the process;
Products = products and materials (e.g. by-products) exported from the installation;
Transfers = include substances discharged to sewers, substances deposited into landfill and substances removed from an installation for destruction, treatment, recycling, reprocessing, recovery or purification;
Accumulations = material accumulated in the process;

Emissions = releases to air, water, soil and groundwater; emissions include both routine and accidental releases, as well as spills;
Uncertainties = uncertainty quantities associated with the different parts of the equation.

Although mass balances seem a straightforward method of emission estimation, the uncertainties involved must be well known. Therefore, mass balances are only applicable in practice when accurate input, output and uncertainty quantities can be determined. Inaccuracies associated with individual material tracking, or other activities inherent in each material handling stage, can result in large deviations for the total emissions from the installation. A slight error in any step of the operation can significantly affect emission estimates. For example, small errors in data or calculation parameters, including those used to calculate the mass elements for the mass balance equation, can result in potentially large errors in the final estimates. In addition, when sampling of input and/or output materials is conducted, a failure to use representative samples will also contribute to the uncertainty. In some cases, the uncertainty may be quantifiable; if so, this is useful in determining whether the values are suitable for their intended use [3, COM 2003].

Examples of the application of a mass balance include fuel analysis (see Section 4.4.2) and solvent management plans (see Section 4.5.4.3).

Even if a mass balance cannot be used to estimate emissions, it can in some cases be a useful tool to better understand emission and consumption levels, e.g. a mercury balance in a mercury cell chlor-alkali plant [140, COM 2014].

3.3.3.3.3 Emission factors

Emission factors are numbers that can be multiplied by an activity rate (e.g. the production output, water consumption, number of animals), in order to estimate the emissions from the installation. They are applied under the assumption that all (agro)industrial units of the same product line have similar emission patterns. These factors are widely used for determining emissions at small installations, e.g. in particular for livestock farming. They are also commonly used for the determination of diffuse emissions (see for example the BREFs for Iron and Steel Production (IS BREF) [142, COM 2012] and the Refining of Mineral Oil and Gas (REF BREF) [143, COM 2015]).

Emission factors are generally derived through the testing of a population of similar process equipment (e.g. boilers using a particular fuel type) or process steps for a specific (agro)industrial sector. This information can be used to relate the quantity of material emitted to some general measure of the scale of activity (e.g. for boilers, emission factors are generally based on the quantity of fuel consumed or the heat output of the boiler) [141, Environment Australia 1999]. In the absence of other information, default emission factors (e.g. literature values) can be used to provide an estimate of the emissions (e.g. there are different emission factors available for ammonia or odour units emitted per animal place for different types of animals).

Emission factors require activity rates, which are combined with the emission factor to determine the emission rate. The generic formula is:

Emission Rate = *Emission Factor* × *Activity Rate*
(mass per unit of time) (mass per unit of throughput) (throughput per unit of time)

Appropriate conversion factors for units may need to be applied. For example, if the emission factor is expressed as kg pollutant/m^3 of fuel burnt, then the activity data required would be expressed in terms of m^3 fuel burnt/h, thereby generating an emission estimate of kg pollutant/h.

EN ISO 11771:2010 [5, CEN 2010] specifies a generic method for the determination and the reporting of time-averaged mass emissions (i.e. emission rates) from a specific installation or from a family of installations (or common source type), using data collected by measurements, and by establishing:

- emission rates by the simultaneous measurement of concentration and gas flow, using standardised manual or automated methods, and also the estimation of the measurement uncertainty;
- time-averaged emission rates using time series of emission rate values, their uncertainty characteristics, and also the determination of the expanded uncertainty of the average;
- time-averaged emission factors for a specific installation or for a family of installations and their associated uncertainty characteristics;
- a quality management system to assist the process of inventory quality assurance and verification.

Emission factors are often generated for emission inventory purposes and can be obtained from several sources (e.g. EMEP/EEA [6, EEA 2013], US EPA AP 42 [7, US EPA 2013] or VDI 3790 Part 3:2010 [8, VDI 2010]). They are usually expressed as the mass of a substance emitted divided by the unit of mass, volume, distance, calorific value of fuel, or duration of the activity emitting the substance (e.g. kilograms of sulphur dioxide emitted per tonne of fuel burnt).

The main criterion affecting the selection of an emission factor is the degree of similarity between the equipment or the process selected in applying the factor, and the equipment or process from which the factor was derived.

Emission factors developed from measurements for a specific process may sometimes be used to estimate emissions at other installations. If a company has several processes of a similar nature and size, and emissions are measured from one process source, an emission factor can be developed and applied to similar sources presenting a comparable situation.

3.3.3.3.4 Other calculations

Theoretical and complex equations, or models, can be used for estimating emissions from industrial processes. Estimations can be made by calculations based on the physico-chemical properties of the substance (e.g. vapour pressure) and on physico-chemical relationships (e.g. ideal gas law).

The use of models and related calculations requires that all necessary corresponding input data are available. Usually models provide a reasonable estimate:

- if they are based on valid assumptions, as demonstrated by previous validations;
- if their inherent uncertainty is sufficiently low;
- if suitable sensitivity analyses results are presented alongside them;
- if the scope of the model corresponds to the case studied;
- if input data are reliable and specific to the conditions of the installation.

An example of such a calculation is the estimation of methane emissions from landfills based on a first order decay of the organic material under anaerobic conditions [266, IPCC 2006].

3.4 Quality assurance

3.4.1 Overview

Data quality is the most critical aspect of monitoring. Reliable data are needed for assessing and comparing the performances of emission control techniques, for decision-making concerning allowable levels of emissions, and for the prevention of accidents, etc. Thus, quality assurance is essential for the whole data production chain and for any type of monitoring.

Since 2005, several changes have occurred in the regulatory framework and in the standardisation of measurement methods that have had a significant effect on the quality assurance of measurements and the quality of data received. In April 2009, the European co-operation for Accreditation (EA) [9, EA 2013] was established according to Regulation No 756/2008 [10, EC 2008], and this required Member States to introduce a uniform accreditation body and system by 1 January 2010, if not already available. Accreditation ensures a common interpretation of standards and covers, among others, laboratories carrying out testing (measurements) and calibration in air and water. Laboratories can be run by plant operators, authorities or third parties (e.g. consultants, experts), but have to fulfil the same requirements.

The EN standard used for the accreditation of testing laboratories is EN ISO/IEC 17025:2005 and this requires that each laboratory applies a proven quality management system. This also covers the validation of methods, data treatment, the determination of the measurement uncertainty and the reporting of results. Applying the rules given in EN ISO/IEC 17025:2005 guarantees a certain level of quality assurance in accredited laboratories, and of the results provided by them [1, CEN 2005]. In 2016, the standard was under review and a second committee draft was published [79, ISO 2016].

For periodic measurements of emissions to air, CEN/TS 15675:2007 [13, CEN 2007] supplements the requirements of EN ISO/IEC 17025:2005.

For measurement uncertainty, EN ISO/IEC 17025:2005 refers to the Guide to the Expression of Uncertainty in Measurement [11, JCGM 2008]. Based on this Guide, a European Standard for estimating the measurement uncertainty in air quality measurements is available, including for measurements of stationary source emissions (EN ISO 20988:2007 [12, CEN 2007]).

In the following sections, the main quality assurance principles are described.

3.4.2 Personnel and laboratory qualification

EN ISO/IEC 17025:2005 specifies general requirements for the competence of testing and calibration laboratories using standard methods, non-standard methods and laboratory-developed methods. Laboratories adhering to the standard have to establish a management system to assure the quality of the measurement results. The standard also includes technical requirements on personnel, laboratory facilities and equipment, measurement and calibration methods and their validation in the case of laboratory-developed and non-standard methods, measurement traceability, sampling and reporting [1, CEN 2005].

EN ISO/IEC 17025:2005 requires a high level of personal and technical qualifications for managerial and technical staff: 'When using staff who are undergoing training, appropriate supervision shall be provided. Personnel performing specific tasks shall be qualified on the basis of appropriate education, training, experience and/or demonstrated skills, as required.' [1, CEN 2005]. CEN/TS 15675:2007 includes an informative annex with example competence criteria for personnel carrying out measurements of emissions to air [13, CEN 2007].

Some Member States (e.g. Belgium (Flanders) [14, BE VLAREL 2010]) have introduced additional guidance or standards to provide more detailed information and criteria for the application of EN ISO/IEC 17025:2005, covering also personnel qualification and making use of EN ISO/IEC 17024:2012 [15, CEN 2012]. For the determination of emissions, knowledge of the various techniques, including of operational processes causing emissions and of abatement techniques, is required. Among others, audits and measurement reports are used to prove the knowledge in different technical fields.

In some Member States, different levels of personnel qualification are defined and related to the required experience and skills. For example in the United Kingdom, the terms trainee (entry level), technician (level 1) and team leader (level 2) are used. Each level requires an increasing level of knowledge and experience. For levels 1 and 2, formal exams are set and the personnel concerned can obtain a certificate [17, MCERTS 2011], [18, MCERTS 2016].

In other Member States, requirements for the manning of laboratories are set. For example in Germany, laboratories carrying out determination of air pollutants at stationary sources are required to have at least one technical supervisor, at least one deputy technical supervisor and competent laboratory personnel consisting of at least two more persons. The qualification of these persons is assessed during (re-)accreditation and regular audits by the accreditation body [19, VDI 2011].

EN ISO/IEC 17025:2005 also requires laboratories to participate in inter-laboratory comparisons or proficiency testing programmes [1, CEN 2005]. General requirements for the development and operation of proficiency testing schemes and for the competence of their providers are given in EN ISO/IEC 17043:2010 [20, CEN 2010].

Following an accreditation procedure and fulfilling all its requirements is challenging and requires a significant effort. The fulfilment of these requirements is assessed through an extensive procedure during the initial accreditation and again during a complete re-accreditation every four to five years. Between re-accreditations, an auditing scheme is applied with a tight time schedule, including inspection visits every year or two, up to three times at fixed intervals [21, UKAS 2013], [22, DAkkS 2015].

A non-accredited laboratory may achieve the same quality of measurement results as an accredited one. But if the results are questionable, the comparability and reliability of the applied methods will have to be demonstrated by the non-accredited laboratory even if it applies EN standards. For accredited laboratories, this is already carried out systematically and in a transparent manner during accreditation and can be proven at any time. In particular in cases of compliance assessment, the majority of Member States therefore only accept the results of measurements carried out by accredited laboratories.

Laboratories accredited according to EN ISO/IEC 17025:2005 can be run by plant operators, authorities or third parties (e.g. consultants, experts), but need to be independent [1, CEN 2005].

In general, measurements of emissions to air are carried out by third-party laboratories, whereas measurements of emissions to water are carried out to a large extent by plant operators. This is related to several factors detailed below.

In the case of emissions to water, the key environmental parameters measured are often the same as the key parameters to control the abatement equipment. It is essential to measure these to run the waste water treatment plant in an optimised way, and to do so, plant operators, in general, have their own analytical laboratory. Furthermore, waste water sampling is relatively easy compared to waste gas sampling, and the results can also be used to show the amount of pollutants released to the environment.

In the case of emissions to air, the key parameters measured to control the process and/or the abatement equipment generally differ from the key environmental parameters (except for CO for combustion processes or NO_X for selective catalytic reduction (SCR) or selective non-catalytic reduction (SNCR)). In addition, the measurement of emissions to air, including sampling and determination of the auxiliary parameters, is much more complicated. Generally, complex and expensive sampling equipment is needed, independent from the analytical equipment for on-site measurements. For these reasons, it is common practice that measurements of emissions to air are mainly carried out by (accredited) third parties, in particular periodic measurements and the calibration of continuous measurement equipment.

In the United Kingdom, a special Operator Monitoring Assessment (OMA) scheme is in place for emissions to air [23, MCERTS 2013] and water [132, MCERTS 2013] from industrial installations regulated under the Environmental Permitting Regulations to strengthen the auditing of operators' self-monitoring arrangements. The OMA scheme is used by the Environment Agency, among others, to assess the quality and reliability of operators' self-monitoring (including monitoring undertaken on behalf of operators by contractors) as required by their permit and to identify monitoring shortfalls and potential areas for improvements.

The use of data generated by accredited laboratories also has an advantage during the drawing up or review of BREFs, where a lot of datasets are provided which may sometimes show variations that cannot be easily explained. Therefore, accreditation may serve as an additional criterion for assessing data quality. In essence, data from accredited laboratories that are regularly audited and that participate in proficiency testing programmes are ultimately more trustworthy than data from non-accredited laboratories.

3.4.3 Standardised methods

According to Directive 98/34/EC, the European standardisation bodies are CEN (European Committee for Standardization), CENELEC (European Committee for Electrotechnical Standardisation), and ETSI (European Telecommunications Standards Institute) [25, EC 1998]. The preparation and amendment of European Standards (EN standards) involves the national standardisation bodies of 33 member countries including all EU Member States.

All European standards developed by CEN need to be converted into national standards without any alteration. Additionally, all conflicting national standards are to be withdrawn. This generates a harmonised basis for measuring methods all over Europe. Using these standards in the accreditation of laboratories guarantees that these laboratories are working according to these standards and applying them in a harmonised way.

Standards for the measurement of emissions to air and water are listed in Annexes A.1 and A.2, respectively.

The precedence of EN standards for the monitoring of emissions in the context of the IED is reflected in Article 70 concerning installations producing titanium dioxide, in Annex V, Part 3, concerning large combustion plants, and in Annex VI, Part 6, concerning waste (co-)incineration plants: 'Monitoring shall be carried out in accordance with CEN standards or, if CEN standards are not available, ISO, national or other international standards which ensure the provision of data of an equivalent scientific quality.'

This hierarchy of standards was taken on for the formulation of the BAT on monitoring in many adopted BAT conclusions: 'BAT is to monitor emissions to (…) in accordance with EN standards. If EN standards are not available, BAT is to use ISO, national or other international standards which ensure the provision of data of an equivalent scientific quality.'

The development of EN standards requires a validation during the standardisation process as described in CEN Guide 13 on Environmental test methods [26, CEN 2008]. Validation means the demonstration of the suitability of the measuring principle for the intended measurement objective. This includes the determination and specification of the performance characteristics to be met by the user of the method. The validation process includes laboratory and field tests carried out by different European testing laboratories at industrial plants in different parts of Europe.

The IED gives second priority to ISO, national or other international standards. The process for the development of ISO standards is not always the same as for EN standards, but in many cases, in particular for water analysis, ISO standards are adopted as EN standards without any alteration. The technical cooperation between ISO and CEN including provisions for the parallel adoption of standards was formalised in 1999 with the Vienna agreement [144, ISO and CEN 2014]. The development process of national or other international standards may also differ from the one used for EN standards. In contrast to EN standards, the experiences and quality requirements of some Member States may not be included in these standards.

In the case of laboratory-developed and non-standard methods, EN ISO/IEC 17025:2005 requires their validation [1, CEN 2005]. During validation, performance characteristics such as the measurement range as well as the accuracy and precision of the results have to be assessed. This typically includes determining the measurement uncertainty, the limit of detection, the selectivity of the method, the linearity, the repeatability and/or reproducibility, the robustness against external influences and/or the cross-sensitivity against interference from the matrix of the sample/test object. Judgements on the scientific quality of the measurement results rely on an analysis of these performance characteristics.

Guidance on the validation of methods is available in some EN standards, e.g. in CEN/TS 15674:2007 for the measurement of emissions to air (see Section 4.3.3.1) [76, CEN 2007] and in CEN/TS 16800:2015 for the measurement of emissions to water (see Section 5.3.1) [264, CEN 2015].

For the measurement of emissions to air, EN 14793:2017 specifies a validation procedure to show if an alternative method (AM) can be used instead of a standard reference method (SRM) [27, CEN 2017]. For water analysis, no similar EN standard was available in 2016. However, ISO/TS 16489:2006 and DIN 38402-71:2002 describe statistical procedures to test the equivalency of results obtained by two different analytical methods [263, ISO 2006] [43, DIN 2002].

The national requirements for compliance assessment of several Member States largely rely on the use of standardised methods, and in particular on EN standards, e.g. in Germany [28, DE UBA 2008], [29, DE 2014], Ireland [16, IE EPA 2014], the Netherlands [30, NL InfoMil 2012], Poland [31, PL 2012] and the United Kingdom [32, MCERTS 2016], [33, SEPA 2011], [34, MCERTS 2015].

Indicative or simplified test methods are usually not used for compliance assessment. Nevertheless, there might be cases when it is advisable to use them in addition to standardised methods. They might also be appropriate when an indication of the emissions is sufficient, e.g. between periodic measurements carried out for compliance assessment.

Another important factor that can have an influence on the use of standardised methods is the potential environmental risk associated with the pollutant in combination with the location of the installation. If the environmental risk is high because there are sensitive subjects in the surroundings, it is advisable to always use standardised methods to ensure a higher level of transparency and reliability, and probably to gain a higher level of acceptance of the results by the public or in court cases, if the use of standardised methods is not already required by laws, regulations and permits.

In practice, not all measurements are related to compliance assessment. For example, in the case of the measurement of key process parameters, it is not necessary to use standardised methods. It is up to the operator to decide what level of accuracy, repeatability and reproducibility is needed (unless it is stated otherwise by a specific piece of legislation).

In summary, the uniform use of EN standards guarantees comparable, reliable and reproducible measurement results all over Europe, in particular if the EN standards are applied by accredited laboratories that are regularly audited and that participate in proficiency testing programmes. ISO or national standards might be used if they ensure the provision of data of an equivalent scientific quality. The usefulness of simplified indicative methods is very limited.

3.4.4 Data treatment

3.4.4.1 Overview

When evaluating and comparing monitoring data, it is important to have information on how the measurement results were processed. Information on the averaging of measurement results (see Section 3.4.4.2) and the measurement uncertainty related to these results (see Section 3.4.4.3) is of fundamental importance. Furthermore, some performance characteristics of the analytical method, such as the limit of detection and the limit of quantification (see Section 3.4.4.4), have to be taken into account when assessing data as well as outlier values, their detection and their treatment (see Section 3.4.4.5).

3.4.4.2 Averaging measurement results

How to average measurement results or how to aggregate data are questions which arise after every measurement series. The choice strongly depends on the measurement frequency (continuous - periodic) and the compliance assessment regime applied.

For **continuous measurements,** it is obvious that averaging is necessary to summarise the results. Depending on the time period and the number of validated values, the result of the measurement can for example be a half-hourly, hourly, daily, monthly or yearly average. In some cases, a validation is carried out before averaging the measurement results (e.g. by taking into account the measurement uncertainty (see Section 3.4.4.3) or by removing outliers (see Section 3.4.4.5)). If the number of validated results is sufficient, the result is considered representative of the operating conditions covered.

For **periodic measurements**, the result of a measurement is an average over the sampling period, which can be, for example, 30 minutes for measurements of emissions to air (see Section 4.3.3.8) or 24 hours for measurements of emissions to water (see Section 5.3.5.4.1). Establishing how many samples are necessary to determine a representative daily, monthly or yearly average is a very complex task which requires taking into account several criteria.

Depending on the measurement objective of periodic measurements, it might be useful not to average the real-time data provided by portable instrumental analysers, e.g. for calibrating permanently installed systems or for carrying out assessments of process control.

In most cases, it is not possible to guarantee representativeness solely by the number of samples taken. Other assumptions need to be made (see Sections 4.3.3 and 5.3.5). If the samples are taken under well-defined and controlled normal operating conditions, it is generally assumed that the results of the measurements are representative of these conditions.

For the averaging of results obtained by continuous and periodic measurements, there are different approaches depending on the legislation and the environmental media. The averaging periods range from 10 minutes, 30 minutes, 1 hour, and 24 hours to up to one year. In particular, the monthly or yearly averages of continuous measurement of emissions to air can be based on 10-minute, half-hourly, hourly or daily averages.
To avoid misinterpretation of the monitoring results, clear and unambiguous definitions should be used. Table 3.2 gives examples of averaging periods that are or could be used in BAT

conclusions or permits. The definitions are subject to modification, according to the specifities of the BREF to be drawn up/reviewed or to the required permit conditions.

Table 3.2: Examples of averaging periods defined in BAT conclusions

	Averaging period	Definition
Emissions to air		
a	Daily average	Average over a period of 24 hours of valid half-hourly or hourly averages obtained by continuous measurements (1)
b	Monthly/Yearly average	Average calculated from the 10-minute, half-hourly, hourly, or daily averages obtained by continuous measurements during one month/year (1)
c	Average over the sampling duration	Average over at least 30 minutes obtained by periodic measurements (2)
d	Average of samples obtained during one year	Average calculated from the results obtained by periodic measurements during one year
e	Daily/Monthly/Yearly average (3) as specific load	Average over a period of one day/month/year expressed as mass of emitted substances per unit of mass of products/materials generated or processed
Emissions to water		
f	Daily average	Average over a sampling period of 24 hours derived from a flow-proportional composite sample
g	Monthly/Yearly average	Average (4) calculated from all daily averages obtained during one month/year
h	Average of samples obtained during one month	Average (4) of at least four (i.e. at least one sample every week) 24-hour flow-proportional composite samples taken during one month
i	Average of samples obtained during one year	Average (4) of at least 12 (i.e. at least one sample taken every month) 24-hour flow-proportional composite samples taken during one year
j	Daily/Monthly/Yearly average (3) as specific load	Average over a period of one day/month/year expressed as mass of emitted substances per unit of mass of products/materials generated or processed

(1) Continuous measurement means, according to EN 14181:2014, measurements with an automated measuring system (AMS) permanently installed on site for the continuous monitoring of emissions or measurement of peripheral parameters [36, CEN 2014].
(2) Periodic measurement means, according to EN 15259:2007, determination of a measurand at specified time intervals [45, CEN 2007].
(3) The averaging period of the specific load and the minimum monitoring frequency have to be defined according to the requirements of the specific industrial sector.
(4) Weighted average considering the daily flows.

In practice, there are two common approaches for assessing the results of periodic measurements.

In some Member States (e.g. Germany, the United Kingdom) each measurement result is assessed individually. This procedure is also used in the IED, Annex VI, Part 8, for emissions of heavy metals and polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDDs/PCDFs) to air from waste (co-)incineration plants [24, Directive 2010/75/EU 2010]. Directive 91/271/EEC concerning urban waste water treatment also uses this approach, based on 24-hour composite samples and, in addition, a 'maximum permitted number of samples which fail to conform' is defined [35, EEC 1991].

Other Member States (e.g. Italy, the Netherlands) use an average over all individual measurements carried out periodically (e.g. three consecutive measurements for emissions to air). Averaging the results of all individual measurements is also used in the IED, Annex VII, Part 8, for emissions of organic compounds to air from installations and activities using organic solvents [24, Directive 2010/75/EU 2010].

Averaging the results of individual measurements may require some additional provisions, such as how to deal with values below the limit of detection/quantification (see Section 3.4.4.4) or how to take into account the measurement uncertainty (see Section 3.4.4.3). For instance, in the Netherlands, the total measurement uncertainty has to be divided by $\sqrt{n}$ before it is subtracted from the calculated average of *n* measurements [4, NL 2012].

3.4.4.3 Measurement uncertainty

The Guide to the Expression of Uncertainty in Measurement (GUM) published by the Joint Committee for Guides in Metrology establishes general rules for evaluating and expressing uncertainty in measurement that are intended to be applicable to a broad spectrum of measurements [11, JCGM 2008]. EN ISO/IEC 17025:2005 uses the concept of measurement uncertainty referring to the GUM, giving the following definition: 'parameter associated with the result of a measurement that characterises the dispersion of the values that could reasonably be attributed to the measurand' [1, CEN 2005]. EN ISO 20988:2007 applies the general recommendations of the GUM to the conditions of air quality measurements, including stationary source emission measurements [12, CEN 2007]. In the field of water analysis, the Eurachem/CITAC guide is often used for the evaluation of the measurement uncertainty, based on the GUM [269, Eurachem/CITAC 2012].

The various standards generally distinguish between three different types of uncertainties [11, JCGM 2008], [12, CEN 2007], [265, INERIS 2016], [269, Eurachem/CITAC 2012]:

- The **standard uncertainty** is the uncertainty of the result of a measurement expressed as a standard deviation.
- The **combined standard uncertainty** is the standard uncertainty of the result of a measurement when that result is obtained from the values of a number of other input quantities. It is equal to the positive square root of a sum of terms, the terms being the variances or covariance of these other quantities weighted according to how the measurement result varies with changes in these quantities.
- The **expanded uncertainty**, also referred to as the overall uncertainty, is the interval within which the value of the measurand is believed to lie with a higher level of confidence. The expanded uncertainty is obtained by multiplying the combined standard uncertainty with a coverage factor. In many cases, a coverage factor of $k = 1.96$ with a confidence level of 95 % is chosen.

For each (new) EN standard dealing with measurement methods, there is the requirement to address the measurement uncertainty [26, CEN 2008]. Every accredited laboratory applying these standards needs to define a procedure describing how uncertainty is addressed and should always apply this procedure for the expression of measurement results [1, CEN 2005].

Therefore, every (accredited) laboratory should be able to state the estimated uncertainty for each measurement result, according to the related standards (e.g. EN standards) or to the related directive. The estimated uncertainty is often necessary for compliance assessment.

As described in general terms in EN ISO/IEC 17025:2005, the following factors, among others, contribute to the total measurement uncertainty, even if their single contribution might not be quantifiable separately [1, CEN 2005]. Some of them will be, or are already, discussed in this document, for example:

- qualification of personnel and human factors;
- laboratory facilities and environmental conditions;
- test and calibration methods and method validation;
- equipment and software used;
- measurement traceability;

- sampling plan, procedures and process;
- transportation and handling of test and calibration items.

There are different ways to take these factors into account when determining the measurement uncertainty.

According to EN ISO 20988:2007, the measurement uncertainty in the case of emissions to air can be determined either in a direct approach by a single experimental design or in an indirect approach by a combination of different experimental designs. In a direct approach, all influencing factors that can cause variations of the measurement result are investigated in a single experiment, including the whole data production chain with all intermediate steps. This leads directly to the expanded uncertainty, which defines an interval within which the measurement result falls. A common direct approach is the use of independent paired measurements with two separate sampling and analysis systems. In an indirect approach, the variations are evaluated separately for the individual intermediate steps of the applied measurement method (see also the factors mentioned above). To calculate the measurement uncertainty, an analytical equation ('method model equation') is needed that combines all contributing intermediate steps. Finally, the indirect approach leads to a combined uncertainty, which needs to be multiplied by a coverage factor to obtain an expanded uncertainty. The focus of the GUM is on the indirect approach but without excluding the direct approach [11, JCGM 2008], [12, CEN 2007], [37, VDI 2009].

Examples of a direct approach are inter-laboratory comparisons where personnel from different laboratories and with different equipment measure the same substance/parameter at the same time. Compared to the GUM, this set-up also includes uncertainties due to sampling, equipment (e.g. DAHS (Data Acquisition and Handling System)), and human factors. However, the influencing factors do not vary at all or to a lower degree. For emissions to air, such inter-laboratory comparisons have been carried out at specifically designed test benches. Experience shows that the measurement uncertainty obtained from such inter-laboratory comparisons is generally higher than the one obtained by using the GUM approach [265, INERIS 2016].

Requirements on maximum permissible measurement uncertainties may be found in standards or legislation. For this purpose, EN ISO 14956:2002 gives guidance to evaluate the suitability of a measurement procedure for ambient air and stack emission measurements by comparison with a required measurement uncertainty [268, CEN 2002].

For periodic measurements of emissions to air, maximum permissible measurement uncertainties are set for some SRMs (Table 3.3).

Table 3.3: Maximum permissible expanded uncertainties of SRMs

Parameter/substance(s)	Standard	Maximum permissible expanded uncertainty of SRM (1)
Carbon monoxide (CO)	EN 15058:2017	± 6.0 %
Dust	EN 13284-1:2001	NS (2)
Gaseous chlorides	EN 1911:2010	± 30.0 %
Nitrogen oxides (NO_X)	EN 14792:2017	± 10.0 %
Oxygen (O_2)	EN 14789:2017	± 6.0 % (3)
Sulphur oxides (SO_X)	EN 14791:2017	± 20.0 %
Water vapour	EN 14790:2017	± 20.0 %

(1) The expanded uncertainty refers to a coverage factor of $k = 1.96$ and a confidence interval of 95 %. It is calculated on a dry basis (except for water vapour) and before correction to the reference oxygen level. In the case of oxygen and water, it applies at the measured value and is expressed as a percentage of that value; otherwise, it applies at the ELV level and is expressed as a percentage of that ELV.
(2) EN 13284-1:2001 was under review in 2016. A maximum permissible expanded uncertainty of ± 20.0 % is proposed in prEN 13284-1:2015.
(3) Or 0.3 % as a volume concentration.
NB: NS = not specified.
Source: [71, CEN 2010], [72, CEN 2017], [73, CEN 2017], [74, CEN 2017], [75, CEN 2001], [181, CEN 2017], [193, CEN 2017], [265, INERIS 2016], [270, CEN 2015]

For continuous measurements of emissions to air, the measurement uncertainty is determined at two stages. For equipment certification, EN 15267-3:2007 requires that the total uncertainty of automated measurement systems (AMS) is at least 25 % below the maximum permissible uncertainty to allow for a sufficient margin for the uncertainty contribution from the individual installation of the AMS (see also Section 4.3.2.2.1 on quality assurance level 1 (QAL1)) [66, CEN 2007]. When the equipment is in operation, the measurement uncertainty is determined according to EN 14181:2014 via the variability, i.e. the standard deviation of the differences of parallel measurements between the SRM and the AMS (see Section 4.3.2.2.2 on QAL2) [36, CEN 2014].

Examples of maximum permissible uncertainties in legislation can be found in the IED which sets requirements for AMS for the measurement of emissions to air from large combustion plants (Annex V, Part 3, Point 9) and waste (co-)incineration plants (Annex VI, Part 6, Point 1.3) (Table 3.4) [24, Directive 2010/75/EU 2010]. The IED refers to values of the 95 % confidence intervals which, according to EN 14181:2014, correspond to expanded uncertainties [36, CEN 2014].

Table 3.4: Maximum permissible expanded uncertainties of AMS for large combustion plants and waste (co-)incineration plants in Annexes V and VI to the IED

Parameter/substance(s)	Maximum permissible expanded uncertainty of AMS (1)	
	Large combustion plants	Waste incineration plants
Carbon monoxide (CO)	10 %	10 %
Dust	30 %	30 %
Hydrogen chloride (HCl)	NA	40 %
Hydrogen fluoride (HF)	NA	40 %
Nitrogen oxides (NO_X)	20 %	20 %
Sulphur dioxide (SO_2)	20 %	20 %
TVOC	NA	30 %

(1) The expanded uncertainties refer to a coverage factor of $k = 1.96$ and a confidence interval of 95 %. They apply at the ELV levels given in Annexes V (monthly ELVs) and VI (daily ELVs) to the IED and are expressed as a percentage of these ELVs.

NB: NA = not applicable.

Source: [24, Directive 2010/75/EU 2010]

For compliance assessment, the expanded uncertainty may be taken into account for each measurement result or for the average before comparing the value(s) with the ELV given in a permit. With respect to the comparison, there are different approaches in the Member States. For emissions to air, the most common approach is to subtract the measurement uncertainty from the result and to use the resulting value for further assessment. In general, it is good practice to describe if/how the measurement uncertainty is taken into account.

In the IED, the measurement uncertainty is taken into account for emissions to air from large combustion plants (Annex V, Part 3, Point 10) and waste (co-)incineration plants (Annex VI, Part 8, Point 1.2). In both cases, validated average values are calculated by subtracting the 95 % confidence interval (i.e. the expanded uncertainty) from the measured average values [24, Directive 2010/75/EU 2010].

The subtraction of the measurement uncertainty may lead to negative results. It is thus good practice to describe how to handle such data. For example, according to the Austrian ordinance on the measurement of emissions to air from boilers and gas turbines, validated average values (i.e. half-hourly average values after subtraction of the measurement uncertainty) which are negative have to be set as zero [42, AT 2011].

Generally, the **relative** measurement uncertainty, expressed as a percentage of the measured value, increases with decreasing emission levels [265, INERIS 2016].

Commission Implementing Decision 2012/119/EU on the collection of data and on the drawing up of BREFs stipulates in Section 5.4.7.2 that an indication of the measurement uncertainty should be included when submitting emission data during the data collection, where applicable. Moreover, Section 3.3 stipulates that rounded values may be used to define BAT-AEPLs including BAT-AELs in order to take into account technical issues such as the measurement uncertainty [39, EU 2012]. However, BAT-AEPLs in BAT conclusions are generally expressed without mentioning the measurement uncertainty. Nevertheless, information on the measurement uncertainty obtained during the data collection could be reported in the BREF (see for example the final draft of the BREF for Large Combustion Plants BREF (LCP BREF) [277, COM 2016]).

3.4.4.4 Limit of detection and limit of quantification

Laboratories adhering to EN ISO/IEC 17025:2005 are required to validate laboratory-developed and non-standard methods and to determine their performance characteristics [1, CEN 2005]. Validation usually includes the determination of the limit of detection (LoD) and of the limit of quantification (LoQ).

In the field of water analysis, there was no generic EN standard or specification in 2016 defining LoD or LoQ. However, a definition is given in Directive 2009/90/EC laying down technical specifications for chemical analysis and monitoring of water status pursuant to the Water Framework Directive [40, EC 2009]:

- **Limit of detection** means the output signal or concentration value above which it can be affirmed with a stated level of confidence that a sample is different from a blank sample containing no determinand of interest.
- **Limit of quantification** means a stated multiple of the limit of detection at a concentration of the determinand that can reasonably be determined with an acceptable level of accuracy and precision. The limit of quantification can be calculated using an appropriate standard or sample, and may be obtained from the lowest calibration point on the calibration curve, excluding the blank.

Even though the monitoring of industrial waste water is not covered by Directive 2009/90/EC, the aforementioned definitions can be equally applied.

For measurements of emissions to air, a similar but more general definition is given in EN 14793:2017 [27, CEN 2017]:

- **limit of detection** means the smallest measurand concentration which can be detected, but not quantified, in the experiment conditions described for the method;
- **limit of quantification** means the smallest measurand concentration which can be quantified, in the experiment conditions described for the method.

Further specifications are given in some individual standards (e.g. in EN 1948-3:2006 for the measurement of PCDD/PCDF emissions to air from stationary sources [41, CEN 2006]).

There are several other terms in use, such as limit of determination, limit of application, practical reporting limit or demonstrability limit, but it appears that they are mostly used in the sense of limit of quantification (LoQ).

Any measurement method applied should have an appropriate LoD/LoQ in relation to the emission level to be measured. In many cases, the LoD is required to be less than 10 % of the ELV in order to guarantee that the LoQ is clearly below the ELV. Some Member States have set stricter performance requirements, e.g. in France the LoQ should be less than 10 % of the ELV [133, FR 2013].

Directive 2009/90/EC for chemical analysis and monitoring of water status pursuant to the Water Framework Directive is an example of EU requirements in the field of water analysis, which is, however, not relevant for emissions from IED installations. The Directive requires that the LoQ for all methods of analysis shall be equal to or below a value of 30 % of the relevant environmental quality standards [40, EC 2009].

The LoD and LoQ strongly depend on the performance of the laboratory and the possible modifications or adaptations to specific circumstances. For instance, for periodic measurements, the sampling time can be adapted and/or the analytical method can be chosen to reach an acceptable LoQ. Therefore, it is essential that, together with the measurement results, the LoD, and preferably also the LoQ, is reported. This allows a better use of data when assessing measurement results.

In that sense, Commission Implementing Decision 2012/119/EU on the collection of data and on the drawing up of BREFs specifies in Section 5.4.7.2 that the LoD and LoQ should be given as reference information accompanying emission data during the data collection, if available. Moreover, the aforementioned Decision stipulates in Section 3.3 that it is acceptable to use an expression of the type '< X to Y', when the lower end of the range cannot be accurately defined, e.g. when the data reported are close to the LoD [39, EU 2012].

If the LoQ is not known or not reported, it can be estimated as a multiple of the LoD, for example by multiplying the LoD given in the relevant (EN) standard by a factor of three. However, the use of laboratory-specific performance characteristics of the method is preferable.

For the averaging of measurement results, the way in which values below the LoD or LoQ are taken into account needs to be defined. This implies also judging if the measured pollutant is relevant for the installation under investigation and therefore whether it may be present in the release. If the best available information indicates that a pollutant is not released, there is no need to measure that pollutant or report any data. If there are indications that the pollutant could be released, even if it is not detectable at present, the data should be reported and the LoD and the LoQ should be expressed.

There are different ways to explicitly handle values below the LoD or LoQ, for example:

- Article 5 of Directive 2009/90/EC for chemical analysis and monitoring of water status pursuant to the Water Framework Directive specifies the following rules for the calculation of average values [40, EC 2009]:
    - Where the amounts of physico-chemical or chemical measurands in a given sample are below the limit of quantification, the measurement results shall be set to half of the value of the limit of quantification concerned for the calculation of mean values.
    - Where a calculated mean value of the measurement results referred to in paragraph 1 is below the limits of quantification, the value shall be referred to as 'less than limit of quantification'.
    - Paragraph 1 shall not apply to measurands that are total sums of a given group of physico-chemical parameters or chemical measurands, including their relevant metabolites, degradation and reaction products. In those cases, results below the limit of quantification of the individual substances shall be set to zero.
- In Denmark, the approach of Directive 2009/90/EC is modified for the monitoring of industrial waste water in order not to lose useful information for pollutants with very low concentrations (e.g. organic micro-pollutants) [38, DK EPA 2012]:
    - If less than 10 % of all samples have concentrations above the LoD, no average will be calculated.
    - If more than 10 % but less than 50 % of all samples have concentrations above the LoD, the measurement result for all values below the limit of detection will be set to zero for the calculation of the average.

  - If 50 % or more of all samples have concentrations above the LoD, the measurement result for all values below the limit of detection will be set to half the value of the limit of detection for the calculation of the average.
- For the reporting to the Scottish Pollutant Release Inventory, the measurement results should be set as zero when multiple results for a pollutant are all below the LoD and there is no other reason to believe that the pollutant is present. When there is reason to believe that a pollutant is present, the measurement results should be taken as half the value of the LoD. When some values are above the LoD and some are below, then those above the LoD should be taken as the measured values, unless it can be demonstrated that the measurements are false, and the readings below the LoD should be taken as half the value of the LoD [33, SEPA 2011].
- In France, for summing up and averaging measurement results for emissions to air, the individual result is taken as half the value of the LoQ for concentrations below the LoQ and as zero for concentrations below the LoD [133, FR 2013].

In other Member States, there might be different approaches for taking the LoD and/or the LoQ into account when measurement results are averaged. Therefore, it is good practice to always report the approach taken together with the results. This also applies to average emission data submitted for the drawing up or review of BREFs.

If relevant, it is useful to clearly state in the permit the necessary arrangements for dealing with values below the LoD or LoQ, if it is not stated elsewhere in the national regulation. This is particularly important in the case of ELVs expressed as calculated averages when the LoQ is not far below the ELV, as the approach may have an influence on the final result and the subsequent compliance assessment.

3.4.4.5 Outliers

ISO 5725-1:1994 defines an outlier as a member of a set of values which is inconsistent with the other members of that set [271, ISO 1994]. CEN/TR 15983:2010 gave a similar definition for the measurement of emissions to air whereby an outlier, also referred to as an invalid data point, is an observation that lies at an abnormal distance from other values in a set of data, and therefore has a low probability of being a valid data point. CEN/TR 15983:2010 has been withdrawn [272, CEN 2010].

In this document (i.e. the ROM), outliers are understood as invalid data points for which the invalidity is rooted in the measurement.

In the context of monitoring of emissions to air and water, two cases need to be distinguished. Outliers may occur in a series of data pairs when comparing the results of two different measurement methods, but also in a series of measurement data when using the same measurement method [273, CEWEP and ESWET 2016].

When comparing the results of two different methods, the Grubbs' test is typically used to statistically determine outliers (e.g. for emissions to air in EN 14793:2017 [27, CEN 2017] and for emissions to water in DIN 38402-71:2002 [43, DIN 2002]). An outlier check is also required by EN 14181:2014 during the QAL2 procedure (see Section 4.3.2.2.2) [36, CEN 2014]. Guidance for the determination of outliers to meet the requirements of EN 14181:2014 is for example given in the Monitoring Quick Guide 14 [44, MCERTS 2012]. The Grubbs' test is based on the assumption of a normal distribution of the data set. This assumption should thus be checked before applying the test [274, NIST/SEMATECH 2017].

In a series of measurement data, the question is to determine whether an abnormal value is due to exceptional emissions or if it is an outlier due to the measurement [273, CEWEP and ESWET 2016]. As the operating conditions of a plant are not normally distributed [273, CEWEP and ESWET 2016], statistical tests alone will thus not be sufficient to identify outliers.

A close analysis of the operating conditions is an important step for the identification of an outlier. Other actions for identifying potential outliers may include checking all concentrations against the preceding and following observations and against permits, and possibly taking past outliers in previous monitoring periods into account [3, COM 2003].

This checking should generally be carried out by skilled staff, although automated procedures may also be put in place. However, strong variations in observations need to be examined by a skilled database operator [3, COM 2003].

Errors during sampling or analysis are a common cause of deviating results when an operational cause for an abnormal value cannot be identified. In this case, the laboratory in question can be notified with reference to a critical revision of their performance and monitoring data [3, COM 2003].

If an abnormal value is due to the measurement (i.e. it is an outlier as described above), it may be left out from the calculation of average concentrations, etc. and, finally, should be clearly distinguished from data related to normal or other than normal operating conditions when reported.

The basis for the identification of an outlier, as well as all actual data, should always be reported to the competent authorities, but also during the data collection for the drawing up or review of BREFs.

3.5 Normal and other than normal operating conditions – corresponding measurement conditions

Article 3(13) of the IED defines emission levels associated with the best available techniques (BAT-AELs) as the range of emission levels obtained under normal operating conditions (NOC) using a best available technique or a combination of best available techniques, as described in BAT conclusions, expressed as an average over a given period of time, under specified reference conditions. Furthermore, Article 15(3) specifies that the competent authority shall set ELVs that ensure that, under normal operating conditions, emissions do not exceed the relevant BAT-AELs. Article 14(1)(f) gives examples of other than normal operating conditions (OTNOC) such as start-up and shutdown operations, leaks, malfunctions, momentary stoppages and definitive cessation of operations [24, Directive 2010/75/EU 2010]. The aforementioned example conditions may be caused by regular and irregular events as well as planned and unplanned ones.

Therefore, the operating conditions should be carefully considered when granting or updating permits. Moreover, Commission Implementing Decision 2012/119/EU stipulates in Section 2.3.7.2.4 that emission and consumption data used for the drawing up or review of BREFs will be qualified as far as possible with details of relevant operating conditions [39, EU 2012].

The linking of BAT-AELs to NOC does not imply that provisions for emissions under OTNOC could not be defined in the IED, permits, and BAT conclusions. Indeed, Article 14(1)(f) of the IED requires permits to contain measures relating to OTNOC. Another example can be found in the IED, Annex VI, Part 3, Point 2, concerning waste incineration plants, where it is stipulated that a certain ELV for total dust 'shall under no circumstances' be exceeded, which includes all operating conditions [24, Directive 2010/75/EU 2010]. Moreover, Commission Implementing Decision 2012/119/EU stipulates in Section 3.1 that BAT conclusions should address OTNOC when these are considered of concern with respect to environmental protection [39, EU 2012]. OTNOC should be particularly addressed if it is obvious that relevant environmental impacts can be expected, e.g. possible emissions of toxic substances or of high concentrations of odorous substances close to residential areas.

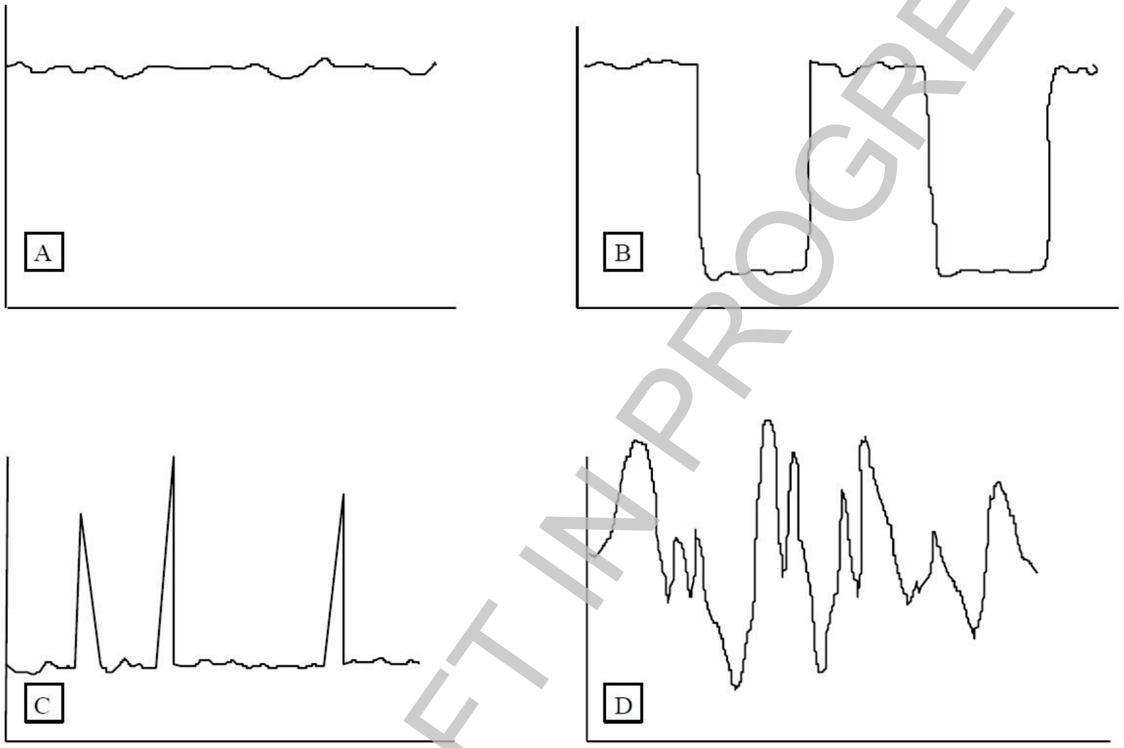
In order to classify measurement results related to NOC or OTNOC, the operating conditions need to be documented in the measurement report, together with contextual information on the emission (e.g. reference conditions) and clearly linked to specific values if the complexity of the source(s) under investigation allows this. This implies that different NOC should be identified if they have an influence on the emissions, e.g. different process modes during production, different raw materials or fuels, plant operating at a specified load or capacity, batch processing or production.

If the averaging of values is necessary, only the ones unambiguously related to comparable NOC or OTNOC should be included in the calculation.

For continuous measurements, the monitoring results will cover both NOC and OTNOC. Therefore, criteria for the classification of the different operating conditions of the plant should be established beforehand, so that the averaging of the values can be carried out separately for NOC and, if necessary, also for OTNOC, as long as the results are within the defined (calibration) range. This ensures that the reported averages are only related to comparable operating conditions.

For periodic measurements, operating conditions should already be taken into account when defining the measurement plan [45, CEN 2007], [46, CEN 2006]. If different NOC occur with significant differences in emissions, it is recommended to carry out periodic measurements that are representative of each distinguishable NOC, or at least representative of the one with the highest expected emissions (see also Sections 4.3.3.4 and 5.3.5.2). Whether periodic measurements are also deemed necessary for OTNOC will depend on the specific situation and the expected emissions. Ensuring representative periodic measurements under OTNOC may be a challenging task, in particular in the case of non-routine events.

Some examples (A, B, C and D) of how emissions can vary over time are given in Figure 3.2, where the horizontal axis (x-axis) represents the time and the vertical axis (y-axis) the emission level.



Source: [3, COM 2003]

Figure 3.2: Examples of how emission levels can vary over time

In the examples given in Figure 3.2, NOC and OTNOC and the associated monitoring regime can be summarised as follows:

- **Process A** represents a very stable process. It can be assumed that NOC are prevailing. The results of measurements will be similar, independent of when they are carried out. Periodic measurements with a minimum frequency might be sufficient. If the expected value is close to an ELV, continuous measurements might be advisable if not already required by the IED or national legislation.
- **Process B** represents an example with alternating but stable high and low emission levels, which are typical for cyclic or batch processes. It can be assumed that the whole process represents NOC with two distinct emission levels.

  The monitoring approach chosen will depend on the duration of the distinct emission phases and the specific requirements of the permit.
  If continuous emission measurements are carried out, the overall average emission level or the emission level of each distinct phase can be easily quantified.
  If periodic measurements are carried out, it needs to be clarified in advance if the overall average emission level (e.g. for estimating loads) or the emission level of each distinct phase should be determined. It might be advisable to measure during the two different emission phases or, depending on the case, to measure only during the phase with the highest expected emission.

Accordingly, BAT-AEPLs and/or ELVs may reflect this emission situation and an appropriate monitoring regime should be chosen.

- **Process C** represents a relatively stable process with occasional short but high peaks. A similar situation might consist of regular peaks which always occur after a certain measure, such as after the start-up of a process after the weekend.

  In these cases, it is necessary to assess if the peaks are caused by NOC or OTNOC. Also, the contribution of the peaks to the total emission and their potential environmental impact should be taken into account when defining monitoring requirements.
  Continuous measurements cover the peaks as well as intermediate periods and allow differentiation between NOC and OTNOC. But, depending on the duration of the peaks, it might also be sufficient to measure periodically under stable conditions and to measure only occasionally during peak times. This might require the shortening of the sampling duration. Whether the peaks need to be reflected in BAT conclusions and/or in permits depends on the relevance of the emission and on the qualification as NOC or OTNOC.
- **Process D** represents a highly variable process which nevertheless probably represents NOC. It seems to be difficult to distinguish between NOC and OTNOC, although, after looking at the process, OTNOC might be identifiable.

  If the whole emission occurs under NOC, it is necessary to evaluate its contribution to the total emissions of the installation, and, provided that the contribution is significant, continuous measurements might be the only possible monitoring solution to cover all the emission variations.
  It is unlikely that periodic measurements would be used for emissions of such a process type. Only if the contribution to the total emission of the installation is very low, or if, despite the fluctuations, the emission levels are expected to be consistently below the ELV, might it be appropriate to develop a measurement plan which guarantees that measurements are carried out during periods of highest emission levels.
  A BAT-AEPL and/or an ELV for such a process should reflect the special conditions and be associated with an appropriate monitoring regime.

As outlined above, different operating conditions or emission patterns will affect the monitoring regime. This will be covered in more detail in Section 4 for emissions to air and in Section 5 for emissions to water.

4 MONITORING OF EMISSIONS TO AIR

4.1 Overview

This chapter covers the monitoring of emissions to air including information on:

- air pollutants (see Section 4.2);
- continuous/periodic measurements (see Section 4.3);
- surrogate parameters (see Section 4.4);
- diffuse emissions (see Section 4.5);
- odour (see Section 4.6);
- biomonitoring (see Section 4.7);
- costs (see Section 4.8).

General aspects of monitoring are described in Chapter 3.

4.2 Air pollutants

Table 4.1 gives some examples of definitions of air pollutants that are or could be used in BAT conclusions or permits. The definitions are subject to modification, according to the specifities of the BREF to be drawn up/reviewed or to the required permit conditions.

Table 4.1: Examples of definitions of air pollutants

Parameter/substance(s)	Definition
CO	Carbon monoxide
Dust	Total particulate matter (in air)
Gaseous chlorides	Gaseous chlorides, expressed as HCl
Gaseous fluorides	Gaseous fluorides, expressed as HF
H_2S	Hydrogen sulphide
Mercury and its compounds	The sum of mercury and its compounds, expressed as Hg
NH_3	Ammonia
NO	Nitrogen monoxide
NO_2	Nitrogen dioxide
NO_X	The sum of nitrogen monoxide (NO) and nitrogen dioxide (NO_2), expressed as NO_2
Odour concentration	Number of European odour units (ou_E) in one cubic metre at standard conditions measured by dynamic olfactometry according to EN 13725 [52, CEN 2003]
PCBs	Polychlorinated biphenyls
PCDDs/PCDFs	Polychlorinated dibenzo-*p*-dioxins/dibenzofurans
SO_2	Sulphur dioxide
SO_X	The sum of sulphur dioxide (SO_2), sulphur trioxide (SO_3), and sulphuric acid aerosols, expressed as SO_2
TVOC	Total volatile organic carbon, expressed as C
VOC	Volatile organic compound; defined in Directive 2010/75/EU [24, Directive 2010/75/EU 2010] as any organic compound as well as the fraction of creosote having at 293.15 K a vapour pressure of 0.01 kPa or more, or having a corresponding volatility under the particular conditions of use

Information on specific monitoring aspects for the most common air pollutants including on the measurement principles is provided in Section 4.3.2.4 for continuous measurements and in Section 4.3.3.10 for periodic measurements.

4.3 Continuous/periodic measurements

4.3.1 Continuous versus periodic measurements

Continuous measurements are carried out with an automated measuring system (AMS) which is permanently installed on site for the continuous monitoring of emissions ([36, CEN 2014]). Periodic measurement is defined as the determination of a measurand at specified time intervals ([45, CEN 2007]).

Table 4.2 provides an overview of important characteristics of continuous and periodic measurements, including advantages and disadvantages.

Table 4.2: Important characteristics of continuous and periodic measurements

Characteristic	Continuous measurement	Periodic measurement
Sampling period	Measurement covers all or most of the time during which substances are emitted	Snapshots of the long-term emission pattern
Speed	Almost always real-time results	Real-time results if instrumental analysers are used; delayed results if a manual method with a laboratory end-method is used
Averaging of results	Results continuously gathered and can be averaged over a given period, e.g. 30 minutes, 1 hour or 24 hours	Results over the sampling period, typically 30 minutes to several hours
Calibration and traceability	AMS require calibration against a standard reference method (SRM) (2) and adjustment with certified reference materials in the maintenance interval	Standard reference methods can be used for periodic measurements; these can be manual or automated methods
Accreditation	Quality assurance of the calibration and maintenance of AMS according to EN 14181:2014 [36, CEN 2014] and EN ISO/IEC 17025:2005 [1, CEN 2005]	Quality assurance for periodic measurements according to CEN/TS 15675:2005 [13, CEN 2007] and EN ISO/IEC 17025:2005 [1, CEN 2005]
Certification of equipment	Certification of equipment available (see Section 4.3.2.2.1)	Certification of portable equipment available
Investment costs (1)	Higher than the costs of periodic monitoring equipment	Lower than the costs of AMS
Operating costs (1)	Normally higher than the costs of periodic measurements, in particular if it includes QAL2, QAL3, AST, etc. (see Section 4.3.2.2.2)	Normally lower than the costs of AMS

(1) For detailed information on costs see Section 4.8 and Annex A.5.

(2) An alternative method (AM) can be used for calibration where the equivalence has been demonstrated in accordance with EN 14793:2017 [27, CEN 2017].

Source: [34, MCERTS 2015].

In addition to Table 4.2, when deciding whether to use continuous or periodic measurements, the following aspects may be taken into consideration [3, COM 2003]:

- the environmental relevance of the emission;
- the environmental risk associated with the exceedance of an ELV (see Section 3.3.1);
- the variability of the emission levels, in particular if they are close to an ELV (see Section 3.5);
- legal requirements (e.g. in national legislation, the IED, BAT conclusions);
- local conditions (e.g. air quality standards);
- the availability and reliability of equipment (e.g. continuous measurements might not be feasible under certain conditions such as high water vapour or dust contents in the waste gas);
- the required measurement uncertainty;
- the need to continuously monitor and/or control the operating conditions including the pollution abatement system;
- the perception of the public.

The IED requires continuous measurements for some activities, e.g. in Annex V, Part 3, for large combustion plants with a total rated thermal input of 100 MW or more (e.g. for SO_2, NO_X and dust) and in Annex VI, Part 6, for waste incineration plants (e.g. for NO_X, provided that ELVs are set, and for CO, total dust, TOC, HCl, HF, and SO_2). In both cases, the IED includes provisions that specify under which circumstances continuous measurements may be replaced by periodic measurements [24, Directive 2010/75/EU 2010].

In some Member States (e.g. Belgium (Flanders) [57, BE (Flanders) 2014], Denmark [58, DK 2002], France [60, FR 2016], Germany [61, DE 2002]) and Portugal [137, PT 1993]), generic mass flow thresholds are used to decide if continuous measurements are required. In general, it is assumed that below these thresholds periodic measurements are sufficient, unless the conditions of the individual case require a different approach. Some examples of such mass flow thresholds for the most common pollutants are given in Annex A.3, Table 7.4.

In other Member States (e.g. in the Netherlands and the United Kingdom), a risk-based approach is used that considers the increase in emissions upon failure of abatement equipment as a basis for requiring continuous measurements or filter leak monitoring [4, NL 2012].

A mass flow threshold for installations and activities using organic solvents is also defined in Annex VII, Part 6 of the IED: Channels to which abatement equipment is connected and which at the final point of discharge emit more than an average of 10 kg/h of TOC are required to use continuous monitoring [24, Directive 2010/75/EU 2010].

Decisions on BAT conclusions regarding monitoring in the sectoral BREFs are based on the practices in the individual industrial sector and the information provided. The aforementioned aspects and examples might help to decide whether it is more appropriate to monitor continuously or periodically.

4.3.2 Continuous measurements

4.3.2.1 Generic EN standards

Table 4.3 lists general EN standards relevant for continuous measurements of emissions to air. One of them is also related to ambient air measurements.

For the general use of EN standards and other standardised methods see Section 3.4.3.

Table 4.3: Generic EN standards relevant for continuous measurements of emissions to air

Standard	Title
EN ISO 9169:2006	Air quality - Definition and determination of performance characteristics of an automatic measuring system (ISO 9169:2006)
EN 14181:2014	Stationary source emissions - Quality assurance of automated measuring systems
EN 15259:2007	Air quality - Measurement of stationary source emissions - Requirements for measurement sections and sites and for the measurement objective, plan and report
EN 15267-1:2009	Air quality - Certification of automated measuring systems - Part 1: General principles
EN 15267-2:2009	Air quality - Certification of automated measuring systems - Part 2: Initial assessment of the AMS manufacturer's quality management system and post certification surveillance for the manufacturing process
EN 15267-3:2007	Air quality - Certification of automated measuring systems - Part 3: Performance criteria and test procedures for automated measuring systems for monitoring emissions from stationary sources

EN ISO 9169:2006 provides definitions and specifies methods to determine the performance characteristics of AMS for ambient air and stack emission measurements. Tests are carried out under stable laboratory conditions or field conditions. The standard applies to measuring systems for which it is possible to apply several reference materials with accepted values with known uncertainty for the measurand, within the range of application [267, CEN 2006].

EN 14181:2014 defines quality assurance procedures for AMS in operation, namely the calibration and validation which represents quality assurance level 2 (QAL2), the ongoing quality assurance during operation which represents QAL3, and the annual surveillance test (AST) (see Section 4.3.2.2.2) [36, CEN 2014]. In conjunction with this standard, more specific EN standards for AMS are available for some pollutants/parameters such as dust [62, CEN 2004], mercury [232, CEN 2005] and methane [233, CEN 2010], as well as velocity and volume flow rate [234, CEN 2013].

EN 15259:2007 applies mainly to periodic emission measurements, but it also specifies a procedure for finding the best available sampling point for AMS (see Section 4.3.2.3) [45, CEN 2007].

EN 15267, Parts 1 to 3 describe the certification of AMS, also referred to as suitability evaluation, which constitutes quality assurance level 1 (QAL1). The certification procedure is carried out before the AMS is installed at the emission source (see Section 4.3.2.2.1) [64, CEN 2009] [65, CEN 2009] [66, CEN 2007].

In 2017, a working group of the Technical Committee CEN/TC 264 'Air quality' was working on a series of new EN standards on the quality assurance of data received by data acquisition and handling systems (DAHS) from AMS that are used to monitor emissions from stationary sources. This EN series is expected to specify requirements for the handling and reporting of data (Part 1), for DAHS (Part 2) and for the performance tests and certification of DAHS (Part 3) [78, CEN 2017].

4.3.2.2 Quality assurance

4.3.2.2.1 Certification

QAL1 is a procedure defined in EN 15267, Parts 1 to 3, and referred to in EN 14181:2014, to demonstrate that an AMS is suitable for its intended purpose **before** installation on site [36, CEN 2014]:

- EN 15267-1:2009 specifies general principles, including common procedures and requirements of the certification [64, CEN 2009].
- EN 15267-2:2009 specifies requirements for the manufacturer's quality management system, the initial assessment of the manufacturer's production control, and the continuing surveillance of the effect of subsequent design changes on the performance of a certified AMS [65, CEN 2009].
- EN 15267-3:2007 specifies the performance criteria and test procedures for AMS [66, CEN 2007].

The QAL1 suitability test is a complex procedure, divided into a laboratory and a field testing phase [28, DE UBA 2008], [66, CEN 2007]. Manufacturers of measuring instruments normally commission third parties to carry out the suitability tests to obtain the certification. In 2016, the suitability tests in Europe were carried out or coordinated by the following organisations:

- Monitoring Certification Scheme of the Environment Agency of England (MCERTS);
- TÜV Rhineland and German Federal Environment Agency (UBA).

The suitability tests include a **certification range**, which is the range over which the AMS has been certified. The certification range is related to the ELVs given in relevant EU directives of the processes for which the AMS will be used. For example, EN 15267-3:2007 states that the certification range shall be no greater than 1.5 times the daily ELV for waste incineration plants and 2.5 times the daily ELV for large combustion plants [66, CEN 2007], [67, MCERTS 2015]. When an ELV changes, an existing AMS may no longer fulfil the requirements for the certification range. This generally requires an assessment to ascertain if the AMS is still fit for purpose.

A certified AMS meets a number of performance standards including the maximum expanded uncertainty according to the requirements given in the IED, Annexes V and VI. EN 15267-3:2007 requires that the total uncertainty is at least 25 % below the maximum permissible uncertainty to allow for a sufficient margin for the uncertainty contribution from the individual installation of the AMS in order to successfully pass QAL2 and QAL3 of EN 14181:2014 (see Section 4.3.2.2.2). The standard also requires that the limits of quantification for dust and gaseous compounds except oxygen which are determined in laboratory tests are ≤ 8 % of the upper limit of the certification range [66, CEN 2007].

Older AMS (e.g. before 2007) might not be able to fulfil the criteria of EN 15267 [256, CONCAWE 2013].

For the measurement of emissions to air, certified AMS are available for the pollutants and peripheral parameters listed in Annex A.1, Table 7.2.

Continuously measured emission data need to be stored and further processed. A variety of systems are used for this purpose, with a clear preference for automatic data loggers, which might also be able to communicate with a remote central processing unit. There are also certified digital data transfer and evaluating systems available [129, DE UBA and TÜV 2016], [138, MCERTS 2017], which are not included in Table 7.2.

For the certification of continuous dust arrestment plant monitors, EN 15859:2010 provides performance criteria and test procedures. Two types of dust arrestment plant monitors are covered by this standard [63, CEN 2010]:

- a filter dust monitor which can be calibrated in mass concentration units (e.g. in mg/m3) and used for dust arrestment control purposes;
- a filter leakage monitor, which indicates a change in the emission level or a change in the magnitude of the dust pulses created by the cleaning process.

Continuous dust measurements certified according to EN 15859:2010 may be used in cases, where only qualitative monitoring of the arrestment plants is needed, as an alternative to the more expensive quantitative AMS, even if the measurements made by these dust monitors do not necessarily fulfil all the requirements of EN 14181:2014.

A filter leakage monitor, as referred to above, may be used as an indicative surrogate parameter (see Section 4.4.1.1).

4.3.2.2.2 Quality assurance in operation

EN 14181:2014 describes procedures for the quality assurance levels QAL2 and QAL3 as well as the annual surveillance test (AST) for AMS in operation [36, CEN 2014].

QAL2 as defined in EN 14181:2014 involves testing laboratories that are accredited (see Sections 3.4.1 and 3.4.2) or approved directly by the relevant competent authority. The QAL2 tests are performed **after** the AMS has been installed. A calibration function is established from the results of a number of real emission measurements performed in parallel with the AMS and the standard reference method (SRM). The variability of the measured values obtained with the AMS is subsequently evaluated against the maximum permissible measurement uncertainty [36, CEN 2014].

The SRMs are defined in specific EN standards (see Annex A.1, Table 7.2). An alternative method (AM) can be used where equivalency has been demonstrated in accordance with EN 14793:2017 [27, CEN 2017].

The QAL2 procedure needs to be repeated periodically at least every five years. More frequent repetitions may be required by legislation, by the competent authority, or after major changes of the AMS or of the process/operating conditions. QAL2 comprises at least 15 parallel measurements with the AMS and the SRM (or AM) under normal operating conditions. EN 14181:2014 does not allow the use of reference materials alone to obtain the calibration function because they do not sufficiently replicate the matrix stack gas. The measurements are performed within a period of four weeks and are uniformly spread both over at least three days and over each of the measuring days. In general, the concentrations during the calibration should vary as much as possible within the normal operating conditions of the plant. If normal operating conditions consist of distinct operating modes (e.g. use of different fuels, manufacture of different products), the need for additional calibrations has to be checked [36, CEN 2014].

As the QAL2 procedure is based on real emission measurements, the resulting **calibration range** is different from the certification range (e.g. it might be lower or higher). EN 14181:2014 contains provisions that specify to which extent the valid calibration range may be extended above the highest measured value obtained during calibration. The **measuring range** is the range at which the AMS is set to operate during use. National competent authorities usually require that the measuring range encompasses the maximum short-term ELV. The measuring range can be different from the certification range (e.g. it might be lower or higher). For measurements outside the valid calibration range, EN 14181:2014 stipulates that the calibration curve should be extrapolated. If greater confidence in the performance of the AMS at the ELV is required when the plant is emitting outside its calibration range, reference materials should be used during calibration to confirm the suitability of the linear extrapolation [36, CEN 2014].

The calibration of an AMS is generally difficult when the emission levels are close to the limit of quantification. In 2016, INERIS reported cases where clouds of data points resulted in calibration lines with poor regression coefficients or even negative slopes [265, INERIS 2016]. As the possibilities to vary the operating conditions of the plant are often limited, EN 14181:2014 provides for the possibility to use reference materials if there are limited variations in the parallel measurement results and the measured concentrations are well below the ELV [36, CEN 2014]. However, such reference materials are not available for dust measurements [265, INERIS 2016].

QAL3, as defined in 14181:2014, describes a frequent quality assurance procedure to maintain and demonstrate the required quality of the AMS during its normal operation. The implementation and performance of the QAL3 procedure is the responsibility of the plant operator. In contrast to QAL1 and QAL2, QAL3 does not require an accredited or approved laboratory to carry out the procedures. The aim of the QAL3 procedure is to ensure that the AMS is maintained in the same operational condition compared to its installation and calibration during the QAL2 procedure. This is achieved by confirming that the drift and precision determined during certification (i.e. QAL1) remain under control [36, CEN 2014].

The QAL3 procedure requires regular and ideally frequent measurements at zero and span points using reference materials of known quantity and quality. Control charts are used which plot the zero and span readings against the time. Depending on the type of control chart, the drift and precision of the AMS are determined either combined or separately. This makes it possible to identify when an adjustment or maintenance is necessary (e.g. by the manufacturer) [36, CEN 2014].

The required frequency of the QAL3 procedure is at least once within the period of the maintenance interval which is defined during certification (i.e. QAL1), typically between eight days and one month. Some AMS have much longer maintenance intervals (e.g. from three to six months) offering the benefits of a proven long-term stability and of a higher availability for monitoring, as span measurements can be time-consuming [36, CEN 2014].

The **AST** (annual surveillance test) involves testing laboratories that are accredited (see Sections 3.4.1 and 3.4.2) or approved directly by the relevant competent authority. It is an annual procedure to test the AMS in order to evaluate (i) that it functions correctly and its performance remains valid, and (ii) that its calibration parameters remain as previously determined (i.e. during QAL2). In general, an AST consists of a functional test and at least five parallel measurements between the AMS and the SRM (or AM). The measured data are used in a test of the variability and the calibration function of the AMS [36, CEN 2014].

4.3.2.3 Measurement/sampling site, section, plane and point

The following terms are frequently used [45, CEN 2007], [102, UK MCERTS 2016]:

- **Measurement/sampling site (also referred to as measurement/sampling location):** the place at the waste gas duct in the area of the measurement plane(s) where the measurements or the sampling are carried out. It consists of structures and technical equipment, for example working platforms, measurement ports, and energy supply.
- **Measurement/sampling section:** the region of the waste gas duct which includes the measurement plane(s) and the inlet and outlet sections.
- **Measurement/sampling plane:** the plane normal to the centreline of the duct at the sampling position.
- **Measurement/sampling point:** the position in the measurement plane of the waste gas duct at which the measurement data are obtained directly or the sample stream is extracted.

EN 14181:2014 requires that the working platform of an AMS is easily accessible, clean, well ventilated, well lit and in accordance with EN 15259:2007. Suitable protection for the personnel and the equipment is required if the working platform is exposed to the weather [36, CEN 2014]. According to EN 15259:2007, the working platforms shall have a sufficient load-bearing capacity and shall provide sufficient working space (i.e. area and height) to manipulate the AMS [45, CEN 2007].

Continuous measurements are usually restricted to measurement/sampling at a single point or along a single line of sight. EN 15259:2007 requires that these measurement/sampling points are located in a position that allows **representative** measurement/sampling of the emission. For this purpose, the standard provides a procedure to determine the best available measurement/sampling point based on grid measurements (see also Section 4.3.3.6) [45, CEN 2007].

4.3.2.4 Analysis

4.3.2.4.1 Extractive and non-extractive AMS

In general, two different kinds of AMS are available for the continuous measurement of emissions: extractive and non-extractive AMS. For most of the parameters listed in Table 7.2 both types of AMS are available.

In the case of an **extractive AMS,** a gas sample is taken from the main gas stream by a sampling system and sent to the measurement device, which is physically separated from the sampling point (Figure 4.1). This requires suitable sampling equipment, but allows, if necessary, a special treatment of the sampled gas stream. In general, the sampling path should be kept as short as possible, to enable short response times and to avoid possible sample losses. All gas sampling lines and components of the measurement device are made of suitable material; on the one hand to prevent corrosion and on the other hand to avoid reactions between these materials and the measured component. Probes, filters and sample gas tubing, up to the sample gas cooler (if used for condensate separation), are heated to above the dew point temperature [28, DE UBA 2008].

Source: [253, INERCO 2012]

Figure 4.1: Example of an extractive sampling device

In the case of a **non-extractive AMS**, the measurement device is installed across the stack in the gas stream or in a part of it (*in situ* measurement). Therefore, no extractive sampling is necessary. In principle, a non-extractive AMS is more prone to interferences from other waste gas components than an extractive AMS, as there is usually little or no sample pretreatment. For example, a high humidity in the waste gas stream may require the use of an extractive AMS. Because the measurements are carried out in wet conditions and at the operating temperature in the stack, this needs to be considered in the data processing.

4.3.2.4.2 Methods of certified AMS

Methods of certified AMS for the most common air pollutants are summarised in Table 4.4. More detailed information can be found in Annex A.1, Table 7.2.

Table 4.4: Methods of certified AMS for the most common air pollutants

Pollutant	Monitoring methods	Remarks
Ammonia (NH_3)	FTIR, NDIR with GFC, TDL	ISO 17179:2016 specifies the fundamental structure and the most important performance characteristics of automated measuring systems (AMS) for ammonia [262, ISO 2016].
Carbon monoxide (CO)	FTIR, NDIR	—
Dust	Light attenuation or scattering, triboelectric effect (i.e. the probe electrification induced by dust particles)	EN 13284-2:2004 defines specific quality assurance requirements related to AMS for dust [62, CEN 2004]. In 2016, no certified AMS was available for the continuous measurement of particle size distributions.
Hydrogen chloride (HCl)	FTIR, NDIR with GFC, TDL	In 2012, the European Commission issued a mandate to CEN to prepare a new European standard to measure gaseous hydrogen chloride by an automated method including on specific quality assurance requirements [250, COM 2012].
Hydrogen fluoride (HF)	FTIR, TDL	—
Methane (CH_4)	FID, FTIR, NDIR	EN ISO 25140:2010 defines the principle, the essential performance criteria, and specific quality assurance requirements related to AMS for methane [233, CEN 2010].
Mercury (Hg)	AAS, DOAS	EN 14884:2000 defines specific quality assurance requirements related to AMS for total gaseous mercury measurements [232, CEN 2005]. For more details on continuous mercury measurements, see Section 0.
Metals and their compounds	—	Certified AMS were only available for mercury (Hg).
Nitrogen oxides (NO_X)	Chemiluminescence, FTIR, NDIR, NDUV, DOAS	AMS for measuring NO and NO_2 separately were also available.
Polycyclic aromatic hydrocarbons (PAHs)	—	No certified AMS was available in 2016.
PCDDs/PCDFs and dioxin-like PCBs	—	In 2016, certified systems were only available for continuous isokinetic sampling.
Sulphur dioxide (SO_2)	FTIR, NDIR, NDUV, DOAS	—
Sulphur oxides (SO_X)	—	No certified AMS was available in 2016. A typical option is to continuously measure SO_2 and to apply a correction factor that takes into account the contribution of sulphur trioxide and sulphuric acid aerosols. The correction factor may be determined by periodic measurements of SO_X, e.g. at the time of calibrating the continuous measurement device.
Total volatile organic carbon (TVOC)	FID	PIDs are not used for continuous measurements due to the high variability of response factors and to difficulties with sample conditioning [231, MCERTS 2016].

NB: AAS = atomic absorption spectrometry; DOAS = differential optical absorption spectroscopy; FID = flame ionisation detection; FTIR = Fourier transform infrared spectrometry; GFC = gas filter correlation; NDIR = non-dispersive infrared spectrometry; NDUV = non-dispersive UV spectrometry; PID = photo ionisation detector; TDL = tunable diode laser absorption spectrometry.

Source: [104, MCERTS 2017], [129, DE UBA and TÜV 2016]

4.3.2.4.3 Continuous mercury measurements

Continuous measurements of total gaseous mercury are based on extractive gas sampling, filtration, conversion, possibly amalgamation, and measurement (e.g. with atomic absorption spectrometry (AAS) or atomic fluorescence spectrometry (AFS)). Sample gas conditioning plays a special role, as AAS and AFS only detect metallic mercury. Other volatile mercury compounds, mainly mercury chlorides (Hg_2Cl_2/$HgCl_2$), are thus reduced to metallic mercury prior to analysis. This is either achieved by wet chemical reduction (e.g. with tin chloride solution) or by dry reduction with converters at low (~ 250 °C) or high temperatures (~ 700 °C). Any particle-bound mercury is not included in the result [198, Boneß and Greiter 2011], [199, UNEP 2015], [220, Laudal 2015].

Given that mercury measurements in waste gases require a more advanced sample conditioning and may need to be carried out in concentration ranges of < 1 µg/m^3 to 10 µg/m^3, the requirements on an AMS are comparatively high [198, Boneß and Greiter 2011].

4.3.2.5 Reference/Standard conditions

4.3.2.5.1 Overview

BAT-AELs as defined in Article 3(13) of the IED refer to specified reference conditions, but the IED does not provide a definition of the term reference conditions [24, Directive 2010/75/EU 2010]. EN 14181:2014 defines standard conditions as those conditions to which measured values have to be standardised to verify compliance with ELVs [36, CEN 2014].

In the context of the IED and the BREFs, the terms reference conditions and standard conditions are often used in the same sense and are thus interchangeable. This usually means that the measured emission concentrations are converted to a temperature of 273.15 K and a pressure of 101.3 kPa after the deduction of the water vapour content (thereby referring to dry gas). In many cases, the standard conditions also include a reference oxygen level (e.g. for flue-gases from combustion or incineration processes).

In non-IED related contexts, other definitions of the terms reference/standard conditions might apply. For example, the standard conditions defined by IUPAC exclusively address the temperature (273.15 K) and the pressure (100 kPa) [275, IUPAC 2017].

In order to compare emission levels to air, it is generally necessary to convert them to standard conditions. In most cases, this involves the correction for the temperature, the pressure, and the water vapour content.

The correction for the oxygen content is usually carried out in the case of combustion and incineration processes in order to account for the dilution of the waste gas that is caused by the combustion air. The reference oxygen levels differ from one process/sector to another. On the other hand, emission levels in waste gases from non-combustion processes are generally not corrected to a reference oxygen level. Examples for the latter include the BAT-AELs for emissions of chlorine and chlorine dioxide in the BREF for the Production of Chlor-alkali (CAK BREF) [140, COM 2014], for emissions from non-kiln activities in the BREF for the Production of Cement, Lime and Magnesium Oxide (CLM BREF) [183, COM 2013], for emissions from non-melting activities in the BREF for the Manufacture of Glass (GLS BREF) [182, COM 2013], and for emissions from sources other than particle board and oriented strand board dryers in the BREF for the Production of Wood-based Panels (WBP BREF) [195, COM 2016]).

While the emission levels of thermal oxidisers treating oxygen-free waste gas streams may be reasonably related to a reference oxygen level, this practice is normally not meaningful in the case of high-oxygen or air-rich streams. In the latter case, the amount of supplementary fuel added to ensure a minimum reaction temperature for reliable pollutant destruction is very small. Depending on the waste gas preheat level, this will lead to residual oxygen levels that are so high that large correction factors will need to be applied (e.g. > 10) even if a high reference oxygen level is set (e.g. 11 vol-%) [276, VDI 2014].

Several documents provide information on the calculations necessary to convert the measured mass concentration and the measured flue-gas volume to standard conditions [30, NL InfoMil 2012], [34, MCERTS 2015], [45, CEN 2007]. The equation for calculating the emission concentration at the reference oxygen level is given in the IED and in many BAT conclusions [24, Directive 2010/75/EU 2010]:

Equation 4.1: $$E_R = \frac{21 - O_R}{21 - O_M} \times E_M$$

where E_R = emission concentration at the reference oxygen level O_R;
O_R = reference oxygen level (vol-%);
E_M = measured emission concentration;
O_M = measured oxygen level in (vol-%).

The equation implies that errors in the measured oxygen level O_M will have a higher impact on the resulting emission concentration at the reference oxygen level E_R if the reference oxygen level O_R is higher.

When calculating emission rates, for example in kg/h, different temperature, pressure, oxygen and water vapour levels do not affect the calculated result, provided that the mass concentration (e.g. in mg/m^3) and the volume flow rate (e.g. in m^3/h) are expressed at the same conditions. Therefore, no conversion to standard conditions is needed for the calculation of emission rates [34, MCERTS 2015], [45, CEN 2007].

4.3.2.5.2 Specific considerations for continuous measurements

As laid out above in Section 4.3.2.5.1, the continuous measurement of a pollutant often requires the simultaneous continuous measurement of peripheral parameters, also referred to as reference quantities, such as temperature, pressure, oxygen level and water vapour content (see for example IED Annexes V and VI [24, Directive 2010/75/EU 2010]). EN 14181:2014 defines a peripheral AMS as an AMS used to gather the data required to convert the AMS measured value to standard conditions. The measurement uncertainty of the peripheral AMS contributes to the measurement uncertainty of the pollutant measured with the AMS [36, CEN 2014].

4.3.2.6 Data treatment

An AMS provides short-term data. The response time ranges from about 5 seconds up to a maximum of 200 seconds for particulate matter and gaseous compounds, except for NH_3, HCl and HF for which the response time may be as high as 400 seconds [66, CEN 2007]. EN 14181:2014 defines the response time as the time interval between the instant of a sudden change in the value of the input quantity to an AMS and the time from which the value of the output quantity is reliably maintained above 90 % of the correct value of the input quantity [36, CEN 2014].

Averaging periods usually vary from 10 to 60 minutes, depending on the permit requirements. Most commonly, half-hourly or hourly averages are calculated. In the same way, data from peripheral measurements (e.g. oxygen, water vapour) are averaged and the half-hourly or hourly averages of the pollutant concentrations are converted to the corresponding standard conditions (see Section 4.3.2.5).

In some cases, the measurement uncertainty is subtracted from the standardised half-hourly or hourly results to obtain validated averages. Negative validated averages are usually accounted for as equivalent to zero (see Section 3.4.4.3). Based on these validated averages, other averages such as daily, monthly or yearly averages can be calculated and used for further assessment.

4.3.2.7 Reporting

The measurement report usually includes:

- the results of the calibration (QAL2 report) and of the annual surveillance test (AST report) of the AMS as described in EN 14181:2014 (see Section 4.3.2.2.2) [36, CEN 2014];
- the measurement results, including reference conditions (temperature, oxygen, water vapour, pressure) and operating conditions.

It is good practice to report measurement results on a daily, monthly and/or yearly basis, depending on the specific requirements set by the permit. The daily and/or monthly reports should contain sufficient data to serve as background information to the yearly report. In particular, to allow a full assessment of the daily/monthly/yearly emissions, it is advisable that the reports contain at least the following data:

- data related to the daily operating conditions and hours indicating normal and other than normal operating conditions;

- half-hourly/hourly averages, standardised half-hourly/hourly averages, and validated half-hourly/hourly averages of the specific day (or for any other required averaging period);
- frequency distribution of the half-hourly/hourly, daily and/or monthly averages for the calendar year;
- declaration of measurement results related to special (operating) conditions, with an indication of the event;
- indication of the measurement results outside the valid calibration range and data related to the validity of the calibration function;
- date and duration of power outages of the AMS;
- date and duration of times for testing and maintenance of the AMS.

Under certain conditions, measurement results/reports are made publicly available, for example according to IED Article 24(3)(b) [24, Directive 2010/75/EU 2010].

4.3.2.8 Drawing up or review of BREFs

During the data collection for the drawing up or review of BREFs, complete data sets (e.g. all half-hourly or hourly averages) are usually not provided. Instead, the data collection usually includes the relevant averages (e.g. daily, monthly and/or yearly), the measurement uncertainty (see Section 3.4.4.3), minimum and maximum values, and the 95th/97th percentile, if available, together with unambiguous information on the operating conditions to distinguish between normal and other than normal operating conditions.

For further information on data gathering and reference information accompanying emission data, see the 'BREF guidance' [39, EU 2012].

4.3.3 Periodic measurements

4.3.3.1 Generic EN standards

Table 4.5 lists some generic EN standards and technical specifications relevant for periodic measurements of emissions to air. Some of them are also related to ambient air measurements. Specific standards for the measurement of emissions to air are listed in Annex A.1, Table 7.1.

For the general use of EN standards and other standard methods see Section 3.4.3.

Table 4.5: Generic EN standards and technical specifications relevant for periodic measurements of emissions to air

Standard	Title
EN 14793:2017	Stationary source emissions - Demonstration of equivalence of an alternative method with a reference method
EN 15259:2007	Air quality - Measurement of stationary source emissions - Requirements for measurement sections and sites and for the measurement objective, plan and report
EN 15267-4:2017	Air quality - Certification of automated measuring systems - Part 4: Performance criteria and test procedures for automated measuring systems for periodic measurements of emissions from stationary sources
CEN/TS 15674:2007	Air quality - Measurement of stationary source emissions - Guidelines for the elaboration of standardised methods
CEN/TS 15675:2007	Air quality - Measurement of stationary source emissions - Application of EN ISO/IEC 17025:2005

EN 14793:2017 specifies a validation procedure to show if an alternative method (AM) can be used instead of the standard reference method (SRM), both implemented to determine the same measurand. Statistical tools and different criteria are provided to evaluate the AM [27, CEN 2017].

EN 15259:2007 applies to periodic emission measurements using manual or automated reference methods and aims for reliable and comparable results that are representative of the emissions. The standard specifies requirements for the measurement objective and the measurement plan (see Section 4.3.3.3), for measurement sites, sections, planes and points (see Sections 4.3.3.5 and 4.3.3.6), for the number, timing and duration of the individual measurements (see Sections 4.3.3.7 and 4.3.3.8), as well as for the reporting (see Section 4.3.3.13) [45, CEN 2007].

EN 15267-4:2017 specifies the general performance criteria and test procedures for portable automated measuring systems (P-AMS) (see Section 4.3.3.2.1) [257, CEN 2017].

CEN/TS 15674:2007 gives recommendations and specifies requirements for the development of standardised reference methods for emission measurements from stationary sources [76, CEN 2007].

CEN/TS 15675:2007 describes the quality assurance for periodic measurements of emissions to air (see Section 4.3.3.2.2) [13, CEN 2007].

4.3.3.2 Quality assurance

4.3.3.2.1 Certification

In 2016, the certification of equipment was only available for portable automated measuring systems (P-AMS). EN 15267-4:2017 applies to P-AMS used for periodic measurements of stationary source emissions. P-AMS are based on measurement techniques specified by a standard reference method (SRM) or an alternative method (AM). The performance tests for P-AMS are carried out similarly to those for stationary AMS according to EN 15267-3:2007 (see Section 4.3.2.2.1). Both tests may be combined if AMS are designed for stationary and portable use [257, CEN 2017].

4.3.3.2.2 Quality assurance in operation

CEN/TS 15675:2007 supplements the requirements of EN ISO/IEC 17025:2005, and is suitable for the demonstration of competence of laboratories that undertake periodic emission measurements from stationary sources including the taking of representative samples and subsequent laboratory analysis, the determination of reference quantities in the field (e.g. temperature, pressure, water vapour, and oxygen content) and the use of portable instruments in the field [13, CEN 2007].

4.3.3.3 Measurement objective and measurement plan

The measurement objective is defined by the customer and specifies the scope of the work to be carried out. According to EN 15259:2007, the measurement objective specifies at least [45, CEN 2007]:

- the purpose of the measurement;
- the dates and times of the measurements;
- the operating conditions under which the measurements are performed (normal operating conditions (NOC) and/or other than normal operating conditions (OTNOC), if known in advance);
- the measurement site;
- the measurands (i.e. pollutants and reference quantities) and the expected values;
- the competence of the testing laboratory.

The measurement objective may also specify the measurement methods to be used and the requirements on the measurement uncertainty [45, CEN 2007].

The measurement plan, drawn up by the testing laboratory, takes these considerations into account and outlines the procedure to fulfil the measurement objective. According to EN 15259:2007, the measurement plan specifies a number of issues, some of which also form part of the measurement objective [45, CEN 2007]:

- the dates and times of the measurements;
- the operating conditions under which the measurements are performed (see Section 4.3.3.4);
- the measurement sites and sections (see Section 4.3.3.5);
- the measurement points (see Section 4.3.3.6);
- the number of individual measurements (see Section 4.3.3.7);
- the timing and duration of the individual measurements (see Section 4.3.3.8);
- the measurands (i.e. pollutants and reference quantities);
- the measurement methods (see Section 4.3.3.10);

- the technical supervisor, necessary personnel and auxiliary help for carrying out the measurements;
- the reporting (see Section 4.3.3.13).

It is also good practice to assess the feasibility of the measurement objective considering NOC and possible OTNOC, if appropriate. The measurement plan should ensure that, depending on the measurement objective, the operating conditions, i.e. NOC or OTNOC, are clearly specified and that measures are taken so that these conditions are present during the measurements.

4.3.3.4 Operating conditions

For compliance assessment, measurements are often carried out at the highest emission state of the operating conditions under investigation (usually NOC). The highest emission state is characterised by the highest emission mass flow which does not necessarily correspond to the maximum emission concentration of a pollutant. Depending on the permit conditions, the measurement objective can refer to concentrations or to mass flows or to both. The highest emission state usually corresponds to the maximum (permitted) plant output. However, the type and composition of the feed materials may also influence the expected emissions. Furthermore, the individual emission behaviour of pollutants can proceed in opposite directions depending on the conditions (e.g. CO and NO_X in combustion processes) [45, CEN 2007].

To identify the conditions associated with the highest emission state, it is advisable to make use of the following [45, CEN 2007]:

- specialist discussions with the operator of the plant and, if necessary, with the competent authorities;
- site visits to the plant and the measurement sites;
- knowledge of the plant type and the associated emission behaviour based on measurements which have already been carried out at the plant in question or at comparable plants;
- literature knowledge (e.g. emission factors).

In some cases, technical constraints may not allow a plant to operate at the highest emission state (e.g. due to constraints imposed by the grid operator on combined cycle combustion plants) [255, EURELECTRIC 2013].

4.3.3.5 Measurement/sampling site, section and plane

Definitions of measurement/sampling sites, sections, planes and points are given in Section 4.3.2.3.

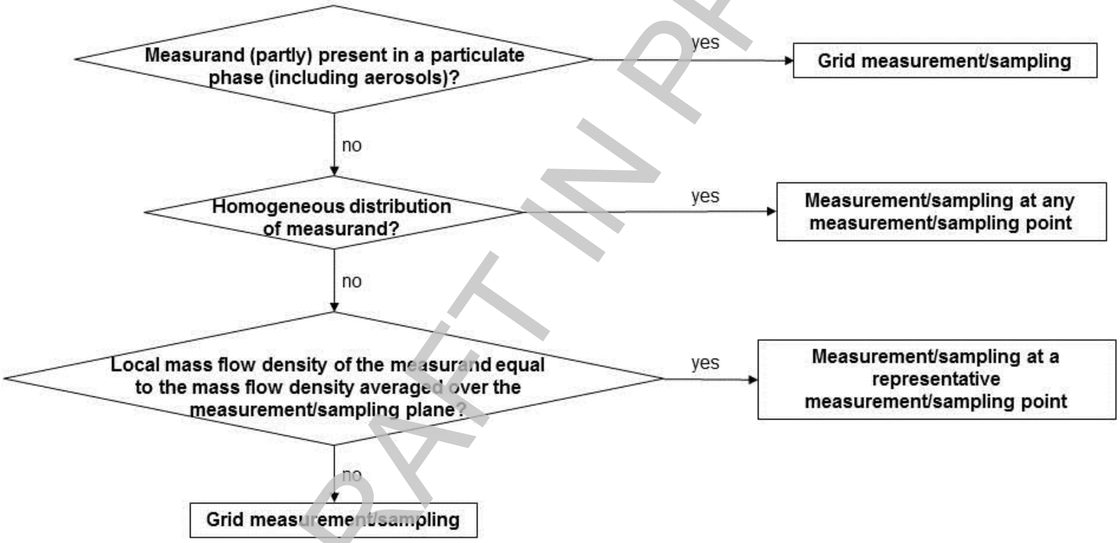
According to EN 15259:2007, measurement sites and sections should be designed to enable representative sampling of the waste gas and to measure the distribution of the pollutants and the reference quantities. The latter are also referred to as peripheral parameters. The measurement site should allow easy access to the sampling points for typical sampling equipment, e.g. via a platform that enables personnel performing the measurement to work safely and efficiently [45, CEN 2007].

Furthermore, defined flow conditions are required in the measurement plane, i.e. an ordered and stable flow profile without vortexing and backflow, so that the waste gas velocity and the mass concentration of the measurand can be determined representatively. According to EN 15259:2007, the measurement plane shall be situated in a section of the waste gas duct where homogeneous flow conditions and concentrations can be expected. The requirement for homogeneous flow conditions is generally fulfilled if the measurement plane is [45, CEN 2007]:

- as far downstream and upstream as possible from any disturbance that could produce a change in the flow direction (e.g. disturbances can be caused by bends, fans or partially closed dampers);
- in a section of the duct with at least five hydraulic diameters of straight duct upstream of the sampling plane and two hydraulic diameters downstream, and, in addition, five hydraulic diameters from the top of a stack (hydraulic diameter: ratio of four times the area and the perimeter of the measurement plane); and
- in a section of the duct with a constant shape and cross-sectional area.

4.3.3.6 Measurement/sampling point

In order to ensure representative measurement/sampling, EN 15259:2007 requires that the provisions on the measurement plane (see previous Section 4.3.3.5) are complemented with a sampling strategy. The sampling strategy consists of a decision tree in order to decide on (a) representative measurement/sampling point(s) (Figure 4.2) [45, CEN 2007]:



Source: Adapted from [45, CEN 2007]

Figure 4.2: Sampling strategy as described in EN 15259:2007

Grid measurement/sampling takes place in a given grid of measurement/sampling points in the measurement/sampling plane. It is required for pollutants which are present in both a particulate and a gaseous phase (e.g. metals and PCDDs/PCDFs). This also includes pollutants which are present in both an aerosol and a gaseous phase (e.g. hydrogen chloride) [45, CEN 2007].

In the case of gaseous compounds and the flow rate, EN 15259:2007 requires a homogeneity test to verify the concentration/flow rate profile across the measurement plane of the waste gas. This test is usually only carried out once, by determining the measurand in a given grid of measurement/sampling points and simultaneously at one measurement/sampling point. For the grid measurement/sampling, EN 15259:2007 describes the identification of the number of measurement/sampling points, their placement, and the sampling duration at each measurement/sampling point. Depending on the outcome of the homogeneity test, the subsequent measurement/sampling is carried out at any measurement/sampling point, at a representative measurement/sampling point or over a grid of measurement/sampling points (Figure 4.2) [45, CEN 2007].

Grid measurements are also required for determining a representative measurement/sampling point for AMS (see Section 4.3.2.3) [45, CEN 2007].

The representative measurement/sampling of particulate matter and aerosols requires **isokinetic sampling** which means sampling at a flow rate such that the velocity and direction of the gas entering the sampling nozzle are the same as the velocity and direction of the waste gas at the sampling point [45, CEN 2007], [75, CEN 2001]. If the sampling flow rate is too low, a percentage of smaller particles will not be sampled, whereas more of the larger particles will enter the sampling nozzle. This could lead to an overestimation of the dust concentration. If the sampling flow rate is too high, more of the smaller particles will be collected in comparison to the original particle-size distribution. This could lead to an underestimation of the dust concentration [30, NL InfoMil 2012], [34, MCERTS 2015].

Generally, the sampling should be carried out without changing the composition of the waste gas (e.g. avoidance of water condensation or particulate filtration) and/or the sample should be converted into a more stable form. This implies, among others, that the sampling device should be designed in such a way that:

- it can be heated to avoid condensation;
- it can be cooled to assist absorption;
- it allows different sampling flow rates; and
- the gas volume extracted can be measured either dry or wet (e.g. for odour measurements).

Changes to the sample composition during transportation and storage need to be avoided too.

4.3.3.7 Number of individual measurements

The number of consecutive individual measurements in one measurement series should be specified in accordance with the measurement objective and in relation to the stability of the emission. When measuring a stable emission, best practice is to take a minimum of three samples consecutively in one measurement series. In the case of unstable emissions, the number of samples can be increased to meet the measurement objective [45, CEN 2007]. Depending on the permit conditions and the related averaging (see Section 3.4.4.2), it might be sufficient to carry out three measurements with a longer sampling duration (e.g. two to three hours), to measure a representative average of the unstable emission.

The minimum number of individual measurements in one measurement series is usually specified in the relevant legislation or in the permit.

In some Member States, the minimum number of individual measurements depends on the distance of the measurement result to the ELV. For example in France, the minimum number of individual measurements in one measurement series may be reduced from three to one if the results of the three previous measurement series were lower than 20 % of the ELV [133, FR 2013].

4.3.3.8 Timing and duration of individual measurements

The timing and duration of the emission measurement should be specified in the measurement plan in accordance with the measurement objective [45, CEN 2007]. The most common sampling duration is 30 minutes, but 60 minutes is applied as well, but this also depends on the pollutant and the emission pattern of the process.

The sampling duration depends on the mass of pollutant needed for the subsequent measurement. For this reason, some EN standards specify that the sampling duration is dependent on the expected concentration of the pollutant in the waste gas and on the measurement range of the analytical method used by the laboratory including the limit of detection (see Section 3.4.4.4). It is therefore crucial that the performance of the analytical method is considered when deciding on a suitable sampling duration. This might lead to longer sampling durations than commonly applied.

The following three process categories are distinguished in EN 15259:2007 for the selection of the most appropriate sampling timing and duration [45, CEN 2007]:

- continuous processes with a constant emission pattern;
- continuous processes with a variable emission pattern;
- discontinuous processes, such as batch or loading processes.

Continuous processes with a constant emission pattern are characterised by largely constant characteristics of the fuels and raw materials used as well as largely constant operating conditions. Therefore, the emission pattern is relatively constant over longer time periods. For this reason, the emission can be measured at any point in time. Examples of typical continuous processes are combustion plants with non-variable fuel(s), drying plants, coating plants, rotary kiln plants and crushing and classification plants [45, CEN 2007].

Continuous processes with a variable emission pattern can be characterised by largely constant material feed, but time-dependent process steps that can affect the emission pattern. The timing of the emission measurements should give adequate consideration to these conditions and take the changes in the emission pattern over time sufficiently into account. Examples of typical continuous processes having variations over time are firing processes in brick manufacture (e.g. trolley charging in tunnel kilns) and glass manufacture in regenerative tank furnaces [45, CEN 2007].

Discontinuous processes are predominantly characterised by the fact that the emission pattern is controlled, or can be controlled, by operating procedures, which may vary depending on the material used and/or with time. The timing of the emission measurements should take these circumstances into account. Especially in the case of very short-term emission events, a check should be made as to whether several similar emission events can be combined in one sample/measurement in order to enable evaluation of the operating state. Examples of typical batch processes can be found in the chemical industry, in non-ferrous metal melting plants, in the production of steel and in the textile industry [45, CEN 2007].

4.3.3.9 Measurement frequency

In general, the measurement plan, as described before, refers to one or a set of measurement series, each consisting of at least three consecutive measurements at a certain date and time. In addition, it is also advisable to define the time intervals at which periodic measurements should be performed (measurement frequency). In practice, the following frequencies related to measurement series of at least three consecutive measurements are generally applied, taking into account also cost aspects and potential impacts for the environment (see Section 3.3.1):

- **Once or twice per year:** Generally, this is the typical frequency for NOC, also taking into account that reporting to competent authorities according to the IED should be carried out yearly. Furthermore, it may be advisable to use indirect methods between measurements to ensure that no severe changes in emissions occur between direct measurements.
- **Once every three years:** This may be the appropriate frequency if it can be shown over several years (e.g. five years) that the emission level for NOC is clearly below the ELV or if the measurement is carried out for other purposes (e.g. to determine emission loads for reporting). The reduced frequency is applied unless emission increases are expected due to changes in the NOC of the production process. In particular, in these cases it is

advisable to use indirect methods to ensure that no severe changes in emissions to air occur between direct measurements.

- **Higher frequencies** (e.g. weekly, monthly, every two months, quarterly): This might be required in cases where higher emissions than under NOC are expected, e.g. due to OTNOC or during commissioning or decommissioning. In these cases, the higher monitoring frequency should be maintained until an acceptable emission level under NOC is reached.

The planning of the periodic measurements is challenging in the case of plants with frequent, unplanned start-ups and shutdowns (e.g. power plants with a limited number of operating hours per year depending on the electricity demand) [255, EURELECTRIC 2013]. In this sense, the final draft of the BREF for Large Combustion Plants (LCP BREF) stipulates that the given monitoring frequencies do not apply where a plant would have to be operated for the sole purpose of performing an emission measurement [277, COM 2016].

4.3.3.10 Analysis

4.3.3.10.1 Overview

For periodic measurements, the waste gas sample is extracted from the emission source and the pollutant is either analysed on-line by portable monitoring devices or fixed in an absorption liquid, on a filter or on an adsorbent. Afterwards, this liquid or solid sample is analysed in the laboratory. Therefore, the collection, storage and transport of the samples are critical for achieving a reliable measurement result.

The following sections provide information on specific monitoring aspects for the most common air pollutants including on the measurement principles. A list of specific standards and methods for the measurement of emissions to air together with information on measurement ranges and limits is given in Annex A.1, Table 7.1.

4.3.3.10.2 Ammonia

BAT-AELs for emissions of ammonia to air were defined in several BAT conclusions (e.g. in the BREFs for the Production of Cement, Lime and Magnesium Oxide (CLM BREF) [183, COM 2013], the Manufacture of Glass (GLS BREF) [182, COM 2013], the Non-Ferrous Metals Industries (NFM BREF) [229, COM 2014], the Production of Pulp, Paper and Board (PP BREF) [160, COM 2015], and the Refining of Mineral Oil and Gas (REF BREF) [143, COM 2015]). In 2016, however, no EN or ISO standards for ammonia measurements from stack emissions were available [59, CEN 2016], [112, ISO 2016]. Examples of national or industry standards that are used are given in Annex A.1, Table 7.1.

4.3.3.10.3 Carbon monoxide

EN 15058:2017 is the standard reference method (SRM) for the measurement of carbon monoxide using non-dispersive infrared spectrometry (NDIR). Interferences from other absorbing gases, in particular from water and carbon dioxide, as well as detector instability and drift are suppressed, e.g. by measuring at a specific wavelength, by employing dual cell monitors, and/or by using gas filter correlation (GFC) [72, CEN 2017].

4.3.3.10.4 Dust

The SRM for the measurement of dust is EN 13284-1:2001. It is based on isokinetic sampling (see Section 4.3.3.6), filtration with a plane filter, and gravimetry. Deposits upstream of the filter in the sampling equipment are also recovered and weighed. Dust measurements in waste gases saturated with water vapour are more difficult than in dry waste gases and lead to higher LoDs [75, CEN 2001].

In order to better qualify the environmental impact of total dust emissions, it may be advisable or even necessary to determine the dust particle size distribution, in particular PM_{10} and $PM_{2.5}$ (e.g. according to EN ISO 23210:2009 [69, CEN 2009]). This type of characterisation may have to be repeated whenever the process generating dust emissions undergoes significant changes (e.g. fuels, raw materials, catalysts used).

Particle size distributions cannot be determined when the waste gas is saturated with water vapour due to the presence of droplets [69, CEN 2009].

4.3.3.10.5 Formaldehyde

BAT-AELs for emissions of formaldehyde to air were defined in some BAT conclusions (e.g. in the BREFs for the Manufacture of Glass (GLS BREF) [182, COM 2013] and the Production of Wood-based Panels (WBP BREF) [195, COM 2016]). In 2016, however, no EN or ISO standards for formaldehyde measurements from stack emissions were available [59, CEN 2016], [112, ISO 2016]. Therefore, the European Commission identified the development of such a standard as a new action under the annual Union work programme for European standardisation for 2016 [222, COM 2016].

Examples of national or industry standards that are used are given in Annex A.1, Table 7.1, and the WBP BREF [195, COM 2016]. They differ considerably regarding sampling and analytical measurements. In 2014, a study carried out by Eurofins Italy for the European Panel Federation revealed that the methodological differences may result in significantly different measurement results. Formaldehyde shows a strong tendency to dissolve in water droplets and to bind to particles. In the case of waste gases containing aerosols or dust, the sampling method (i.e. isokinetic or non-isokinetic) therefore significantly influences the measurement result. Moreover, other factors may also come into play such as filter/probe heating and probe washing [196, EPF and Eurofins Italy 2014]. For these reasons, the BAT conclusions of the WBP BREF specify several sampling details for the measurement of formaldehyde [195, COM 2016].

4.3.3.10.6 Gaseous chlorides/fluorides and HCl/HF

EN 1911:2010 and ISO 15713:2006 are the SRMs used to measure gaseous chlorides and fluorides, respectively. In both cases, a known volume of waste gas is extracted, filtered and passed through absorption solutions (i.e. water). The resulting chloride/fluoride is determined by using water analytical methods. All chlorine/fluorine-containing compounds that are volatile at the filtration temperature and produce soluble chloride/fluoride compounds upon reaction with water are measured by these methods [71, CEN 2010], [180, ISO 2006]. Generally, almost all of the produced chloride/fluoride originates from HCl/HF, respectively. However, in specific cases, other gaseous halogen compounds such as elementary chlorine (Cl_2) might contribute to the measurement result.

Depending on the nature of the waste gas, the legislation, or the permit, it might be necessary to measure HCl/HF or gaseous chlorides/fluorides. For example, IED Annex VI for waste incineration plants refers to HCl/HF [24, Directive 2010/75/EU 2010]. On the other hand, some BAT-AELs defined in BAT conclusions refer to gaseous chlorides/fluorides (e.g. in the BREFs for Iron and Steel Production (IS BREF) [142, COM 2013], the Manufacture of Glass (GLS BREF) [182, COM 2013], the Non-Ferrous Metals Industries (NFM BREF) [229, COM 2014], and the Production of Cement, Lime and Magnesium Oxide (CLM BREF) [183, COM 2013]).

4.3.3.10.7 Gaseous organic compounds

In 2016, no EN or ISO standards for the measurement of individual gaseous organic compounds from stack emissions were available [59, CEN 2016], [112, ISO 2016]. However, a CEN technical specification was published in 2014 and could become an EN standard after successful validation. CEN/TS 13649:2014 describes the determination of individual gaseous organic compounds. It specifies procedures for the sampling by adsorption on sorbents, the sample preparation by solvent extraction or thermodesorption and the analysis by gas chromatography [283, CEN 2014].

4.3.3.10.8 Mercury and its compounds

The SRM for the measurement of total mercury is EN 13211:2001. A known volume of waste gas is extracted isokinetically (or non-isokinetically if the mercury content in dust and droplets corresponds to $< 1\ \mu g/m^3$), filtered and passed through an absorption solution. The filter is digested. The filter digestate and the absorption solution are analysed by atomic absorption spectrometry (AAS) (see Section 5.3.5.8.9). The result represents the concentration of mercury and its compounds, independent of their state (gaseous, dissolved in droplets, solid, adsorbed on particles) [197, CEN 2001].

Due to the challenges associated with continuous mercury measurements (see Section 0), an alternative emerged in the last years: sorbent trap sampling. Known volumes of waste gas are extracted through sorbent media traps at an appropriate flow rate. Typically, duplicate samples are extracted in parallel using probes inserted into the gas stream. The sorbent material used mainly consists of halogenated carbon. At the end of the sampling period, the sorbent traps are manually replaced, and the used traps are analysed, either by traditional water analytical methods or small thermal desorption systems. Standard sorbent traps are intended to measure gaseous mercury, but particulates containing mercury can also be drawn into the sorbent traps. These particulates are analysed and the measured mercury amount is added to the mercury amount bound to the carbon bed to give the total mercury amount. However, the sampling is not isokinetic and therefore not accurate for measuring particle-bound mercury. Compared to continuous measurements, sorbent trap sampling is easier to install and to operate. If the measurement frequency is not too high, it will also be less expensive. Sorbent traps ensure continuous sampling while providing good sensitivity and accuracy for a wide range of concentrations [199, UNEP 2015], [221, Senior 2015].

The final draft of the BREF for Large Combustion Plants (LCP BREF) stipulates that continuous sampling combined with frequent analysis of time-integrated samples, e.g. by a standardised sorbent trap monitoring method, may be used as an alternative to continuous measurements [277, COM 2016].

However, no EN or ISO standards for mercury measurements with sorbent traps were available in 2016 [59, CEN 2016], [112, ISO 2016]. The European Commission identified the development of such a standard as a new action under the annual Union work programme for European standardisation for 2016 [222, COM 2016]. In the United States, method 30B specifies the use of sorbent traps for measuring mercury emissions from coal-fired combustion sources [223, US EPA 2014]. Related performance benchmarks are described in performance specification 12B [224, US EPA 2014].

4.3.3.10.9 Metals and their compounds

EN 14385:2004 specifies the determination of the mass concentration of the following elements: the metalloids antimony (Sb) and arsenic (As), as well as the metals cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), lead (Pb), manganese (Mn), nickel (Ni), thallium (Tl), and vanadium (V). A known volume of waste gas is extracted isokinetically, filtered and passed through an absorption solution. The filter, the absorption solution and the rinsing solutions are recovered for analysis. The filter is digested. The liquid samples are finally analysed, e.g. by inductively coupled plasma mass spectrometry (ICP-MS), inductively coupled plasma optical emission spectrometry (ICP-OES), or AAS (see Section 5.3.5.8.10). The result includes all metal compounds, independent of whether they are gaseous, dissolved in droplets, solid or adsorbed on particles [47, CEN 2004].

4.3.3.10.10 Methane

EN ISO 25139:2011 is the SRM for the measurement of methane. The sample gas is extracted from the waste gas duct, filtered and introduced into a gas chromatograph (GC). After separation on a packed or capillary column, methane is determined by flame ionisation detection (FID) [217, CEN 2011].

4.3.3.10.11 Nitrogen oxides

NO_X is defined as the sum of nitrogen monoxide (NO) and nitrogen dioxide (NO_2), expressed as NO_2. In flue-gases from conventional combustion systems, the nitrogen oxides consist of more than 95 % NO. The remaining nitrogen oxides predominantly consist of NO_2. The ratio of NO to NO_X may be different in other processes, and other nitrogen oxides may be present [193, CEN 2017].

The SRM for NO_X measurements is EN 14792:2017 which is based on chemiluminescence detection. In the reaction chamber of the analyser, the sampled gas is mixed with ozone which reacts with NO to NO_2. Some of the NO_2 created during this reaction emits light, the intensity of which is proportional to the NO content. The emitted radiation is filtered by means of a selective optical filter and converted into an electric signal by means of a photomultiplier tube. For the determination of NO_X, the sampled gas is fed through a converter where the NO_2 is reduced to NO, and the latter is analysed in the same way as described before. The concentration of NO_2 can then be calculated from the difference between the NO_X concentration and that obtained for NO only (when the sampled gas has not passed through the converter). When a dual-type analyser is used, both NO and NO_X are determined at the same time. In a single-type analyser, the reaction chamber is alternately fed with the raw gas and with the gas having passed the converter that reduces NO_2 to NO. Therefore, NO and NO_X are determined alternately [193, CEN 2017].

4.3.3.10.12 Polycyclic aromatic hydrocarbons (PAHs)

In 2016, two ISO standards were available for the measurement of PAHs, but no EN standard [59, CEN 2016], [112, ISO 2016]. ISO 11338-1:2003 describes the sampling by the heated filter/condenser/adsorber method, the dilution method, or the cooled probe/adsorber method. All three methods are based on isokinetic sampling [218, ISO 2003]. ISO 11338-2:2003 describes the sample preparation, clean-up, and determination using high-performance liquid chromatography (HPLC) or gas chromatography mass spectrometry (GC-MS) [219, ISO 2003].

In the atmosphere, PAHs containing four or more rings tend to adsorb onto particles, while PAHs containing two to four rings tend to be present in gaseous form. In waste gases, the distribution of PAHs between the gaseous phase and particles depends on a number of factors such as temperature, mass of emitted particles, particle size, and water vapour, as well as type and concentration of PAHs [219, ISO 2003].

The toxicity, in particular the carcinogenicity of PAHs, varies considerably from one substance to another. Benzo[*a*]pyrene is considered to be one of the most toxic PAHs and is sometimes used as an indicator for the total concentration of PAHs in a waste gas. This approach is for example used in the NFM BREF [229, COM 2014] and in Germany [61, DE 2002]. Alternatively, the concept of toxic equivalence factors may be applied, similarly to PCDDs/PCDFs (see Section 4.3.3.10.13) [225, Safe 1998], [226, Jung et al. 2010], [227, MDH 2016]. This approach is for example used in Denmark [58, DK 2002].

4.3.3.10.13 PCDDs/PCDFs and dioxin-like PCBs

The measurement of PCDDs/PCDFs and dioxin-like PCBs is covered by a series of EN standards. EN 1948-1:2006 describes the isokinetic sampling by the filter/condenser method, the dilution method, or the cooled probe method [49, CEN 2006]. Subsequently, EN 1948-2:2006 covers the extraction and clean-up [70, CEN 2006]. Finally, EN 1948-3:2006 and EN 1948-4:2010 address the identification and quantification of PCDDs/PCDFs and dioxin-like PCBs, respectively, both using isotope dilution GC-MS [41, CEN 2006], [51, CEN 2010].

In addition to those standards, the technical specification CEN/TS 1948-5:2015 describes the long-term sampling of PCDDs/PCDFs and PCBs. Similarly to the use of sorbent traps for the measurement of mercury (see Section 4.3.3.10.8), this long-term sampling aims at determining the average concentration levels over a longer period, typically four weeks. CEN/TS 1948-5 relies on the same sampling principles as EN 1948-1 [216, CEN 2015]. The European Commission identified the validation of this technical specification as a new action under the annual Union work programme for European standardisation for 2015 [222, COM 2016].

The sampling time for the measurement of PCDDs/PCDFs is typically six to eight hours [24, Directive 2010/75/EU 2010], [49, CEN 2006].

According to IED Annex VI for waste incineration plants and to EN 1948-1:2006, measurement results for PCDDs/PCDFs are expressed in the unit ng I-TEQ/m^3, where I-TEQ means international toxic equivalent, derived by applying international toxic equivalence factors (I-TEFs; also referred to as international toxic equivalency factors). These factors indicate the toxic potential of a single PCDD or PCDF congener relative to the toxic effect of 2,3,7,8-TCDD, which is the congener with the highest toxicity. The IED sets I-TEFs for 17 PCDD/PCDF congeners including 2,3,7,8-TCDD [24, Directive 2010/75/EU 2010], [49, CEN 2006].

If there is a need to also cover dioxin-like PCBs, it is advisable to use the unit ng WHO-TEQ/m^3, applying toxic equivalence factors from the World Health Organisation (WHO-TEFs; also referred to as WHO toxic equivalency factors) which, in addition to I-TEFs, include toxic equivalence factors for the 12 dioxin-like PCBs. Another difference between the two concepts is that WHO-TEFs differ from I-TEFs for a few PCDDs/PCDFs [50, Van den Berg et al. 2006], [51, CEN 2010].

Toxic equivalence factors are listed in Annex A.4, Table 7.5.

4.3.3.10.14 Sulphur oxides

SO_X is defined as the sum of sulphur dioxide (SO_2), sulphur trioxide (SO_3) and sulphuric acid aerosols (H_2SO_4), expressed as SO_2. For most industrial emission sources, SO_2 is the dominating sulphur oxide species (i.e. typically > 90 %).

The SRM for the measurement of SO_2 is EN 14791:2017. A known volume of waste gas is extracted, filtered and passed through an absorption solution containing hydrogen peroxide which oxidises SO_2 to sulphate. The latter is determined by ion chromatography or titration. SO_3 is included in the measurement result as it is equally absorbed and oxidised to sulphate [181, CEN 2017]. Therefore, the standard actually measures SO_X.

Since early 2017, a technical specification for an instrumental technique for sampling and determining the concentration of gaseous sulphur dioxide emissions from stacks has been available. CEN/TS 17021:2017 is applicable to both periodic measurements and the calibration of AMS permanently installed on stacks, for regulatory or other purposes. The technical specification does not prescribe a specific technique, but sets performance criteria for the analyser and the associated sampling system, hence for the complete measuring system which is a portable automated measuring system (P-AMS). The actual measurement may be based on different techniques including IR or UV absorption, UV fluorescence or electrochemical cells [211, CEN 2017].

Depending on the nature of the waste gas, the legislation, or the permit, it might be necessary to measure SO_2 or SO_X. For example, IED Annex V for large combustion plants and IED Annex VI for waste incineration plants refer to SO_2 [24, Directive 2010/75/EU 2010]. Some BAT-AELs defined in BAT conclusions also refer to SO_2 (e.g. in the BREFs for the Non-Ferrous Metals Industries (NFM BREF) [229, COM 2014], the Production of Pulp, Paper and Board (PP BREF) [160, COM 2015], and the Refining of Mineral Oil and Gas (REF BREF) [143, COM 2015]), but others refer to SO_X (e.g. in the BREFs for the Iron and Steel Production (IS BREF) [142, COM 2013], the Manufacture of Glass (GLS BREF) [182, COM 2013], and the Production of Cement, Lime and Magnesium Oxide (CLM BREF) [183, COM 2013]).

In some cases, SO_X emissions may be determined by fuel analysis (see Section 4.4.2).

4.3.3.10.15 Total volatile organic carbon (TVOC)

EN 12619:2013 defines TVOC as the sum of all gaseous and vaporous organic compounds, expressed as total carbon. The measurement relies on an FID with a sample gas cleaning system that prevents contamination by particles and/or condensation inside the instrument. Hydrocarbons of a higher order, entering the analyser as solids, are filtered and consequently not measured. Although IED Annex VI for waste incineration and Annex VII for installations and activities using organic solvents refer to the measurement of TOC (total organic carbon), the FID analyser does not actually measure organic compounds bound to particles. According to EN 12619:2013, this is generally accepted in the industry and by competent authorities [48, CEN 2013].

The FID ionises organically bound carbon atoms in a hydrogen flame and the ionisation current is measured. One advantage of the FID is that it shows negligible interference from a number of inorganic compounds (e.g. CO, CO_2, NO, and H_2O). However, the oxygen level influences the signal and calibrations are carried out with similar levels of oxygen as present in the stack gas. The FID sensitivity depends mostly on the number of carbon atoms, but also on the molecular structure (i.e. single or double bonds, number and nature of heteroatoms, chain length, and ring structure). For example, the FID is usually less sensitive for oxygen-containing organic compounds compared to pure hydrocarbons with the same number of carbon atoms per molecule [48, CEN 2013], [231, MCERTS 2016].

The response factor is a function of the specific design of the detector and the adjusted operating conditions. EN 12619:2013 prescribes the use of propane (C_3H_8) for the calibration, setting its response factor to 1.00 while taking into account the number of carbon atoms (i.e. three). In the case of waste gases containing one or a limited number of organic compounds in stable proportions, the concentration(s) of the individual compound(s) may be determined provided that the response factors have been determined beforehand [48, CEN 2013].

In the case of waste gases from **non-combustion processes** (e.g. from the use of organic solvents), TVOC may be measured with EN ISO 13199:2012. The extracted waste gas is filtered and split into two streams. The first stream passes through a catalytic converter for the complete oxidation of organic compounds to CO_2 which is then measured by NDIR. The second stream is directly led to the NDIR analyser for CO_2 measurement. The difference in the CO_2 concentrations between the two streams is equal to the CO_2 concentration originating from the organic compounds. The advantages compared to an FID include greater safety (no flame, no hydrogen), equal response factors of individual organic compounds with the same number of carbon atoms, and no interference due to oxygen [194, CEN 2012]. On the other hand, TVOC measurements based on catalytic oxidation show two disadvantages: the catalysts can be poisoned and the conversion of the organic compounds to CO_2 may not always be complete [231, MCERTS 2016].

Photo ionisation detectors (PIDs) may be used alternatively to measure organic compounds. PIDs work in the same way as FIDs except that UV light is used for the ionisation. As for FIDs, the sensitivity depends on the number of carbon atoms and the molecular structure. Moreover, the PID sensitivity also depends on the type of UV lamp used. For example, for butanol the relative response for 9.8 eV, 10.6 eV, and 11.7 eV lamps is 1, 15, and 50, respectively [192, Honeywell 2004].

FIDs and PIDs have different sensitivities and are calibrated with different gases. Therefore, analytical results are **not comparable**. In broad terms, FIDs respond more to carbon chain length, whereas PIDs respond more to functional groups. For example, an FID shows a relatively similar response to propane, isopropanol, and acetone (slightly decreasing in this order [230, Dietz 1967]), because these compounds all have three carbon atoms, whereas a PID is not very sensitive to propane, moderately sensitive to isopropanol, and very sensitive to acetone. The relative order of sensitivity is as follows [192, Honeywell 2004]:

FID: Aromatics, long-chain compounds > short-chain compounds (methane) > halogenated compounds.
PID: Aromatics, iodinated compounds > olefins, ketones, ethers, amines, sulphur compounds > esters, aldehydes, alcohols, aliphatics > chlorinated aliphatics, ethane > methane (no response).

PIDs generally do not respond to methane and therefore actually measure non-methane volatile organic carbon (NMVOC). While FIDs measure TVOC including methane, they may be modified to measure NMVOC by adding a methane-cutting catalyst [190, Wilford 2006].

Compared to FIDs, PIDs are simpler and intrinsically explosion-proof (no hydrogen flame), and therefore often used in portable instruments (see Section 4.5.3). PIDs can detect much lower levels of organic compounds than FIDs, while FIDs are more linear in higher concentration ranges. Moreover, FIDs are generally free from humidity effects [190, Wilford 2006], [192, Honeywell 2004].

In 2016, no EN or ISO standards for the measurement of organic compounds from stack emissions with PIDs were available [59, CEN 2016] [112, ISO 2016].

Depending on the nature of the waste gas (e.g. if the waste gas contains methane), the legislation, or the permit, it might be necessary to measure TVOC or NMVOC. As mentioned before, IED Annexes VI and VII refer to TOC and thus to TVOC [24, Directive 2010/75/EU 2010]. Moreover, some BAT-AELs defined in BAT conclusions refer to TOC or TVOC (e.g. in the BREFs for the Non-Ferrous Metals Industries (NFM BREF) [229, COM 2014] and the Production of Cement, Lime and Magnesium Oxide (CLM BREF) [183, COM 2013]). However, the BAT-AELs in the BAT conclusions of the BREF for the Refining of Mineral Oil and Gas (REF BREF) refer to NMVOC [143, COM 2015]. A special case can be found in the BAT conclusions of the BREF for the Production of Wood-based Panels (WBP BREF) where the BAT-AELs generally refer to TVOC, but the methane content is subtracted in the case of emissions originating (partly) from the dryer when using fuels such as natural gas and liquefied petroleum gas. This subtraction aims at differentiating between the emission sources (i.e. from the drying process or the heater) [195, COM 2016]. The E-PRTR refers to NMVOC [147, EC 2006]).

4.3.3.11 Reference/Standard conditions

General information on reference/standard conditions is given in Section 4.3.2.5.1.

The periodic measurement of a pollutant often requires the simultaneous measurement of reference quantities, also referred to as peripheral parameters. EN standards for the periodic measurement of oxygen and water vapour are available [73, CEN 2017], [74, CEN 2017]. Moreover, the measurement of reference quantities is also needed for the AMS calibration with the SRM during the QAL2 procedure (see Section 4.3.2.2.2) [36, CEN 2014].

Specific standard conditions apply for the measurement of the odour concentration with dynamic olfactometry (i.e. a temperature of 293.15 K without correction for the water vapour content; see Section 4.6.3.2).

4.3.3.12 Data treatment

The measurement results are converted to the corresponding standard conditions (see Sections 4.3.2.5 and 4.3.3.11) [45, CEN 2007].

How to average the measurement results of periodic measurements strongly depends on the number of individual measurements per measurement series, the measurement frequency, and the compliance assessment regime applied (see Section 3.4.4.2).

In some cases, the measurement uncertainty is subtracted from the measured values (see Section 3.4.4.3).

4.3.3.13 Reporting

The measurement report should describe, in a transparent and traceable way, where and how the measurements were carried out and should also provide sufficient detail to enable the results to be traced back through the calculations to the collected raw data and operating conditions [45, CEN 2007]. In several Member States, standard report formats are specified for regulatory purposes, but they do not necessarily have a comparable content and level of detail. To allow a Europe-wide comparison of measurement results, it is advisable that at least the requirements given by EN 15259:2007, as mentioned below, are taken into account.

According to EN 15259:2007, an emission measurement report includes at least the following information [45, CEN 2007]:

- general information, such as the operator's name, the address of the installation, the name and the address of the testing laboratory;
- definition of the project by specification of the measurement objective(s);
- description of the installation and materials handled;
- identification of the measurement site and section;
- identification of the measurement methods and apparatus according to individual standards for the measured pollutants and reference quantities;
- operating conditions of the production process during the measurement, including the waste gas treatment units;
- identification of deviations from the measurement plan;
- reference to how to access and use the original data for verification purposes;
- measurement results and other relevant data necessary for the interpretation of the results, including sampling date (hour, day, month and year) and measurement uncertainties;
- calculation procedures, such as the conversion of data to specific standard conditions;
- presentation of the results.

Furthermore, any deviation from EN standards (e.g. EN 15259:2007) and from the measurement plan should be justified and documented in the measurement report [45, CEN 2007].

Also, each EN standard contains a section on how the measurement method and the performance parameters should be specified in any report and how the achieved results should be reported [76, CEN 2007].

In addition, every testing laboratory uses dedicated measurement or work files with much more detailed information for internal documentation. These files should allow, among others, to trace the storage and handling of every sample, from the measurement point to the analysis of the sample, including the data treatment, and the documentation of the results.

Under certain conditions, measurement results/reports are made publicly available, for example according to IED Article 24(3)(b) [24, Directive 2010/75/EU 2010].

4.3.3.14 Drawing up or review of BREFs

During the data collection for the drawing up or review of BREFs, complete measurement reports for periodic measurements are usually not provided. Instead, the data collection usually includes the individual measurement results, measurement uncertainties, sampling durations, reference conditions, number of consecutive measurements in one measurement series, and the measurement frequency, together with unambiguous information on the operating conditions to distinguish between normal and other than normal operating conditions.

If averaged values are reported in addition, the number of individual measurements, the minimum and the maximum values, and the way the LoD/LoQ has been considered are also relevant for the data assessment and should thus be provided.

The provided data are the basis for defining BAT and BAT-AEPLs, where appropriate. For BAT-AEPLs, the associated monitoring regime needs to be defined. In 2016, the following general conditions for periodic measurements were widely used in BAT conclusions:

- reference conditions (temperature 273.15 K, pressure 101.3 kPa, dry gas, defined oxygen content);
- a sampling duration of at least 30 minutes;
- at least three consecutive measurements in one measurement series;
- a measurement frequency of at least once (or twice) per year, if appropriate;
- measurements at the time of the highest emission state under normal operating conditions, if appropriate.

Depending on the industrial sector and the pollutant, the monitoring regime for periodic measurements might be adapted. Examples include the specific standard conditions for the measurement of the odour concentration with dynamic olfactometry at 293.15 K without correction for the water vapour content (see Section 4.6.3.2) or an increased sampling duration for the measurement of PCDDs/PCDFs (see Section 4.3.3.10.13). Also, more than three consecutive measurements and a lower or higher measurement frequency might be appropriate in some cases.

For further information on data gathering and reference information accompanying emission data, see the 'BREF guidance' [39, EU 2012].

4.4 Indirect methods

4.4.1 Examples of surrogate parameters

4.4.1.1 Overview

General aspects of surrogate parameters including the distinction between quantitative, qualitative, and indicative surrogate parameters are described in Section 3.3.3.3.1.

Examples of **quantitative surrogate parameters** may include the following [3, COM 2003]:

- TVOC instead of individual organic compounds (see Section 4.3.3.10.15);
- fuel flow rate and fuel composition to determine the flue-gas flow rate of a furnace (e.g. according to EN ISO 16911-1:2013 [254, CEN 2013]);
- Predictive Emission Monitoring Systems (PEMS) which rely on a combination of surrogate parameters (see Section 4.4.1.2).

Examples of **qualitative surrogate parameters** may include the following [3, COM 2003]:

- dust instead of individual metals and their compounds;
- dust instead of PM10 or PM2.5.

Examples of **indicative surrogate parameters** may include the following [3, COM 2003]:

- temperature of the waste gas from a condenser instead of TVOC;
- pressure drop, flow rate, pH and humidity of a biofilter instead of odour;
- combustion temperature and residence time (or flow rate) of a thermal oxidiser instead of the compounds to be oxidised;
- catalyst temperature and residence time (or flow rate) of a catalytic oxidiser instead of the compounds to be oxidised;
- flow rate, voltage, and quantity of removed dust of an electrostatic precipitator instead of the dust concentration;
- flow and temperature of waste gas, flow and pressure of scrubbing liquid, and pressure drop of a wet scrubber instead of the compounds to be scrubbed;
- filter leakage monitor (e.g. according to EN 15859:2010 [64, CEN 2009]) for a fabric filter (see Section 4.3.2.2.1) instead of dust.

4.4.1.2 Predictive Emission Monitoring Systems (PEMS)

Predictive Emission Monitoring Systems (PEMS) are systems used to determine the emission concentrations of a pollutant based on their relationship with a number of characteristic continuously monitored process parameters (e.g. fuel gas consumption, air/fuel ratio) and fuel or feed quality data (e.g. the sulphur content) of an emission source.

PEMS combine up to 25 parameters to calculate the corresponding emission concentrations of the pollutant. The calibration of these systems with direct measurements is complex, because it has to be carried out and validated under a broad range of operating conditions, but the advantage is that the resulting emission concentrations can be determined continuously without an AMS. In any case, PEMS need to be proven to be applicable for a certain process.

In 2017, there were activities in the Technical Committee CEN/TC 264 'Air quality' to draw up a technical specification on the applicability, execution and quality assurance of PEMS used for the determination of stationary source emissions [78, CEN 2017].

In the Netherlands, NTA 7379:2014 provides guidelines for the implementation and quality assurance of PEMS [77, NEN 2014].

4.4.2 Fuel analysis

Fuel analysis is an example of a mass balance (see Section 3.3.3.3.2). Depending on the industrial sector, it can be used to predict emissions of SO_2, metals and other substances based on the application of conservation laws, if the fuel mass flow rate is available. The basic equation used in fuel analysis emission calculations is the following:

Equation 4.2: $$E = Q \times c/100 \times \left(M_W / M_{WE}\right) \times t \times (100 - R)$$

where E = annual load of the chemical species emitted (kg/yr);
Q = fuel mass flow rate (kg/h);
c = concentration of the elemental pollutant in the fuel (wt-%);
M_W = molecular weight of the chemical species emitted (g/mol);
M_{WE} = elemental weight of the pollutant in the fuel (g/mol);
t = operating hours (h/yr);
R = retention factor (wt-%), i.e. the mass fraction of the elemental pollutant remaining in the combustion process (e.g. as ash).

4.4.3 Drawing up or review of BREFs

With the exception of the quantitative surrogate parameter TVOC, indirect methods are less frequently used in BAT conclusions on emissions to air than in BAT conclusions on emissions to water (see Section 5.4.2). Such instances include the following:

- BREF for the Manufacture of Glass (GLS BREF): BAT 7(iii) and BAT 7(viii) stipulate that it is BAT to use surrogate parameters to ensure that the treatment system is working properly between periodic measurements, including for dust, NO_X and SO_2 emissions. Reagent feed, temperature, water feed, voltage, dust removal, and fan speed are listed as examples of surrogate parameters [182, COM 2013].
- BREF for the Intensive Rearing of Poultry or Pigs (IRPP BREF): A mass balance is mentioned in BAT 25 as one option to monitor emissions of ammonia to air [284, COM 2015].
- BREF for Iron and Steel Production (IS BREF): BAT 46 on the reduction of diffuse emissions from coke oven plants relies on the control of the visible emissions from all doors as a surrogate parameter [142, COM 2013].
- BREF for the Refining of Mineral Oil and Gas (REF BREF): Indirect methods are mentioned in BAT 4 on the monitoring of emissions to air. They include estimations through an appropriate combination of measurements of surrogate parameters (such as O2 content, sulphur or nitrogen content in the feed/fuel), calculations and periodic stack measurements. Fuel analysis and PEMS are also mentioned. For combustion units with a rated thermal capacity of > 50 MWth and catalytic cracking, continuous SO2 measurements may be replaced by calculations based on measurements of the sulphur content of the fuel or the feed (i.e. by fuel analysis), where it can be demonstrated that this leads to an equivalent level of accuracy. Furthermore, for sulphur recovery units (SRUs), continuous SO_2 measurements may be replaced by a continuous material balance or other relevant process parameter monitoring, provided appropriate measurements of SRU efficiency are based on periodic (e.g. once every two years) plant performance tests [143, COM 2015].
- BREF for the Production of Wood-based Panels (WBP BREF): BAT 15 stipulates that it is BAT to monitor appropriate surrogate parameters. In the case of scrubbers, these may include waste gas flow and temperature, visual appearance of emissions, as well as water

flow and temperature, while in the case of electrostatic precipitators, this may include the voltage drop [195, COM 2016].

The measurement of the pressure drop across a fabric filter as referred to in various BREFS (e.g. in the NFM, TAN and WBP BREFS [179, COM 2013] [195, COM 2016] [229, COM 2014]) provides information on whether the cleaning mechanism is working adequately (i.e. if filters are cleaned and not blinding which in turn affects energy usage). In the event of a filter failure, however, there is no measurable increase in the pressure drop and therefore no indication of increased emissions [246, UK 2013].

4.5 Diffuse emissions

4.5.1 Overview

The quantification of the total emissions of an installation often requires an assessment of diffuse emissions including fugitive emissions (see definitions in Section 4.5.2), as these emissions can potentially account for a considerable amount of the total emissions and can have relevant impacts on the environment. Sometimes diffuse emissions may also have economic significance for an installation. For these reasons, permits and BAT conclusions include, where appropriate and reasonable, provisions that specify how to properly monitor and reduce these emissions [3, COM 2003].

The quantification of diffuse emissions might not be easy and is, in general, labour- and cost-intensive. Measurement techniques are available, but the measurement uncertainty might be relatively high and, therefore, the level of confidence in the results might be low. Furthermore, due to the extended number of potential sources, the assessment of the total amount of diffuse emissions may be more costly than point source emission measurements [3, COM 2003].

In addition to the following sections, the BREF for Refining of Mineral Oil and Gas (REF BREF) contains detailed information on the monitoring of diffuse VOC emissions from refineries [143, COM 2015].

4.5.2 Definitions

The definitions of diffuse and fugitive emissions vary from one source to another, for example:

- Chapter 5 of the IED for installations and activities using organic solvents defines fugitive emissions as 'any emissions not in waste gases of volatile organic compounds into air, soil and water as well as solvents contained in any products'. Waste gases are defined as 'the final gaseous discharge containing volatile organic compounds or other pollutants from a stack or abatement equipment into air' [24, Directive 2010/75/EU 2010].
- EN 15445:2008 defines fugitive dust emission as 'uncontrolled dust emission to the atmosphere from diffuse emission' and gives examples such as windblown dust from stockpiles, dust from workshop buildings and from the handling of dry bulk goods, and dust from resuspension by traffic. Diffuse emissions are not defined [247, CEN 2008].
- EN 15446:2008 defines fugitive emission as 'emission to the atmosphere caused by loss of tightness of an item which is designed to be tight'.

In this document, diffuse and fugitive emissions are understood as follows [3, COM 2003], [143, COM 2015], [154, COM 2016]:

- **Diffuse emissions:** Non-channelled emissions to the environment.
  Emissions usually concern volatile or dusty substances. Diffuse emission sources can be point, linear, surface or volume sources. Examples include storage facilities during loading and unloading, open-air storage of solid matter, separation pools in oil refineries, doors in coke plants, and electrolysis cells in chlor-alkali plants. Multiple emissions inside a building are normally considered diffuse emissions.
- **Fugitive emissions:** Diffuse emissions from point sources.
  Fugitive emissions are a subset of diffuse emissions and typically originate from leaking equipment.

4.5.3 EN standards

Table 4.6 lists EN standards for the monitoring of diffuse and fugitive emissions.

Table 4.6: EN standards for the monitoring of diffuse and fugitive emissions

Standard	Title
EN 15445:2008	Fugitive and diffuse emissions of common concern to industry sectors - Qualification of fugitive dust sources by reverse dispersion modelling
EN 15446:2008	Fugitive and diffuse emissions of common concern to industry sectors - Measurement of fugitive emission of vapours generating from equipment and piping leaks
EN 16253:2013	Air quality - Atmospheric measurements near ground with active Differential Optical Absorption Spectroscopy (DOAS) - Ambient air and diffuse emission measurements

EN 15445:2008 specifies a reverse dispersion modelling method to qualify the diffuse dust emission rates of industrial installations or sites. The method relies on calculations using a dispersion model and the definition of an experimental set-up for sampling. It takes into account field data such as the number, height and width of diffuse dust emission sources, the results of ambient air dust measurements, sampling distances between emission sources and sampling sites, and meteorological information. The standard does not allow quantification of the dust emission rates in absolute figures, but it is a tool to identify relevant emission sources and to implement prevention and reduction techniques. EN 15445:2008 states that it should not be used for compliance assessment or for the comparison of different installations belonging to the same industrial sector [247, CEN 2008].

EN 15446:2008 applies to the measurement of fugitive emissions of volatile organic compounds (VOCs) from process equipment. VOCs are defined as all products of which at least 20 wt-% show a vapour pressure higher than 0.3 kPa at 20 °C. The method, often referred to as the 'sniffing method', uses portable instruments to detect VOC leaks from individual sources. Any detector type is allowed (e.g. based on catalytic oxidation, infrared absorption, flame ionisation, or photo ionisation), provided it meets the specifications and performance criteria of the standard. In addition, EN 15446:2008 describes a procedure to estimate the emission rate from individual sources and the total emissions of the installation over a given reporting period (generally a year) by means of a set of correlations [248, CEN 2008]. Sniffing is often used in leak detection and repair (LDAR) programmes [143, COM 2015], [154, COM 2016].

EN 16253:2013 describes the use of active Differential Optical Absorption Spectroscopy (DOAS) with a continuous radiation source for the determination of gaseous compounds (e.g. NO_2, SO_2, O_3, Hg, benzene, toluene, xylene and other VOCs) in ambient air or in diffuse emissions. DOAS systems support direct multi-constituent measurements. They rely on the absorption of near ultraviolet, visible and/or near infrared light by gaseous compounds along an open monitoring path between a radiation source and a spectrometer. The measurement is conducted at wavelengths typically ranging from 250 nm to 2 500 nm and with a high spectral resolution of 0.1–1 nm. As the technique uses differential absorption instead of absolute absorption, the results are not affected by absorption and scattering due to particles or droplets. DOAS might be used as an alternative measuring technique, on which emission estimates can be based in those cases when direct measurements cannot be used adequately for the monitoring of diffuse emissions, such as emissions from area sources, from sewage treatment plants and from leaks in production areas or pipeline systems [249, CEN 2013].

Independent of the aforementioned EN standards, EN 15259:2007 can also be used if direct emission measurements are carried out at diffuse sources, in particular the planning and reporting aspects of this standard [45, CEN 2007].

In 2012, the European Commission issued a mandate to CEN to prepare a new European standard for the quantification of diffuse and fugitive VOC emissions to air, in particular from the storage, transfer and handling (loading/unloading) of such compounds [251, COM 2012]. In 2016, the Technical Committee CEN/TC 264 'Air quality' was therefore developing a standard covering optical gas imaging (OGI) (see Section 4.5.4.1), differential absorption LIDAR (DIAL) and solar occultation flux (SOF) (see Section 4.5.4.2.1), as well as calculation/estimation methods (see Section 4.5.4.3).

4.5.4 Other methods

4.5.4.1 Measurements at source

Direct measurements
Direct measurements are based on the measurement of a volume flow and a concentration in defined, representative parts of an emission source area, for example under a hood, in a wind tunnel, or at hall openings (windows, gates, ridge turrets) [235, VDI 2005], [236, VDI 2011].

Sniffing
Sniffing is described in EN 15446:2008 [248, CEN 2008] (see Section 4.5.3).

Optical gas imaging
Optical gas imaging (OGI) uses small lightweight hand-held IR cameras which enable the visualisation of gas leaks in real time, so that they appear as 'smoke' on a video recorder, together with the normal image of the equipment concerned. This technique is primarily used to easily and rapidly locate significant VOC leaks, e.g. from process equipment, storage tank fittings, pipeline flanges or vents. Active OGI systems are based on the backscattering of an IR laser beam by the equipment and its surroundings, while passive OGI systems are based on the natural IR radiation emitted from the equipment and its surroundings [143, COM 2015].

An advantage of OGI is the possibility to detect leaks under insulation and to screen from a distance, so that VOC emissions from equipment not accessible for sniffing can be located. However, the sensitivity of OGI systems was reported to be lower than that of traditional sniffing equipment. OGI works particularly well with alkanes, but less so with aromatic compounds. OGI is often used in leak detection and repair (LDAR) programmes [143, COM 2015], [154, COM 2016]. It may also be used to estimate emission rates under certain conditions [237, CONCAWE 2008].

In the Netherlands, NTA 8399:2015 provides guidelines for detecting diffuse VOC emissions using passive OGI systems [134, NEN 2015].

4.5.4.2 Remote measurement methods

4.5.4.2.1 Optical remote sensing

Optical remote sensing (ORS) methods are a specific type of remote measurement methods which are conducted away from the point or area where the pollutant is emitted. ORS methods measure the concentration of air pollutants based on their interaction with electromagnetic radiation (i.e. UV, visible or IR light). Some methods are capable of measuring one or two compounds (e.g. TDL), others are capable of measuring several compounds simultaneously (e.g. UV-DOAS), and others are capable of measuring a large number of compounds simultaneously (e.g. FTIR).When combined with meteorological data, ORS methods allow for a calculation of the emission rates of pollutants downwind of diffuse emission sources [136, US EPA 2011].

Several ORS methods have been used [136, US EPA 2011], [143, COM 2015], [154, COM 2016]:

- DOAS (Differential Optical Absorption Spectroscopy): DOAS is described in EN 16253:2013 [249, CEN 2013] (see Section 4.5.3).
- FTIR spectrometers and tunable diode lasers (TDLs) are similar to DOAS as they also rely on the absorption of light by the pollutant(s). The difference is that FTIR spectrometers record the light intensity over a wide spectral IR range using a Fourier transformation, while in TDLs, the wavelength of the laser is tuned over a selected absorption band of the pollutant [136, US EPA 2011].
- **DIAL** (differential absorption LIDAR): DIAL uses lasers directed into the atmosphere to measure aerosols, dust, or gaseous compounds. Spatial concentrations are obtained from the reflected or backscattered light at two wavelengths: one at the absorption band of the pollutant(s) and the other just outside of it. The latter is used to measure the background light scattering. The ratio of the backscattered light intensity at the two wavelengths is measured and combined with the time delay of the return signal. The ratio allows the concentrations of the pollutant(s) to be determined while the time delay is used to determine the location. By measuring the backscattered light at different angles from the source, the data can be processed to show the two-dimensional plume shape of an emission [136, US EPA 2011].

  The main advantage of DIAL over other ORS methods is its ability to spatially locate the concentrations of the pollutant(s) [136, US EPA 2011]. Moreover, DIAL allows more comprehensive measurements of diffuse emissions, which may be underestimated when using other methods [135, Chambers et al. 2008], [252, Robinson et al. 2011]. However, the number of wavelengths that can be generated by laser technology is limited, and thus so too is the number of pollutants that can be monitored. Additionally, the costs of using DIAL are reported to be high [136, US EPA 2011].
- **SOF** (solar occultation flux): SOF is a passive ORS method which uses the sun as a broadband light source. A SOF system contains three components: a spectrometer to measure the solar radiation (usually an FTIR spectrometer), a sun tracker to maintain the instrumental orientation to the solar zenith, and a GPS for the accurate measurement of the location relative to the gas plume. The SOF system is mounted on a mobile vehicle which moves along a given geographical itinerary, crossing the wind direction and cutting through emission plumes [136, US EPA 2011].

4.5.4.2.2 Other remote measurement methods

Tracer gases

This method consists of releasing a tracer gas at different identified points or areas and at various heights above the surface of the installation. Then the pollutant (e.g. VOCs) and tracer gas concentrations are measured downwind of the installation by portable instruments, which may rely on ORS. The emission rates can be estimated from simple flux assumptions with near stationary conditions and assuming insignificant atmospheric reactions or deposition of gases between the leakage points and the sampling points [3, COM 2003], [136, US EPA 2011].

Ambient air quality measurements

The qualitative monitoring of diffuse emissions may be performed by ambient air quality measurements downwind of the installation (e.g. by diffusive sampling or by analysis of wet and dry depositions), which then allows an estimation of the evolution of diffuse emissions over time, provided that they can be distinguished from background concentrations and other sources [3, COM 2003].

Reverse dispersion modelling (RDM)

RDM allows the estimation of the emissions of a source or an installation from downwind measured air quality data and meteorological data. To cover all potential emission sources, it is common practice to monitor at several points. High plume emissions may not be covered by this approach. The (exact) location of a leak might be difficult to indicate with this method [3, COM 2003]. An RDM method for dust is described in EN 15445:2008 [247, CEN 2008] (see Section 4.5.3).

Biomonitoring
Biomonitoring is described in Section 4.7.

4.5.4.3 Calculations and estimations

Mass balances
Mass balances are described in Section 3.3.3.3.2. A solvent management plan according to Part 7 of Annex VIII to the IED (for installations and activities using organic solvents) constitutes an example of the application of a mass balance to quantify diffuse emissions of organic compounds [24, Directive 2010/75/EU 2010].

Emission factors and/or correlations
Emissions from storage tanks, loading/unloading operations, waste water treatment, and cooling water systems are often calculated based on general emission factors and/or correlations [3, COM 2003]. Emission factors are described in Section 3.3.3.3.3.

4.5.5 Drawing up or review of BREFs

In 2016, a number of BREFs contained BAT on the monitoring of diffuse emissions, including the following:

- BREF for Iron and Steel Production (IS BREF): BAT 16 specifies that it is BAT to determine the order of magnitude of diffuse emissions from relevant sources. Direct measurements are preferred over indirect methods or evaluations based on calculations with emission factors [142, COM 2013].
- BREF for Refining of Mineral Oil and Gas (REF BREF): BAT 6 specifies that it is BAT to monitor diffuse VOC emissions to air from the entire site by using the three following techniques: sniffing, OGI, and calculations of emissions based on emission factors. Moreover, the screening and quantification of site emissions by periodic campaign measurements with optical absorption-based techniques such as DIAL or SOF is considered a useful complementary technique [143, COM 2015].
- BREF for Common Waste Water and Waste Gas Treatment/Management Systems in the Chemical Sector (CWW BREF): BAT 5 specifies that it is BAT to periodically monitor diffuse VOC emissions to air from relevant sources by using an appropriate combination of sniffing, OGI, and calculations of emissions based on emission factors. Where large amounts of VOCs are handled, the screening and quantification of emissions from the installation by periodic campaign measurements with optical absorption-based techniques such as DIAL or SOF is considered a useful complementary technique [154, COM 2016].

When addressing diffuse and fugitive emissions in BREFs, it seems appropriate to clearly define these terms (see Section 4.5.2).

4.6 Odour

4.6.1 Overview

Odour emissions occur in several (agro)industrial sectors, such as the intensive rearing of animals, the food industry, the iron and steel industry, the chemical industry, and waste (water) treatment. They are caused by channelled or, more often, by diffuse sources. Gaseous emissions may contain odorous substances which can be perceived by the human olfactory system. These substances can be inorganic, such as hydrogen sulphide or ammonia, or organic, such as hydrocarbons, sulphur compounds (e.g. mercaptans) or amines.

Depending on the location of the installation, the release of an odorous substance may be perceived by the population living in the vicinity of the installation, causing odour nuisance and complaints. As a consequence, there may be a need to monitor the odour emissions and, if the source can be identified, to take measures to reduce these emissions.

The sensory perception of odours has four major dimensions [52, CEN 2003]:

- detectability: the minimum concentration necessary for detection;
- intensity: the perceived strength of the odour;
- quality: what the odour smells like;
- hedonic tone: the perceived pleasantness or unpleasantness of the odour.

In general, the odour of an emission is composed of several chemical substances. The analysis of a single chemical substance is in most cases not sufficient to describe and quantify the odour emission and can thus cause significant underestimations. As a consequence, odour measurements are performed with human sensors.

Nevertheless, the identification of the main odorous substances may also be needed to choose appropriate techniques to prevent or reduce odour emissions [133, FR 2013].

There are several methods available for monitoring odours quantitatively or qualitatively, by direct or indirect methods. The following sections address parameters to describe odours (e.g. odour concentration, odour intensity and hedonic tone) and some common methods applied in Europe for the measurement of odour emissions.

4.6.2 Definitions

According to the relevant European standards, the following definitions apply:

- **Odour detection:** To become aware of the sensation resulting from adequate stimulation of the olfactory system [52, CEN 2003], [85, CEN 2016], [86, CEN 2016].
- **Detection threshold:** The odorant concentration which has a probability of 50 % of being detected under the conditions of the test [52, CEN 2003]. At the detection threshold, the odour can be perceived by humans but not recognised [85, CEN 2016]. The detection threshold is characteristic for each chemical substance. In the case of mixtures of chemical substances, the detection threshold cannot be estimated from the detection thresholds of the individual substances [246, UK 2013].
- **Odour type:** Odour that can be recognised and assigned to a certain installation or source. Odour types are defined specifically for a survey. One installation can emit more than one odour type and several installations can emit the same odour type [85, CEN 2016], [86, CEN 2016].
- **Odour recognition:** An odour sensation that allows positive identification of the odour type [85, CEN 2016], [86, CEN 2016].

- **Recognition threshold:** The odorant concentration which has a probability of 50 % of being recognised under the conditions of the test [52, CEN 2003].
- **European odour unit (ou$_E$):** Amount of odorant(s) that, when evaporated into one cubic metre of neutral gas at standard conditions, elicits a physiological response from a panel (detection threshold) equivalent to that elicited by one European reference odour mass (EROM) evaporated into one cubic metre of neutral gas at standard conditions [52, CEN 2003].
- **European reference odour mass (EROM):** Accepted reference value for the European odour unit, equal to a defined mass of a certified reference material. One EROM is equivalent to 123 µg *n*-butanol which produces a concentration of 0.040 µmol/mol if it is evaporated into one cubic metre of neutral gas [52, CEN 2003].
- **Odour concentration:** Number of European odour units (ou$_E$) in one cubic metre at standard conditions measured by dynamic olfactometry according to EN 13725 [52, CEN 2003].
- **Odour intensity:** Strength of odour sensation caused by the olfactory stimulus. The odour intensity can be described by an ordinal scale ranging from 0 (no odour) to 6 (extremely strong odour) [56, UK 2011], [80, VDI 1992]. The relationship between the stimulus and the perceived odour intensity is logarithmic. Therefore, the relationship between the odour concentration and the odour intensity is not linear and can follow a different relationship for different (mixtures of) odorants. In addition to the odour concentration, the odour intensity is influenced by both the odour quality and the hedonic tone [52, CEN 2003].
- **Hedonic tone:** Degree to which an odour is perceived as pleasant or unpleasant [85, CEN 2016], [86, CEN 2016]. The measurement scale for hedonic tones typically ranges from +4 for very pleasant odours (e.g. bakeries) to -4 for foul ones (e.g. rotting flesh) [56, UK 2011], [81, VDI 1994]. Outside of a laboratory setting, the hedonic tone can be subject to substantial variation between individuals [93, DEFRA 2010].
- **Odour exposure:** Contact of a human with a defined odour type, quantified as the amount of odorant(s) available for inhalation at any particular moment. As odours have no effect below the detection threshold, exposure to recognisable odours may be characterised as the frequency of occurrence of concentrations above a certain odour concentration (the recognition threshold) [85, CEN 2016], [86, CEN 2016].

4.6.3 EN standards

4.6.3.1 Overview

Table 4.7 lists EN standards for odour measurements.

Table 4.7: EN standards for odour measurements

Standard	Title
EN 13725:2003	Air quality - Determination of odour concentration by dynamic olfactometry
EN 16841-1:2016	Ambient air - Determination of odour in ambient air by using field inspection - Part 1: Grid method
EN 16841-2:2016	Ambient air - Determination of odour in ambient air by using field inspection - Part 2: Plume method

Dynamic olfactometry can be used for inspections at source and allows the determination of the emission rate [52, CEN 2003]. The grid method allows the measurement of the odour exposure (as odour hour frequency) [85, CEN 2016] and the plume method allows the determination of the extent of a plume [86, CEN 2016]. The methods are described in more detail in the following sections.

4.6.3.2 Dynamic olfactometry

EN 13725:2003 specifies a method for the objective determination of the odour concentration of a gaseous sample using dynamic olfactometry with human assessors. Measurement results are expressed in European odour units per cubic metre (ou_E/m^3). The standard includes the methodology for the determination of emission rates from point sources and area sources with or without outward flow [52, CEN 2003].

The standard is widely used in Europe (e.g. in Belgium (Flanders) [14, BE VLAREL 2010], France [53, INERIS 2013], Germany [54, DE 2008], [89, VDI 2015], the Netherlands [55, NEN 2012] and the United Kingdom [56, UK 2011], [87, MCERTS 2015]) and is part of the accreditation of testing laboratories.

Generally, measurements of odour concentrations represent a specific case of periodic emission measurements. Therefore, the generic EN standards for periodic measurements are relevant, in particular EN 15259:2007 [45, CEN 2007] (see Section 4.3.3.1).

Two types of sampling can be carried out: dynamic sampling for direct olfactometry, where the sample is ducted directly to the olfactometer and, more commonly, sampling for delayed olfactometry where a sample is collected and transferred to a sample container for analysis by delayed olfactometry. The advantage of dynamic sampling is the short time period between sampling and measurement which reduces the risk of a sample modification over time. The disadvantage is that it requires the use of ventilated rooms in order to isolate the panel members from the usually odorous ambient environment. This is difficult to implement and often requires very long sampling lines which may lead to a sample modification (e.g. by condensation, adsorption or ingress of air). In contrast, delayed olfactometry reduces the measurement uncertainty by placing the panel in the best possible conditions [52, CEN 2003], [87, MCERTS 2015].

In the case of delayed olfactometry, the sampling is similar to that of other periodic air pollutant measurements (see Section 4.3.3), and comprises, for example, a recommended sampling duration of 30 minutes and at least three consecutive measurements. The most common sampling system follows the 'lung principle', where the sample bag is placed in a rigid container. Subsequently, the air is removed from the container using a vacuum pump. The under-pressure in the container then causes the bag to fill with a volume of sample equal to that which has been removed from the container. By doing so, the contact of the sample with any pump is avoided [52, CEN 2003], [87, MCERTS 2015], [90, VDI 2011].

Maintaining the sample integrity during handling, storage and transport is of crucial importance. This includes [52, CEN 2003]:

- use of odourless materials when they come into contact with the sample;
- if necessary, sample predilution with nitrogen to avoid condensation, adsorption and chemical transformations;
- sample bag conditioning by filling them with sample gas and emptying them again.

EN 13725:2003 sets a maximum storage time of 30 hours. In practice, it is advisable to carry out the olfactometric measurement as soon as possible [52, CEN 2003]. In Germany, proof is to be provided that the odour concentration in the samples has not changed, if the storage time exceeds six hours [90, VDI 2011]. Additional guidance on sampling for olfactometric measurements according to EN 13725:2003 is available in the United Kingdom [87, MCERTS 2015] and Germany [90, VDI 2011].

For the actual measurement, an olfactometer is used to dilute the sample with neutral gas in a defined ratio and to present the diluted gas stream to a panel consisting of at least four selected and trained panel members. The odour concentration is measured by determining the dilution factor required to reach the detection threshold, where the odour concentration, by definition, is

1 ou_E/m^3. The odour concentration of the sample is thus expressed as a multiple of 1 ou_E/m^3 at standard conditions. In contrast to other periodic measurements, the standard conditions for olfactometry refer to room temperature (293.15 K), normal atmospheric pressure (101.3 kPa) and a wet basis. This applies to the olfactometric measurements as well as to the volume flow rates of emissions. The conditions were chosen by convention, to reflect typical conditions for odour perception [52, CEN 2003].

In addition to sampling and measurement, EN 13725:2003 also defines requirements for data recording, calculation, reporting, and quality assurance [52, CEN 2003].

4.6.3.3 Grid method

EN 16841-1:2016 describes the grid method for the determination of the level of odour exposure in ambient air within a defined assessment area. The method relies on qualified human panel members to determine the distribution of the frequency of odour exposure over a sufficiently long period (6 or 12 months) to be representative of the meteorological conditions of that location. The sources of the odorant under study may be located within or outside the assessment area. [85, CEN 2016].

The parameter measured by the human panel members is the 'odour hour frequency' which is the ratio of positive test results (number of odour hours) to the total number of test results for an assessment square (or in special cases for a measurement point). The odour hour frequency is an odour exposure indicator, and can be used to assess the exposure to recognisable odour originating from one or many specific odour source(s) emitting in a particular area of study, independent of whether the odour emissions are channelled or diffuse [85, CEN 2016].

If the odour types are recorded separately, the identification of the source among several installations with different odour types is feasible. However, if several installations emit the same odour type, identifying the emitter can be significantly more difficult and will require analysis of wind measurements [85, CEN 2016].

4.6.3.4 Plume method

EN 16841-2:2016 describes the plume method for determining the extent of recognisable odours from a specific source using direct observations in the field by human panel members under specific meteorological conditions (i.e. specific wind direction, wind speed and boundary layer turbulence) [86, CEN 2016].

The odour plume extent is described by points where a transition from absence to presence of the recognisable odour under investigation occurs. The shape of the plume is delineated by a smooth interpolation polyline through the transition points, the source location and the location determined by the maximum plume reach estimate [86, CEN 2016].

The results are typically used to determine a plausible extent of potential exposure to recognisable odours, or to estimate the total emission rate using reverse dispersion modelling. The plume extent measurement is particularly useful as a starting point for estimating emission rates for diffuse odour sources where sampling at source is impracticable [86, CEN 2016].

4.6.4 Other methods

4.6.4.1 Overview

Practices for odour monitoring vary considerably from one Member State to another. Two examples are described in Section 4.6.4.2. Moreover, a number of monitoring methods are standardised at national level. These methods are based on panels (see Section 4.6.4.3) or surveys (see Section 4.6.4.4). The principles and restrictions of using electronic sensor systems are described in Section 4.6.4.5.

4.6.4.2 Examples of odour monitoring practices in Member States

In Ireland, a procedure is in place which offers a consistent and systematic approach to the assessment of odours on site and in the vicinity of installations that are licensed by the Irish EPA, using a special 'Odour Investigation Field Record Sheet' [124, IE EPA 2010].

In England, several different monitoring methods can be used for the assessment of odours: sniff testing (to check ambient air on or off site); meteorological monitoring; complaints; odour diaries; surrogate chemicals or process parameters; emissions monitoring; and spot samples followed by olfactometric measurements according to EN 13725:2003 [56, UK 2011], [93, DEFRA 2010].

4.6.4.3 Odour monitoring with panels

Examples of national standards for odour monitoring with panels include the following:

- **NF X43-103:1996** describes a method to determine the odour intensity of a particular sample by comparison with that of a reference scale, defined by an orderly series of concentrations of a pure substance, for example, of *n*-butanol. The measurement relies on a panel of six to eight members. For field measurements in the vicinity of (agro)industrial installations, measuring points are defined according to the impact distances of the plant and the direction and velocity of the prevailing winds. Meteorological conditions are registered during measurements. Intensity perception can then be correlated with the examined plant (odour intensity mapping) [82, AFNOR 1996], [123, ADEME 2009].
- **VDI 3882 Part 1:1992** and **VDI 3882 Part 2:1994** describe the use of dynamic olfactometry to determine the odour intensity and the hedonic tone, respectively [80, VDI 1992], [81, VDI 1994]. Compared to the measurement of odour concentrations, these methods require larger panels and a larger range of odour concentrations to be presented to the panel members. The latter can cause serious contamination problems in the dilution system of the olfactometer. Also, care needs to be taken as suprathreshold concentrations can cause adaptation. Therefore, costs are higher compared to the measurement of odour concentrations and the methods are rarely used in practice [91, Both 2013], [246, UK 2013].
- **VDI 3940 Part 3:2010** allows the determination of the odour intensity and hedonic tone in the field. It is mainly applied together with grid or plume measurements (see Sections 4.6.3.3 and 4.6.3.4). The method uses selected and trained panel members [83, VDI 2010].
- **VDI 3940 Part 4:2010** describes a polarity profile method to determine the hedonic tone of odour samples or odours perceived in ambient air on the basis of pairs of opposites. By doing so, it is possible to clearly identify pleasant odours ('fragrance') or unpleasant odours ('stench'). The method uses selected and trained panel members [84, VDI 2010].
- **VDI 3940 Part 5:2013** provides further instructions and examples for the use of VDI 3940 Part 3:2010 and VDI 3940 Part 4:2010 [92, VDI 2013].

4.6.4.4 Odour surveys

Examples of national standards for odour surveys include the following:

- **VDI 3883 Part 1:2015** describes a survey method using questionnaires to determine the actual or potential odour annoyance caused by an odour exposure in a residential area. In each survey area, depending on the survey objective, a minimum number of households has to be investigated, and one person per household needs to be interviewed. The results are intended to identify objectively and quantifiably the odour annoyance level of the residents [238, VDI 2015].
- **VDI 3883 Part 2:1993** describes a survey method for determining the existing odour annoyance by using local volunteers. They are repeatedly questioned as to their momentary odour perception and their rating of the degree of annoyance. This can be carried out using postcards or by telephone. The results of a longer period of time are used to quantify the annoyance caused by odours in a defined survey area [239, VDI 1993].

The objective of the two methods described in VDI 3883 is to assess the degree of annoyance of residents caused by odours in ambient air. They are not aimed at estimating odour emissions. Comparisons with the results of grid measurements and dispersion modelling will help to establish some correlations afterwards.

Other types of odour surveys, such as 'odour diaries', register and analyse the odour complaints of residents in a specific area, together with additional information on the perceived odour [56, UK 2011], [93, DEFRA 2010]. Information from odour complaints may be a direct indication of odour annoyance, but the interpretation of the information collected should be carried out carefully, as the driving force for odour complaints might not be the perceived odour but rather another reason. On the other hand, the absence of odour complaints does not necessarily mean that there is no odour nuisance [238, VDI 2015].

4.6.4.5 Electronic sensor systems

Electronic sensor systems, also called 'electronic noses' or 'e-noses', are multi-gas sensor systems intended to detect gaseous substances [55, NEN 2012]. Because the sensors cannot smell like the human olfactory system, these substances may be both odorous and non-odorous gases. Electronic sensors therefore show a broader sensitivity spectrum than the human nose, the extent of the spectrum depending on the sensor types used.

Electronic sensors include three major parts: a sample delivery system, a detection system, and a data processing system. The **sample delivery system** generates the headspace (volatile compounds) of a sample, which is the fraction injected into the **detection system**, where an array of sensors, usually six, is located. Each sensor is more or less sensitive to all volatile molecules but each in their specific way. Mostly sensor arrays that react upon contact are used: the adsorption of volatile compounds on the sensor surface causes a physical change in the sensor. Commonly used sensors are metal oxide semiconductors, conducting polymers, quartz crystal microbalances, and surface acoustic waves. The **data processing system** records the responses of the sensors, which represent the input for the data treatment. The signals of the sensors are combined and a global fingerprint analysis is performed based on statistical models [126, INERIS 2009], [127, Peris et al. 2009].

To train electronic sensor systems, samples are analysed in parallel by olfactometry and the electronic sensor system, in order to: first, create a qualitative fingerprint database to recognise the gas composition (i.e. the odour), and, second, develop a mathematical model that is able to convert the raw sensor data into odour concentrations. This usually requires a reasonable number of parallel measurements. An electronic sensor system 'trained' for specific sources cannot be used to monitor other sources or another plant without new adapted 'training'.

Moreover, depending on the odorous compounds that constitute the emissions to survey, the 'training' to define a possible correlation between the sensor signals and the odour emission could be very difficult to establish or may only be established with great uncertainty [126, INERIS 2009].

Typical applications for electronic sensor systems are semi-qualitative or semi-quantitative control of material or product qualities as well as of processes, where changes in gas composition need to be detected, including qualitative controls of abatement systems.

In 2016, there was no EN or ISO standard available which describes how to apply electronic sensor systems [59, CEN 2016], [112, ISO 2016]. In the Netherlands, the Netherlands Technical Agreement (NTA) 9055 sets out requirements for the use of electronic ambient air monitoring [125, NEN 2012].

4.6.5 Drawing up or review of BREFs

The impact of odour emissions depends on a number of factors including the distance to the receiver, the local meteorological conditions, the type of source, the odour type, the individual perception, the hedonic tone, and the emission rate.

Because of these factors, BAT conclusions generally focus on techniques to prevent or reduce odour emissions (e.g. in the BREFs for Common Waste Water and Waste Gas Treatment/Management Systems in the Chemical Sector (CWW BREF) [154, COM 2016], the Production of Pulp, Paper and Board (PP BREF) [160, COM 2015], the Production of Wood-based Panels (WBP BREF) [195, COM 2016], and the Tanning of Hides and Skins (TAN BREF) [179, COM 2013]).

In a few cases, BAT on odour monitoring were also defined (e.g. in the BREFs for Common Waste Water and Waste Gas Treatment/Management Systems in the Chemical Sector (CWW BREF) [154, COM 2016] and the Production of Wood-based Panels (WBP BREF) [195, COM 2016]).

In 2017, the TWG for the review of the BREF for Waste Treatment (WT BREF) decided to set a BAT-AEL for odour emissions from the biological treatment of waste as an alternative to the BAT-AEL for ammonia emissions [280, TWG WT BREF 2017].

4.7 Biomonitoring

4.7.1 Overview

Biomonitoring is the use of biological systems to monitor environmental changes over space and time. Biomonitoring can complement direct emission measurements and/or dispersion modelling, by demonstrating possible biological effects, in particular if there are diffuse emissions which do not allow direct emission measurements. In the context of the IED, biomonitoring may be used to assess the effects of industrial emissions, e.g. as part of the permitting or inspection process [240, CEN 2014], [241, CEN 2014], [242, CEN 2016].

4.7.2 Definitions

According to the relevant European standards, the following definitions apply:

- A bioindicator is an organism, a part of it, or an organism community (biocenosis) which documents environmental impacts. Bioindicators include bioaccumulators and response indicators [240, CEN 2014], [241, CEN 2014], [242, CEN 2016].
- A **bioaccumulator** is an organism which can indicate environmental conditions and their modification by accumulating substances present in the environment (air, water or soil) at the surface and/or internally [240, CEN 2014], [241, CEN 2014], [242, CEN 2016].
- A **response indicator**, also referred to as an effect indicator, is an organism which can indicate environmental conditions and their modification, by either showing specific symptoms (molecular, biochemical, cellular, physiological, anatomical or morphological) or by its presence/absence in the ecosystem [240, CEN 2014], [241, CEN 2014], [242, CEN 2016].
- **Active biomonitoring** refers to deliberate field exposure following a standardised methodology [242, CEN 2016].
- **Passive biomonitoring** refers to in situ sampling and/or observation of selected bioindicators currently or previously present in the environment [242, CEN 2016].

4.7.3 EN standards

Table 4.8 lists EN standards for biomonitoring with plants.

Table 4.8: EN standards for biomonitoring with plants

Standard	Title
EN 16413:2014	Ambient air - Biomonitoring with lichens - Assessing epiphytic lichen diversity
EN 16414:2014	Ambient air - Biomonitoring with mosses - Accumulation of atmospheric contaminants in mosses collected in situ: from the collection to the preparation of samples
EN 16789:2016	Ambient air - Biomonitoring with higher plants - Method of the standardised tobacco exposure

EN 16413:2014 describes a method for assessing epiphytic lichen diversity. It provides a framework for assessing the impact of anthropogenic intervention, particularly for estimating the effects of atmospheric pollution. Because the existing epiphytic lichen population is used, it might be necessary to take both regional characteristics of the lichen flora and local conditions into account. The method does not aim to assess the effects of emissions to air from a specific source or installation; however, it could provide an indication of the general ambient air quality [240, CEN 2014].

EN 16414:2014 describes the sampling protocol and the preparation of samples of *in situ* mosses to monitor the bioaccumulation of atmospheric pollutants. All necessary steps from the field sampling of mosses to their final preparation before analysis are covered. The standard can be used to identify and localise one or more emission sources, as well as to monitor background pollution levels [241, CEN 2014].

EN 16789:2016 describes the determination of the impact of ground-level ozone on a tobacco plant species in a given environment. It specifies the procedure for setting up and using a system designed to expose these plants to ambient air. The procedure for leaf injury assessment is also described. The repeated exposure of tobacco on several sites enables the determination of the temporal and spatial distribution of ozone effects [242, CEN 2016].

In 2017, a working group of the Technical Committee CEN/TC 264 'Air quality' was working on a new EN standard dealing with the determination of air quality via standardised grass exposure [78, CEN 2017].

4.7.4 Other methods

Other biomonitoring methods using different plants for active biomonitoring (e.g. gladiolus, spruce, curly kale) or passive biomonitoring (*in situ* sampling of leaves such as grazing land grass, maize plants, garden vegetables and needles) are used in some Member States. Some of these methods allow the determination of ambient air quality in relation to specific industrial sources (e.g. [94, VDI 2004], [95, VDI 2014]) but, as for all the biomonitoring methods mentioned, investigations at source (e.g. emission measurements) and/or dispersion modelling are still necessary.

4.7.5 Drawing up or review of BREFs

As biomonitoring methods do not allow the direct quantification of emissions, they are of limited use for the drawing up or review of BREFs.

4.8 Costs

Qualitative information on the costs of monitoring emissions to air is given in several sections of this chapter, for example in relation to different monitoring regimes (see Section 4.3.1) and different frequencies in the case of periodic measurements (see Section 4.3.3.9).

Moreover, the UK Source Testing Association, whose members comprise testing laboratories, plant operators, instrument manufacturers and regulators, conducted a survey in December 2012 to gather information about the costs of stack emissions monitoring of IED installations in the United Kingdom. The information is split into three tables, which are shown in Annex A.5.

The costs in Table 7.6 are examples provided by plant operators from different industrial sectors (e.g. coal-fired combustion plants, waste incineration plants, cement plants) and include both periodic measurements and continuous measurements with AMS (where applicable). For periodic measurements, the costs cover the entire process, and thus include measurement planning, time spent on site safety inductions and report writing. For continuous measurements, the costs are broken down into investment costs (i.e. purchase, installation, and other items) and operating costs (i.e. maintenance, service and calibration, QAL2, and AST) [68, UK STA 2012]. Costs for construction works (e.g. for the installation of a platform) are not included [245, Cefic and CONCAWE 2013].

The costs in Table 7.7 were provided by a wide range of instrument manufacturers and suppliers, operating in and outside Europe. Even though the costs represent examples from the United Kingdom, they are expected to be similar throughout Europe. The costs in Table 7.8 were provided by testing laboratories which carry out periodic measurements using reference methods. The table includes the costs of single tests, triplicate tests and completion of a QAL2 [68, UK STA 2012].

The costs per stack or per monitoring activity are usually different from one site to another, due to several factors including the following [68, UK STA 2012]:

- Nature of parameters:
  - The costs of an AMS depend to a large extent on the parameters that have to be measured. For example, parameters required for waste incineration plants will be more expensive than those for most other plants, due to the number and complexity of the analysers.
  - Special features of a process may require the measurement of additional parameters, for example ammonia when selective catalytic reduction (SCR) and/or selective non-catalytic reduction (SNCR) is used. This may mean that a multi-gas analyser is required, which can be more expensive than other options.
- Economies of scale:
  - Testing laboratories and plant operators will often combine the calibration of AMS (QAL2/AST) with routine periodic measurements for compliance assessment.
  - AMS suppliers may offer discounts for installing more than one system.
  - For periodic measurements, there may be other monitoring activities, besides measuring emission levels or calibrating AMS. For example, operators of coal-fired combustion plants with flue-gas desulphurisation abatement may need to measure the removal efficiency, which implies measurements at both the inlet and outlet.
- Measurement/sampling site:
  - Monitoring arrangements at an indoor location with a lift are usually less expensive than at an outdoor location that is accessed via vertical ladders.
  - For extractive AMS, an air-conditioned room is often required to house the analysers (Figure 4.3).
  - The greater the distance between the sampling point and the analyser, the greater the costs for materials and installation because of the length of lines,

especially when they need to be heated. Therefore, in the case of a plant with several similar sampling points (e.g. several stacks of a combustion plant), costs are reduced when the sampling points are located close to each other.

- The need to install a platform on a high stack can lead to major additional costs [245, Cefic and CONCAWE 2013].

Source: [253, INERCO 2012]

Figure 4.3: Example of air-conditioned housing for an AMS

The costs for odour measurements, as described in Section 4.6, are significantly affected by the use of human sensors and their salaries. For the measurement of the odour concentration by dynamic olfactometry, at least four panel members are needed (see Section 4.6.3.2). Experience from Germany shows that, depending on the sampling as well as on the performance and ability of the panel members to stay concentrated, costs for a measurement day with approximately 10 to 20 samples are expected to range from EUR 2 500 up to EUR 5 000. The costs for applying the grid method, as described in Section 4.6.3.3, depend to a large extent on the size of the assessment area and the number of measurement sites. Experiences in Germany show that the costs start at approximately EUR 10 000 to EUR 15 000 for a six-month measuring period [91, Both 2013].

5 MONITORING OF EMISSIONS TO WATER

5.1 Overview

This chapter covers the monitoring of emissions to water including information on:

- water pollutants (see Section 5.2);
- continuous/periodic measurements (see Section 5.3);
- surrogate parameters (see Section 5.4);
- toxicity tests and whole effluent assessment (see Section 5.5);
- costs (see Section 5.6).

General aspects of monitoring are described in Chapter 3.

5.2 Water pollutants

Table 5.1 gives some examples of definitions of water pollutants that are or could be used in BAT conclusions or permits. The definitions are subject to modification, according to the specifities of the BREF to be drawn up/reviewed or to the required permit conditions.

Table 5.1: Examples of definitions of water pollutants

Parameter/substance(s)	Definition
Adsorbable organically bound halogens (AOX)	Adsorbable organically bound halogens, expressed as Cl, include adsorbable organically bound chlorine, bromine and iodine
Ammonium nitrogen (NH_4-N)	Ammonium nitrogen, expressed as N, includes free ammonia and ammonium (NH_4-N)
Biochemical oxygen demand (BOD_n)	Amount of oxygen needed for the biochemical oxidation of the organic matter to carbon dioxide after n days. BOD is an indicator for the mass concentration of biodegradable organic compounds
Chemical oxygen demand (COD)	Amount of oxygen needed for the total oxidation of the organic matter to carbon dioxide. COD is an indicator for the mass concentration of organic compounds
Free chlorine	Free chlorine, expressed as Cl_2, includes dissolved elementary chlorine, hypochlorite, hypochlorous acid, dissolved elementary bromine, hypobromite, and hypobromic acid
Hydrocarbon oil index (HOI)	Hydrocarbon oil index includes all compounds extractable with a hydrocarbon solvent (including long-chain or branched aliphatic, alicyclic, aromatic or alkyl-substituted aromatic hydrocarbons), and measured according to EN 9377-2:2000 [97, CEN 2000]
Mercury	The sum of mercury and its compounds, expressed as Hg
Phenol index	The sum of phenolic compounds, expressed as phenol, and measured according to EN ISO 14402:1999 [98, CEN 1999]
Sulphide, easily released	The sum of dissolved sulphide and of those undissolved sulphides that are easily released upon acidification, expressed as S^{2-}
Total inorganic nitrogen (N_{inorg})	Total inorganic nitrogen, expressed as N, includes free ammonia and ammonium (NH_4-N), nitrite (NO_2-N) and nitrate (NO_3-N)
Total Kjeldahl nitrogen (TKN)	Total Kjeldahl nitrogen, expressed as N, includes free ammonia and ammonium (NH_4-N), and organic nitrogen compounds
Total nitrogen (TN)	Total nitrogen, expressed as N, includes free ammonia and ammonium (NH_4-N), nitrite (NO_2-N), nitrate (NO_3-N) and organic nitrogen compounds
Total organic carbon (TOC)	Total organic carbon, expressed as C, includes all organic compounds
Total phosphorus (TP)	Total phosphorus, expressed as P, includes all organic and inorganic phosphorus compounds, dissolved or bound to particles
Total suspended solids (TSS)	Mass concentration of all suspended solids, measured via filtration through glass fibre filters and gravimetry

The determination of emissions to water covers the measurement of single substances, as well as, to a large extent, the measurement of sum parameters. Sum parameters are quantitative surrogate parameters (see Sections 3.3.3.3.1 and 5.4).

In some cases, there may be a need to cover single substances relevant for the specific industrial sector, e.g. specific metals or other hazardous substances. Such a need could be triggered by monitoring results obtained in the context of other legislation such as the Water Framework Directive.

Section 5.3.5.8 provides information on specific monitoring aspects for the most common water pollutants including on the measurement principles.

5.3 Continuous/periodic measurements

5.3.1 Generic EN standards

Table 5.2 lists some generic EN standards and a technical specification relevant for the monitoring of emissions to water. Most of them are related to periodic measurements and might be partly applied to continuous measurements of emissions to water, such as EN ISO 5667-1:2006; whereas, EN ISO 15839:2006 deals specifically with continuous on-line monitoring. Specific standards for the measurement of emissions to water are listed in Annex A.2.

For the general use of EN standards and other standard methods see Section 3.4.3.

Table 5.2: Generic EN standards and a technical specification relevant for the monitoring of emissions to water

Standard	Title
EN 1085:2007	Wastewater treatment - Vocabulary
EN ISO 5667-1:2006	Water quality - Sampling - Part 1: Guidance on the design of sampling programmes and sampling techniques (ISO 5667-1:2006)
EN ISO 5667-3:2012	Water quality - Sampling - Part 3: Preservation and handling of water samples (ISO 5667-3:2012)
EN ISO 5667-14:2016	Water quality - Sampling - Part 14: Guidance on quality assurance and quality control of environmental water sampling and handling
EN ISO 5667-16:2017	Water quality - Sampling - Part 16: Guidance on biotesting of samples (ISO 5667-16:2017)
EN ISO 15839:2006	Water quality - On-line sensors/analysing equipment for water - Specifications and performance tests (ISO 15839:2003)
EN 16479:2014	Water quality - Performance requirements and conformity test procedures for water monitoring equipment - Automated sampling devices (samplers) for water and waste water
CEN/TS 16800:2015	Guideline for the validation of physico-chemical analytical methods

EN 1085:2007 establishes a standardised terminology in the field of waste water treatment in the three official languages of CEN (German, English and French). It focuses on waste water treatment, and, therefore, not all the definitions related to water analysis are included, but it is useful for a common understanding of the waste water treatment terms [149, CEN 2007].

EN ISO 5667-1:2006 gives the general principles for, and guidance on, the design of sampling programmes and sampling techniques for all aspects of water sampling (including waste water, sludges, and bottom deposits). Furthermore, this standard addresses the time and frequency of sampling and gives cross references to flow measurements [46, CEN 2006].

EN ISO 5667-3:2012 establishes general requirements for sampling, pretreatment, preservation, handling, transport and storage of all water samples, including those for biological analyses. This part of EN ISO 5667 is particularly appropriate when spot or composite samples cannot be analysed on site and have to be transported to a laboratory for analysis, which is generally the case. It provides a detailed indication of sample preservation techniques, container types, storage conditions, and maximum storage times for each parameter/substance. EN ISO 5667-3:2012 is complementary to other, more specific measurement standards [128, CEN 2012].

EN ISO 5667-14:2016 specifies quality assurance/control procedures and provides additional guidance on manual sampling. The standard describes potential sources of sampling errors (i.e. materials, methods, personnel, environment, as well as sample preservation and transport) and how to minimise these errors [285, CEN 2016].

EN ISO 5667-16:2017 describes special sampling and pretreatment provisions relevant for toxicity tests [150, CEN 2017].

EN ISO 15839:2006 specifies test procedures for performance testing of on-line sensors/analysing equipment used for continuous measurements of water quality, to be applied in the laboratory and in the field [106, CEN 2006]. The standard requires the construction of test bench facilities and is thus not addressed to end users of the equipment.

EN 16479:2014 defines general requirements, performance requirements and conformity test procedures for automated sampling devices (samplers) for water and waste water that sample from non-pressurised (i.e. open to atmosphere) channels or vessels and sample over extended periods to collect discrete or composite samples based on time-, event- or flow-proportional sampling [151, CEN 2014].

CEN/TS 16800:2015 describes an approach for the validation of physico-chemical analytical methods for environmental matrices. The guidance addresses both the method development and validation at the level of single laboratories (intra-laboratory validation) and the method validation at the level of several laboratories (inter-laboratory validation). The specification is applicable to the validation of a broad range of quantitative physico-chemical analytical methods for the analysis of water (including surface water, groundwater, waste water, and sediment). Analytical methods for other environmental matrices, like soil, sludge, waste, and biota, can be validated in the same way [264, CEN 2015].

In 2016, there was no generic EN standard for the sampling of waste water but one ISO standard and a few national standards existed. **ISO 5667-10:1992** contains details on the sampling of domestic and industrial waste water, i.e. the design of sampling programmes and techniques for collection of samples including safety aspects. The standard covers waste water in all its forms. The sampling of accidental spillages is not included, although the methods described may in certain cases also be applicable to spillages [152, ISO 1992].

5.3.2 Monitoring regimes

EN ISO 5667-1:2006 gives some guidance on measurement and sampling, distinguishing between continuous and periodic measurements, between continuous and periodic sampling, and between composite and spot samples [46, CEN 2006].

An overview of different measurement and sampling types is given in Table 5.3.

Table 5.3: Overview of different measurement and sampling types relevant for the monitoring of emissions to water

Continuous (on-line) measurement		
Sampling type		**Sample type**
Continuous	Direct measurement in the effluent flow without extraction	No discrete samples
	Time-proportional extraction	
	Flow-proportional extraction	
Periodic measurement (analysis of each separate sample)		
Sampling type		**Sample type**
Continuous	Time-proportional extraction	Discrete samples for short time intervals or composite samples for longer time intervals (e.g. 24 hours)
	Flow-proportional extraction	
Periodic	Time-proportional extraction	
	Flow-proportional extraction	
	Instantaneous extraction	Spot samples

In the case of **continuous (on-line) measurements,** no discrete samples are taken. The measurement devices are directly positioned in the effluent flow, or positioned separately, with the requisite that the sample is taken continuously (time- or flow-proportional **continuous sampling**) and pumped to the device.

In the case of **periodic measurements**, sampling may be carried out continuously or periodically:

- For **continuous sampling,** the samples are taken continuously with a fixed or variable flow rate. If the sampling flow rate is adjusted continuously to the waste water flow (flow-proportional), the samples are representative of the bulk water quality. This requires either continuous on-line measurement of the flow rate or a sufficient number of discrete samples for the relevant time period to allow the determination of changes in the waste water composition.
- This method is most suitable for taking representative samples of waste water discharges when the flow rate and concentration of the parameter of interest vary significantly. However, this method can involve higher costs, in particular, depending on the number of samples to be analysed; therefore, it is only applied in extraordinary cases.
- For **periodic sampling,** the samples are taken at different intervals, typically depending on time or waste water volume flow rate. One example is **flow-proportional sampling**, in which a predefined amount of sample is taken for each predefined volume of waste water discharged.

The following main sample types for periodic measurements can be distinguished [152, ISO 1992]:

- **Composite samples are**, by far, the most commonly used samples. They are obtained by mixing appropriate proportions of periodically (or continuously) taken samples. Composite samples provide average compositional data. Consequently, before combining samples, it should be verified that such data are desired and that the parameter(s) of interest do(es) not vary significantly during the sampling period. It is assumed that this is generally the case for industrial waste water. Composite samples are mainly taken in order to reduce the amount of analytical work.
- **Spot samples are** discrete samples taken at random time intervals. They are generally not related to the waste water volume discharged. The application depends on the parameter, its variations, and the waste water matrix in the industrial sector.

For more details on continuous (on-line) measurements, see Section 5.3.4; for periodic measurements using composite and spot samples, see Section 5.3.5.

5.3.3 Continuous versus periodic measurements

Several water parameters can be measured continuously as well as periodically. A number of parameters, such as pH, temperature and turbidity, are typically measured continuously, because the results are used for process control and are important to run the waste water treatment plant properly. Table 5.4 provides an overview of important characteristics of continuous and periodic measurements, including advantages and disadvantages.

Table 5.4: Important characteristics of continuous and periodic measurements

Characteristic	Continuous measurement	Periodic measurement
Sampling period	Measurement covers all or most of the time during which substances are emitted	Coverage depends on the sampling plan (for details see Section 5.3.5.2)
Speed	Almost always real-time output of results	Real-time results if portable instrumental analysers are used; delayed results if analysis is carried out in a laboratory
Stability	Sensors may be prone to fouling (unless automatic cleaning has been installed)	Sample integrity needs to be maintained before analysis
Availability	Only available for a limited number of measurands	Comprehensive range of methods available
Standardisation	Restricted availability of standardised methods	Standardised methods are available with defined performance requirements
Averaging of results	Results are continuously gathered and can be averaged, e.g. over one hour or 24 hours	Results are reported for a specified sampling period, e.g. as 24-hour composite samples (daily average) or as spot samples
Accreditation	Not applicable because of a lack of standardised methods	Accreditation according to EN ISO/IEC 17025:2005 [1, CEN 2005]
Certification of equipment	Certification of measurement equipment is only available in the United Kingdom (MCERTS) and only for a limited number of measurands	Certification of sampling equipment is only available in the United Kingdom (MCERTS). In 2016, certification of laboratory equipment was not available
Investment costs	Tend to be higher than the equivalent periodic measurement method	Tend to be lower than the equivalent continuous measurement method
Source: [103, MCERTS 2015]		

As mentioned in Table 5.4, continuous (on-line) measurements almost always provide a real-time output of results, and so the averaging period needs to be defined. Common averaging periods are, for example, one hour, two hours or 24 hours (daily averages).

Periodic measurements also aim for representative results for a specified time period, e.g. one day. The samples are taken periodically or continuously, kept discrete or directly mixed over a predefined time period, e.g. an entire day, and then analysed afterwards. A typical example of periodic measurements is the collection of 24-hour flow-proportional composite samples, giving the average value for one day. Flow-proportional sampling requires the continuous measurement of the water flow at the sampling point (for details on flow measurements see Section 5.3.4.2).

The choice to measure a water parameter continuously strongly depends on:

- the need to control highly variable and/or excessive waste water discharges;
- the instability of the parameter during sampling, transportation and storage (e.g. volatile compounds);
- the expected impact of the waste water discharge on the environment, taking local conditions into account;
- the need to monitor and control the performance of the waste water treatment plant and, possibly, to promptly react according to the generated data (e.g. physico-chemical parameters);
- the availability and reliability of measurement equipment, depending on the industrial sector and on the waste water discharge;
- the specific requirements of the industrial sector, and/or the specific circumstances of the installation;
- the costs of continuous measurements (economic viability).

A parameter that is almost always measured continuously is the volume flow rate of the waste water discharge (see Section 5.3.4.2).

In some Member States a mass flow threshold is used to decide on the monitoring regime. For example in France, daily measurements of 24-hour flow-proportional composite samples are required for a number of water parameters including COD, TSS, BOD_5, AOX, mercury, cadmium and several organic substances, when certain mass flow thresholds are exceeded [60, FR 2016, Article 60]. In the Netherlands, mass flow thresholds are also used in a limited number of permits. The choice is determined by the specific discharge situation (i.e. short peak discharges, waste water diluted with cooling water) [105, NL 2013]. In general, it is assumed that below such specific mass flow thresholds a lower measurement frequency is sufficient, unless the conditions of the individual case require a different approach.

As mentioned in Table 5.4, the certification of measurement equipment is only available in the United Kingdom. In other Member States, e.g. in the Netherlands and France, the sampling equipment has to meet the requirements of the national standards, and compliance with the standards is supervised by competent authorities.

5.3.4 Continuous measurements

5.3.4.1 Water parameters except waste water flow

In practice, continuous measurements are mainly carried out with sensors that are directly positioned in the effluent flow, or that are positioned separately and the sample is pumped to it. For some parameters, such as TOC, instruments operate as a continuous batch process: a discrete sample is taken from the effluent and analysed and, when completed, the process starts again.

EN ISO 15839:2006 defines on-line sensors and on-line analysing equipment as automated measurement devices which continuously (or at a given frequency) give an output signal proportional to the value of one or more measurands in a solution which it measures [106, CEN 2006].

Examples of water parameters that can be continuously measured include the following [103, MCERTS 2015], [152, ISO 1992]:

- pH, dissolved oxygen, and conductivity by direct electrochemical measurements;
- nitrate and ammonia by specific ion electrodes;
- metals by anodic stripping voltammetry;
- ammonia, phosphate, total phosphorus (TP), and iron by spectrophotometry;
- TOC by combustion and IR spectrometry;
- turbidity.

EN ISO 15839:2006 describes for on-line sensors/analysing equipment [106, CEN 2006]:

- the determination of performance characteristics in the laboratory, such as linearity, limits of detection and quantification, repeatability; and
- the determination of performance characteristics in the field, such as response time, delay time, rise time and fall time.

In general, the regular calibration and maintenance of continuous measurement devices is important to ensure that measurement results of an appropriate quality are produced, with minimum data loss from breakdowns. Maintenance and calibration procedures need to be established and carried out regularly. Depending on the waste water characteristics, daily or weekly maintenance and calibration might be necessary to guarantee a well-functioning system.

In a written schedule, the maintenance and calibration tasks can be described, including who is responsible for the task, e.g. operator, manufacturer or accredited laboratory. Records of all maintenance and calibration activities need to be kept as part of the quality assurance system.

For most continuous measurement devices, the maintenance and calibration procedures are given in manufacturer's instructions and often it might be advisable that the manufacturers themselves install, commission, maintain and calibrate their devices.

As already mentioned in Table 5.4, a certification system exists in the United Kingdom which also covers performance standards and test procedures for continuous water monitoring equipment [107, MCERTS 2010].

5.3.4.2 Waste water flow

The effective monitoring of effluent discharges requires knowledge about the mass flow rate of single substances and of sum parameters. This is achieved by combining flow measurement data (volume/time) with pollutant concentrations (mass/volume). Uncertainties associated with flow measurement can have a significant effect on the calculation of emission loads. In addition, the flow measurement data are also needed to run automated sampling devices. Therefore, waste water flows are often measured continuously.

A wide range of flow-measuring devices and instrumentation layouts are in use. There are several EN, ISO and national standards available dealing with flow measurements in channels and pipes. In principle, the devices can be divided into three separate groups [38, DK EPA 2012]:

- open channel flow meters;
- pipe flow meters for partly filled pipes;
- pipe flow meters for pipes which are completely filled and often pressurised.

Open channel flow is defined as the flow in a conduit in which the upper surface of the liquid is in contact with the atmosphere (free surface). The shape of the channel and the liquid level determine the cross-section of the flow. The flow in an open channel can be measured using a combination of a primary device (a structure restricting flow and causing the liquid level to vary proportionately with the flow) and a secondary device (that measures the variation in the liquid level caused by the primary device). The relationship between the liquid level and the flow rate depends on the shape and dimensions of the primary device, and is calculated using a known equation. Typical primary devices are weirs and flumes. A weir is a calibrated obstruction or dam built across an open channel over which the liquid flows, often through a specially shaped opening or notch. A flume is a specially shaped channel restriction that changes the channel area and slope. Typical secondary measuring devices are floats, capacitance probes, ultrasonic devices and bubblers [153, British Columbia 2003].

In partly filled pipes, it is necessary to measure the cross-sectional area of the flow and the average flow velocity. The waste water flow (e.g. in m^3/h) is calculated by multiplying the cross-sectional area and the flow velocity. Such area-velocity methods can also be used in the case of open channels. The cross-sectional area is determined by measuring the liquid level, e.g. using a pressure transducer, and then by calculating the area based on the diameter of the pipe. The flow velocity can be determined with a number of techniques, e.g. by means of a Doppler flow meter emitting high-frequency sound waves that are reflected by air bubbles and suspended particles in the waste water. The change in the frequency of the reflected sound waves is then used to calculate the flow velocity [38, DK EPA 2012], [153, British Columbia 2003].

Commonly used closed-pipe flow-measuring devices for waste water include electromagnetic flow meters and Doppler flow meters. The measurement of flow in closed pipes is typically more accurate than that in open channel systems. The measuring devices can generally be mounted in any orientation, but best practice is to install them on a pipe in which the waste water is flowing upwards. This precaution prevents the occurrence of partially filled pipes and diffused air entrapment in the pipes. When a Doppler flow meter is used in a closed-pipe flow system, the sensor is typically installed on the outside of the pipe wall. In electromagnetic flow meters, the waste water passes perpendicularly through the magnetic field and induces a voltage between the electrodes placed in the pipe and the magnetic field, which is proportional to the flow velocity in the pipe. The waste water flow is calculated by multiplying the average flow and the cross-sectional area of the pressurised pipe. Many categories and sizes of electromagnetic flow meters are commercially available [38, DK EPA 2012].

As mentioned in Table 5.4, in the United Kingdom, a certification system exists which also covers performance standards and test procedures for water flow meters [108, MCERTS 2013]. Also in the United Kingdom, a standard is in place for the inspection of flow monitoring structures [109, MCERTS 2014].

5.3.5 Periodic measurements

5.3.5.1 Overview

Periodic measurements are defined as the determination of a measurand at specified time intervals. In general, these measurements are based on periodic sampling at fixed intervals, which can be time-, volume- or flow-dependent, followed by an analysis of the parameters under investigation in the laboratory (on-site, off-site). This includes handling, storage and transport of the samples, taking into account the requirements of the subsequent analysis.

In the case of monitoring of emissions to water, the personnel responsible for sampling are often not the same as those responsible for the analysis, but both need to have a sound knowledge and experience in their respective field of responsibility to obtain reliable and comparable results. Provisions on sampling are part of EN ISO/IEC 17025:2005 [1, CEN 2005].

Generic EN standards for the monitoring of emissions to water are described in Section 5.3.1. EN standards dealing with the analysis of specific pollutants and sum parameters are listed in Annex A.2, together with additional information. EN standards are not available for all parameters (e.g. COD) or for all types of (waste) water. Therefore, there is a broad range of other standards in use, e.g. ISO standards, national standards, and/or laboratory-developed and non-standard methods (see Section 3.4.3).

5.3.5.2 Measurement and sampling plan

The purpose of the measurement plan is to ensure that emission measurements are adequate for the given measurement objective (e.g. for the determination of average concentrations over a specified period or for the determination of the highest emission concentrations during normal operating conditions). This requires foremost a representative sampling of the effluent, the quality of which usually varies over time. The sampling plan may be a part of the measurement plan and is sometimes referred to as the sampling programme (e.g. in EN ISO 5667-1). It considers these variations, which may occur under normal and other than normal operating conditions and which may include seasonal and diurnal cycles, business week cycles, random or transient events, and long-term persistence or trends [46, CEN 2006].

The measurement plan includes, among others, a clear description of the following items:

- measurement objective including specification of the measurands;
- collection of data to clearly describe the operating conditions;
- sampling site and sampling point (see Section 5.3.5.3);

- sampling method, including sampling equipment (see Sections 5.3.5.4 and 5.3.5.5);
- volume of waste water that the sampling intends to represent;
- collection of data related to the waste water flow and other parameters, if relevant, such as temperature, pH;
- time and frequency of sampling (see Section 5.3.5.6);
- pretreatment and preservation of samples (see Section 5.3.5.7);
- handling and storage of samples (see Section 5.3.5.7);
- laboratory measurement (see Section 5.3.5.8);
- data treatment (see Section 5.3.6);
- quality assurance measures;
- documentation and reporting (see Section 5.3.7).

The measurement plan might be divided into a sampling plan and an analysis plan, e.g. if the sampling and the analysis are not carried out by the same laboratory. In any case, sampling requirements imposed by the applied analytical method and constraints resulting from sampling need to be taken into account.

In the case of automated sampling devices to be permanently installed, it may be sufficient to draw up one measurement (and sampling) plan before installing the device and then only to update it accordingly after relevant changes in the waste water treatment plant or in the measurement system. For spot samples, the plan may need to be updated for each sampling campaign.

In the following paragraphs, some examples are given of special conditions that can affect the final effluent discharge and that, therefore, need to be reflected in the measurement plan [38, DK EPA 2012].

Changes in production or the **start-up of new plants** might result in an immediate short-term increase or decrease of emissions. By using portable sampling equipment, temporary sampling can easily be established and discharges can be documented.

During specific **production campaigns**, for instance the harvest season for industries producing vegetables and derived products, often an increase in emissions occurs. Then more frequent sampling (e.g. once every day or once every week, instead of once every month) and an estimation of the load based on the actual waste water flow may be needed.

Batch production might require (spot) samples to be taken of the final waste water discharge or after the batch has passed through an equalisation tank if the emission pattern is determined by these batches. If samples are taken from a tank, good mixing is necessary to ensure that the entire volume is homogenised. If mixing is difficult and unmixed zones are inevitable, e.g. when the tank is very big, it is advisable to take several subsamples and to mix them before analysis.

Decommissioning of a production plant might require a specially designed measurement plan, taking into account different and potentially new waste water streams.

Outdoor areas and stocks where storage may be uncovered (e.g. in the metals or wood-based panels industries) can result in contaminated run-off, in particular under exceptional weather conditions (e.g. heavy rainfalls). Flow-proportional samples of run-off are difficult to take, but they allow the load coming from these areas to be determined.

When **accidents or breakdowns** with unforeseen pollutant discharges occur, it is beneficial to have a contingency plan for measurements and documentation in terms of concentrations and loads, in order to allow for an estimation of the possible impact on the receiving water body. The measurement plan is also important when a quick implementation of measures is needed to reduce environmental damage (e.g. closing-off, temporary treatment of stored polluted waste water, collection of spilled pollutants).

5.3.5.3 Measurement/sampling site and point

The **measurement/sampling site**, also referred to as the measurement/sampling location, is the place at the waste water stream where the measurements or the sampling are carried out. The **measurement/sampling point** is then the precise position in the waste water stream at which the measurement data are obtained directly or the sample is extracted [152, ISO 1992].

The location of the sampling point(s) should ensure that the sample is representative of the effluent discharge. It is recommended to accurately describe and mark the sampling point on the process flowsheet, if possible supplemented with photographs to facilitate identification of the exact location.

The following recommendations might be helpful to select the sampling point [38, DK EPA 2012], [103, MCERTS 2015], [152, ISO 1992]:

- a sampling point in a pipe or channel must be sufficiently far downstream of the last inflow in order to guarantee that mixing of the two streams is complete;
- the waste water at the sampling point should be well mixed (turbulent flow), in order to avoid stratification and sedimentation of particles;
- sampling points should be placed away from the sides and the bottom, to avoid contamination of the sample with sediments or biofilms;
- the sampling point should not be affected by recirculating internal flows;
- the sampling point should not be in front of a dam, because intermittent loads may occur;
- for automated sampling devices, the water level at the sampling point should be higher than 50 mm and the suction head placed at a depth of approximately one third of the water level during dry weather conditions.

5.3.5.4 Sample types

5.3.5.4.1 Composite samples

There are two types of composite samples, where subsamples with a defined volume of waste water are taken from the discharge: flow-proportional and time-proportional composite samples. For the flow-proportional composite sample, a fixed sample volume is taken for each predefined volume (e.g. every 10 m^3), while for time-proportional composite samples, a fixed sample volume is taken for each time unit (e.g. every 5 minutes) [103, MCERTS 2015], [152, ISO 1992].

Time-proportional composite samples are representative of an average emission if both the flow and the concentration are constant, if the flow is constant and the concentration varies, or if the flow varies and the concentration is constant. However, if both the flow and the concentration vary, time-proportional composite samples are not representative [38, DK EPA 2012]. When targeting representative results, flow-proportional composite samples are therefore generally preferred and most commonly applied. Consequently, the associated monitoring in BAT conclusions is usually based on flow-proportional composite samples. However, time-proportional composite samples may lead to equally representative results provided that the variations in the concentrations or flows are small. This is also reflected in some BAT conclusions.

In order to obtain representative composite samples, the interval between each subsample should not be too long. For time-proportional composite samples, one source recommends an interval of between 3 minutes (the shortest time that the sampler needs to go through a complete cycle) and 10 to 12 minutes. The maximum recommended time interval between two subsamples is 20 minutes, so that the composite sample is representative of the observed time period [38, DK EPA 2012].

The subsequent analysis of a composite sample gives an average value of the parameter during the period over which the sample was collected. It is common practice to collect composite samples over 24 hours to obtain a daily average value [103, MCERTS 2015]. Shorter sampling periods are also sometimes used, for example two hours or half an hour. This may be due to practical reasons (e.g. external inspections can be carried out during normal working hours) or to the instability of the sample (see below).

Taking composite samples over a period of 24 hours is usually automatic; instruments automatically withdraw a portion of sample at the appropriate volume discharged or time. It is advisable that the total sample volume is as large as is reasonably practicable to accommodate. In addition, it is necessary to consider the stability of the target parameter over the total sample collection time, as samples may deteriorate while being kept in the automated sampling device. In order to preserve the composite sample, it is often cooled and chemicals might be added. Sample instability may lead to shorter sample collection times or even to taking spot samples (see Section 5.3.5.7).

Therefore, it may not be appropriate to automatically collect composite samples for periods longer than 24 hours, due to potential issues with the stability of the parameters being monitored, for example BOD_n, pH, COD, and ammonia, even when automated sampling devices are refrigerated [103, MCERTS 2015].

For weekly, monthly or annual averages, it is good practice to collect a reasonable number of 24-hour flow-proportional composite samples (see Section 5.3.5.6), to analyse them separately, and then to average the measurement results (see Section 5.3.6). It is generally not advisable to mix such composite samples prior to analysis to obtain average concentrations for longer time periods (e.g. weekly and monthly average concentrations), because the information on the daily variations of the parameters will be lost. The mixing of samples, to reduce the number of analyses needed, should only be carried out in individual cases, where concentrations in the effluent remain stable and where longer storage times will not lead to changes in the sample composition.

As mentioned in Table 5.4, a certification system exists in the United Kingdom which also covers performance standards and test procedures for automated sampling devices [111, MCERTS 2017].

5.3.5.4.2 Spot samples

Spot samples, also referred to as grab samples, are discrete samples taken at random times and are not related to the volume discharged [152, ISO 1992]. Spot samples can be used, for example, when [103, MCERTS 2015]:

- the composition of the waste water is relatively constant;
- the quality of the discharged waste water needs to be checked at a particular moment, e.g. for inspection purposes;
- separate phases are present in the discharge and automated sampling is thus not applicable, e.g. an oil layer floating on water;
- the concentrations of the target substances are not stable in the sample, for example due to decomposition (e.g. chlorine), evaporation (e.g. VOCs, chlorine) or precipitation (e.g. dissolved silicates);
- the discharge is not continuous (e.g. from batch or buffer tanks or during special weather conditions), provided that the effluent is well mixed;
- the discharge caused by plant failure or accidental release needs to be evaluated.

When water flows and/or substance concentrations vary significantly, spot samples are generally not suitable. However, specific parameters might only be determined in spot samples, for instance oil components, grease, volatile compounds, dissolved oxygen, bacteriological parameters, chlorine and sulphide [38, DK EPA 2012], or with continuous on-line measurement, if available for the parameter.

5.3.5.5 Sampling equipment

5.3.5.5.1 Sample container

The choice of sample container is of major importance to preserve the integrity of the samples (e.g. to prevent sample contamination or losses due to adsorption or volatilisation). For the sampling of waste water, plastic containers are generally recommended for most parameters. Glass containers are generally used for the measurement of oil, grease, hydrocarbons, detergents, and pesticides [152, ISO 1992].

EN ISO 5667-3:2012 includes detailed provisions on the types of containers to be used, depending on the parameter [128, CEN 2012]. This standard is complementary to other, more specific measurement standards which provide more detailed information on the required type of container and its pretreatment (see the list of standards in Annex A.2).

Other factors to be considered when selecting sample containers include the following [152, ISO 1992]:

- mechanical and thermal resistance;
- sealing efficiency;
- ease of reopening, cleaning, and reuse;
- practicability of size, shape, and mass;
- costs.

Examples of sample containers are shown in Figure 5.1.

Source: [244, LUA NRW 2001]

Figure 5.1: Examples of sample containers

5.3.5.5.2 Manual sampling devices

Typical simple devices used for manual sampling include buckets, ladles, or wide-mouthed bottles that may be mounted on a handle of a suitable length. Another possibility is to use Ruttner or Kemmerer samplers which consist of a tube with a hinged lid at each of its ends.

An example of a sampling ladle and a handle is shown in Figure 5.2.

Source: [244, LUA NRW 2001]

Figure 5.2: Example of a sampling ladle and a handle

In general, the sampling devices are cleaned with detergents and water before use, and finally rinsed with water. If the analytes under study are detergents, special attention is paid to the rinsing step. Often, the sampling devices may be rinsed before use in the waste water stream from which the sample is taken in order to minimise the risk of contamination. However, this procedure is not adequate if it influences the measurement (e.g. analysis of oils and greases, and microbiological analysis) [152, ISO 1992].

5.3.5.5.3 Automated sampling devices

Automated sampling to obtain flow- or time-proportional samples can be carried out with several different devices which may be using a chain pump (paternoster pump), a peristaltic pump or compressed air and/or vacuum. Sampling devices are often portable. Depending on the tasks, several factors are usually taken into account when selecting an appropriate device, including [152, ISO 1992]:

- possibility to take flow- and/or time-proportional composite samples;
- robustness of construction;
- ease of operation and maintenance;
- possibility to lift samples over the required height;
- possibility to operate unattended for a long time period;
- precision and accuracy of the sampled volumes;
- adjustability of time intervals between different samples;
- possibility to sample from pressurised environments;
- possibility to cool samples and/or to add preservatives;
- costs.

An example of an automated sampling device is shown in Figure 5.3.

Source: [244, LUA NRW 2001]

Figure 5.3: Example of an automated sampling device

5.3.5.6 Measurement/sampling frequency

Depending on the numbers of subsamples taken, 24-hour flow-proportional composite samples generally allow a representative characterisation of the long-term emission pattern.

Typical measurement/sampling frequencies related to 24-hour flow-proportional composite samples are:

- once every day (daily);
- once every week (weekly);
- once every two weeks (fortnightly);
- once every month (monthly);
- once every two months (bimonthly);
- once every three months (quarterly).

Measuring every day allows the calculation of a representative yearly average (see Section 5.3.6), whereas with other frequencies, in principle, the calculated average only represents the sampled days. Therefore, it is more accurate to call it an 'average of samples obtained during one year' (see Sections 3.4.4.2 and 5.3.6) than a yearly average. For spot samples, the frequencies might be the same but the samples only represent a short sampling period.

Higher frequencies imply a higher workload and higher costs. In the case of automated sampling devices, the workload for sampling might not be as relevant but the additional analyses will result in a significant additional workload and costs. Therefore, the measurement/sampling frequency should reflect criteria, such as (see also Section 3.3.2):

- emission pattern;
- amount of pollutant released;
- variability of the pollutant concentration;
- possibility to assess the performance of the waste water treatment plant, in particular by measuring sum parameters;
- expected effects of the pollutant on the environment.

It might be necessary to increase the sampling frequency during other than normal operating conditions, e.g. during process/plant start-up or during unexpected low or high influents to the waste water treatment plant. An appropriate weighting of measurement results is needed if results obtained during times of higher sampling frequencies are to be used for calculating average values.

It is good practice to continuously measure the waste water flow to the receiving water body (see Section 5.3.3). This allows the calculation of the emission load at any time.

Contrary to 24-hour flow-proportional composite samples, spot samples only allow a snapshot of the long-term emission pattern. This might be sufficient in individual cases but if it is necessary to provide representative data for longer time periods a higher number of spot samples are required, or it is advisable to take 24-hour flow-proportional composite samples.

5.3.5.7 Handling and storage of samples

EN ISO 5667-3:2012 provides general information on the preservation and handling of water samples, including maximum storage times [128, CEN 2012]. This standard is complementary to other, more specific measurement standards which provide more detailed information on the recommended preservation techniques, the storage temperature, and the sample durability (see the list of standards in Annex A.2).

To preserve pollutant concentrations that may change during sample storage, the following measures may be necessary, depending on the waste water composition and the pollutant concerned:

- storage of the sample in the dark;
- cooling of the sample;
- filtration of the sample;
- stabilisation of the sample with acids, alkalis, or other chemicals;
- redissolution of precipitates.

An example of sample conservation is shown in Figure 5.4.

Source: [244, LUA NRW 2001]

Figure 5.4: Example of sample conservation

The maximum storage time depends on the pollutant/parameter to be measured, but also on the matrix of the waste water. It is a fundamental recommendation that the transport and storage time should be as short as possible. Efforts should be made to start the analysis within 24 hours of sample collection. Where logistics do not allow this, samples may be examined up to 48 hours after collection or may need to be frozen [38, DK EPA 2012]. The maximum storage time also depends on the expected concentrations. If low concentrations are expected, the analysis may need to be carried out immediately.

Usually, it is easy to find an (accredited) laboratory close to the sampling site that is able to carry out analyses of the most common waste water parameters (e.g. TSS, TOC or COD, nutrients, metals). But when the analysis of specific organic pollutants is required, it might be a task for specialised laboratories. Then it becomes important to organise the transportation in such a way as to minimise the time between sampling and analysis [38, DK EPA 2012].

It is important to take into account laboratory instructions on the use of sampling containers and sample preservation before and during sampling. For example, some measurements will require that no air space is left in the container after filling to prevent the loss of volatile components, while others need some space left to allow the addition of extraction solvents upon arrival in the laboratory. Sample containers may need to be treated beforehand, e.g. by adding preservatives before dispatch [103, MCERTS 2015].

Not taking laboratory instructions into account while sampling may lead to invalid analytical results. In particular, when sampling and analysis are carried out by different laboratories, a procedure has to be established to assure the quality of the measurement results [103, MCERTS 2015]. The audit of these procedures is part of accreditation according to EN ISO/IEC 17025:2005 [1, CEN 2005] (see also Sections 3.4.1 and 3.4.2).

5.3.5.8 Analysis

5.3.5.8.1 Overview

General recommendations for water analysis include the following [103, MCERTS 2015]:

- instrument operating instructions, calibration procedures and performance checks need to be fully documented and available to the personnel;
- instrument calibration procedures and performance checks need to be carried out at appropriate intervals and corresponding records need to be kept showing that calibration is maintained;
- all instruments need to be correctly maintained and records of the maintenance need to be kept, whether carried out by a third party, such as the instrument manufacturer, or not;
- traceability of the calibration of equipment, such as balances, thermometers, timers, auto-pipettes, according to EN standards and, where not available, to ISO or national standards is a prerequisite, and any corresponding certificates or other records need to be available;
- calibrated equipment needs to be clearly labelled and identifiable by the personnel.

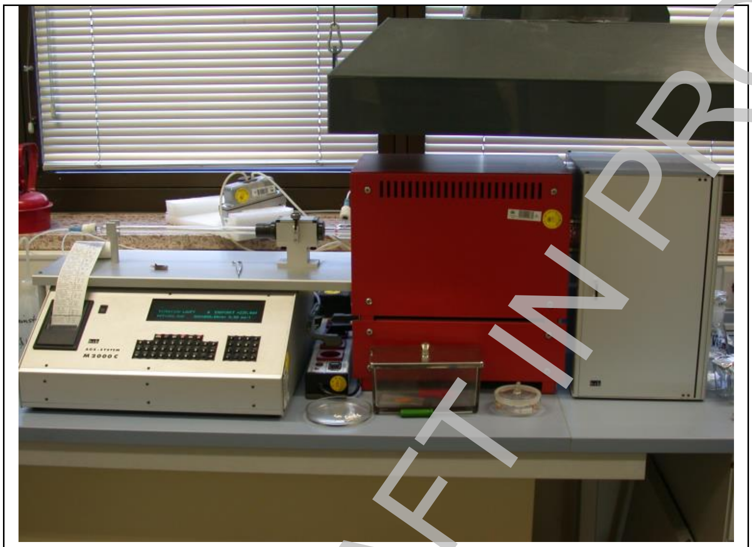
The issues listed above are regularly checked in the case of a laboratory accredited according to EN ISO/IEC 17025:2005 [1, CEN 2005].

The following sections provide information on specific monitoring aspects for the most common water parameters including on the measurement principles. A wider, but still non-exhaustive list of specific standards for the measurement of emissions to water together with information on measurement ranges and limits is given in Annex A.2. Toxicity tests and whole effluent assessment are described in Section 5.5.

5.3.5.8.2 Adsorbable organically bound halogens (AOX)

The parameter AOX is usually determined according to EN ISO 9562:2004. Organic compounds contained in the acidified water sample are adsorbed onto activated carbon by a shaking, stirring, or column procedure. Subsequently, inorganic halides are displaced from the loaded activated carbon by rinsing. Finally, the activated carbon is combusted and the flue-gas passes through an absorption solution. The resulting halide ions are determined by argentometric titration (e.g. microcoulometry). The method is applicable to test samples with AOX concentrations of more than 10 µg/l and chloride concentrations of less than 1 g/l. Alcohols, aromatic compounds, or carboxylic acids may give rise to negative bias (e.g. in case of dissolved organic carbon (DOC) concentrations of more than 100 mg/l) [96, CEN 2004].

An example of an AOX analyser is shown in Figure 5.5.



Source: [243, DE UBA 2016]

Figure 5.5: Example of an AOX analyser

AOX gives an indication of the overall level of organohalogen compounds in water samples (organochlorine, -bromine and -iodine compounds). Organofluorine compounds are not covered by the method. Moreover, the recovery of volatile compounds as well as of some polar and hydrophilic compounds (e.g. chloroacetic acids) is incomplete. High concentrations of organic compounds or chloride may interfere with the AOX measurement and thus require sample dilution or the use of an alternative method [96, CEN 2004].

One alternative method is the EOX (extractable organically bound halogens) which is based on a liquid-liquid extraction of the halogenated organic compounds with a non-polar solvent such as hexane. After phase separation, the solvent is combusted and the flue-gas passes through an absorption solution. The resulting halide ions are subsequently determined by argentometric titration (e.g. microcoulometry) [281, Analytik Jena 2007]. The disadvantage of the parameter EOX is that it only covers non-polar organic compounds, and therefore AOX values are generally higher than EOX values. In 2016, there was no EN standard for the measurement of EOX, but a few national standards existed (see Annex A.2).

Another alternative consists in using a modified AOX method, the SPE-AOX (dissolved adsorbable organically bound halogens after solid phase extraction), which is described in the informative Annex A of EN ISO 9562:2004. In this method, the test sample is filtered and the halogenated organic compounds are subsequently separated from inorganic halides by using solid phase extraction with a styrene-divinylbenzene copolymer. The resulting extract is subsequently analysed according to the traditional AOX method. The SPE-AOX method tolerates chloride concentrations of up to 100 g/l and DOC concentrations of up to 1 g/l. However, compared to the traditional AOX method, the SPE-AOX method does not include halogenated organic compounds that are bound to particles and shows lower recovery rates for polar halogenated organic compounds. Therefore, the comparability of the results obtained by using the SPE-AOX method with those of the traditional AOX method cannot be taken for granted [96, CEN 2004], [282, Wasserchemische Gesellschaft 1999]. Nevertheless, the SPE-AOX method can generally be assumed to give higher recovery rates for halogenated organic compounds than the EOX method. This was for example shown in the case of waste water from a chlor-alkali plant with high chloride concentrations [140, COM 2014].

5.3.5.8.3 Ammonium nitrogen (NH_4-N)

Ammonium nitrogen (NH_4-N) includes free ammonia (NH_3) and ammonium (NH_4^+). NH_4-N is usually measured to control the nitrification step of a biological waste water treatment plant or to control the effluent toxicity, as free ammonia in concentrations above approximately 0.2 mg/l can cause fatalities in several species of fish [200, Sawyer et al. 2003]. The contribution of ammonia to NH_4-N depends on the pH: at pH values below 8, ammonia represents less than 10 %, at pH values below 7, it represents less than 1 %.

In 2016, there were two EN standards available for the measurement of ammonium nitrogen, EN ISO 11732:2005 which is based on flow analysis [201, CEN 2005] and EN ISO 14911:1999 which is based on ion chromatography [210, CEN 1999]. Moreover, a number of ISO and national standards existed (see Annex A.2).

When collecting and assessing data for BREF reviews, it is important that they are in the same format, as concentrations may be expressed for the ion (i.e. the concentration of the NH_4^+ ion) or for the nitrogen concentration that is present in the form of ammonia and ammonium (i.e. NH_4-N).

At the time of writing this document (2016), there was a tendency to not define BAT-AELs for NH_4-N, but rather to use it to describe the performance of a biological waste water treatment plant. Instead, BAT-AELs were defined for total nitrogen (TN) or total inorganic nitrogen (N_{inorg}), as these parameters better reflect the eutrophication potential (see Section 5.3.5.8.13).

5.3.5.8.4 Biochemical oxygen demand (BOD_n)

The parameter BOD_n measures the amount of dissolved oxygen consumed by biochemical oxidation of organic and/or inorganic matter under specified conditions after *n* days, usually five or seven days (BOD_5 or BOD_7). Two EN standards were available in 2016. In the case of EN 1899-1, water samples are diluted and a seed of aerobic microorganisms is added together with allylthiourea to suppress nitrification. In the case of EN 1899-2, undiluted samples are analysed and nitrification is not suppressed. In both cases, incubation is subsequently carried out in completely filled and stoppered bottles at 20 °C in the dark. The BOD_n is determined by measuring the dissolved oxygen concentration before and after incubation [145, CEN 1998], [146, CEN 1998].

BOD_n has long been used and is still used to monitor effluents from biological waste water treatment plants. However, at the time of writing this document (2016), there was a tendency to not define BAT-AELs for BOD_n, but rather to use it to describe the performance of a biological waste water treatment plant, as BOD_n shows some disadvantages:

- the measurement result depends on the local conditions (e.g. inoculum);
- the measurement uncertainty for BODn is higher than for TOC/COD;
- the measurement result is only available after a few days and therefore cannot be used to control the biological waste water treatment plant.

Instead of BOD_n, the parameter TOC may be used because it is faster to determine, although TOC actually represents the amount of organically bound carbon in the sample and not the actual oxygen demand.

5.3.5.8.5 Chemical oxygen demand (COD)/Total organic carbon (TOC)

The parameter COD is commonly used to indirectly measure the amount of organic compounds in water by measuring the mass of oxygen needed for their total oxidation to carbon dioxide. The most widespread COD methods use chromate as an oxidising agent and mercury salts to suppress the influence of inorganic chloride. In 2016, there was no EN standard for the measurement of COD, but a few ISO and national standards existed (see Annex A.2).

Potential interferences of other substances and the degree to which organic compounds are oxidised depend on the oxidising agent and the reaction conditions [278, Janicke 1983]. Therefore, the comparability of the results obtained using different COD methods cannot be taken for granted.

For example, the use of permanganate ('permangante index') is not recommended for determining organic compounds in waste water, as the oxidation is generally incomplete [279, CEN 1995].

The parameter TOC is used to directly measure the amount of organic compounds in water. The most widespread methods use a combustion chamber to completely oxidise the organic substances to carbon dioxide, which is then measured by IR spectrometry. Inorganic carbon (IC) such as carbonate and hydrogen carbonate is not included in the TOC, but elemental carbon, cyanate and thiocyanate are covered. EN 1484:1997 specifies a direct and a differential method for TOC measurements. In the case of the direct method, samples are acidified and IC is purged prior to analysis. The result is sometimes referred to as non-purgeable organic carbon (NPOC). The disadvantage of this method is that VOCs may also (partly) be purged. In the case of the differential method, total carbon (TC) and IC are measured separately, and the TOC is calculated by subtracting IC from TC. The use of the differential method requires that the TOC is higher than the IC or of a similar magnitude, as otherwise the measurement uncertainty becomes high [110, CEN 1997].

In some Member States, there is a tendency to replace COD with TOC for economic and environmental reasons. The use of chromate and mercury, necessary for the COD determination, can be avoided by determining TOC, which is also easier to automatise. Both methods have limitations, which may have an influence on their applicability.

The COD/TOC ratio is usually plant- or site-specific. In general, COD values are higher than TOC values. For organic compounds, the COD/TOC ratio theoretically ranges from 0.67 (oxalic acid) to 5.3 (methane). Higher COD/TOC ratios may be obtained when the waste water contains inorganic oxidisable compounds (e.g. sulphite, Fe^{2+}). In practice, COD/TOC ratios are usually between 2.0 and 4.0. At the end of the 1990s, a study carried out in Germany examined the COD/TOC ratio in the final effluents of a number of industry sectors [88, Braun et al. 1999]. In many cases, a ratio of 3.0 is considered a good approximation (e.g. it is used in the E-PRTR [147, EC 2006]).

5.3.5.8.6 Chromium(VI)

Due to its carcinogenic nature, chromium(VI), also referred to as hexavalent chromium, is sometimes measured in addition to the total chromium content (see Section 5.3.5.8.10). Dissolved chromium(VI) generally consists of chromate (CrO_4^{2-}), hydrogen chromate ($HCrO_4^-$), and dichromate ($Cr_2O_7^{2-}$). The equilibrium between these species depends on the pH and the total chromium(VI) concentration.

In 2016, two EN standards for the measurement of chromium(VI) via flow analysis were available, but only one of them, EN ISO 23913:2009, can be used for waste water. For the measurement, the sample is filtered, if necessary, and fed into a carrier stream so that chromium(VI) reacts with 1,5-diphenylcarbazide to form a red-violet complex that is measured spectrophotometrically at 544 nm [212, CEN 2009]. Alternatively, chromate can also be measured with ion chromatography according to EN ISO 10304-3:1997 [258, CEN 1997].

5.3.5.8.7 Cyanide

In 2016, there were two EN standards available for the measurement of cyanide, EN ISO 14403-1:2012 which is based on flow injection analysis (FIA) [260, CEN 2012] and EN ISO 14403-2:2012 which is based on continuous flow analysis (CFA) [261, CEN 2012]. Both of the aforementioned EN standards distinguish between free cyanide (easily liberatable cyanide) and total cyanide. Free cyanide includes cyanide ions (i.e. CN^-) and the cyanide bound in weak metal cyanide complexes that liberate hydrogen cyanide (i.e. HCN) at pH 3.8. Total cyanide also includes stronger metal-cyanide complexes with the exception of cyanide bound in complexes of cobalt, gold, platinum, rhodium and ruthenium from which recovery can be partial [260, CEN 2012], [261, CEN 2012].

For the determination of total cyanide, complex-bound cyanide is decomposed with UV light at pH 3.8. In the case of EN ISO 14403-1:2012, the resulting hydrogen cyanide is separated by diffusion across a hydrophobic membrane at 30–40 °C and absorbed in a sodium hydroxide solution. In the case of EN ISO 14403-2:2012, the transfer of hydrogen cyanide may also be carried out via online distillation at 125 °C. Subsequently, cyanide absorbed in the sodium hydroxide solution reacts with chloramine-T to cyanogen chloride which in turn reacts with pyridine-4-carboxylic acid and 1,3-dimethylbarbituric acid to give a red dye which is measured spectrophotometrically. The determination of free cyanide is carried out according to a very similar procedure with the main difference being that there is no decomposition step with UV light [260, CEN 2012], [261, CEN 2012].

In addition to the two EN standards, a number of ISO standards existed in 2016 (see Annex A.2). Due to the operational nature of the cyanide definitions in the various standards and also the potential interferences, the comparability of the results obtained using different methods cannot be taken for granted.

5.3.5.8.8 Hydrocarbon oil index (HOI)

EN ISO 9377-2:2000 specifies a method for the determination of the hydrocarbon oil index (HOI) as the sum of the concentrations of compounds extracted and analysed according to a defined procedure. The HOI includes long-chain or branched aliphatic, alicyclic, aromatic or alkyl-substituted aromatic hydrocarbons and can be measured in concentrations above 0.1 mg/l. The content of volatile mineral oil cannot be determined quantitatively. For the measurement, the water sample is extracted with a single hydrocarbon solvent with a boiling point of between 36 °C and 69 °C. Polar substances are subsequently removed from the extract by clean-up with Florisil$^{®}$ (a hard-powdered synthetic magnesia-silica gel). The purified extract is then analysed by gas chromatography (GC) with a flame ionisation detector (FID). The total peak area between *n*-decane ($C_{10}H_{22}$) and *n*-tetracontane ($C_{40}H_{82}$) is measured. The concentration of mineral oil is quantified against an external standard consisting of two specified mineral oils, and the hydrocarbon oil index is calculated [97, CEN 2000].

In the past, the HOI was often determined by extraction with a halogenated solvent followed by Fourier transform infrared spectrometry (FTIR). These methods were discontinued due to the ozone depletion potential of the solvents used. Another HOI method, prEN ISO 9377-1:2000 (ISO/DIS 9377-1:2000) was based on solvent extraction, clean-up with Florisil$^{®}$, solvent evaporation, and gravimetry, but the sensitivity was low compared to EN ISO 9377-2, as only

HOI concentrations above 5 mg/l could be determined [202, Nordic Council 2003]. The draft standard prEN ISO 9377-1:2000 (ISO/DIS 9377-1:2000) was withdrawn in 2003.

Given the operational nature of the definition of the HOI in EN ISO 9377-2:2000, the comparability of the results with those obtained using other methods cannot be taken for granted.

In addition to the HOI, several EN standards for the measurement of individual hydrocarbon compounds are available, e.g. for monocyclic aromatic hydrocarbons, PAHs, and volatile halogenated hydrocarbons [121, CEN 2016].

5.3.5.8.9 Mercury

In 2016, two specific EN standards for the measurement of mercury were available. EN ISO 12846:2012 describes a method using atomic absorption spectrometry (AAS) with or without enrichment (cold-vapour technique). For the measurement without enrichment, mono- and divalent mercury species including organomercury compounds are converted to divalent mercury by oxidation with potassium bromate/potassium bromide and then reduced to elemental mercury with tin(II) chloride. Elemental mercury is subsequently stripped from the solution and measured with AAS. If the enrichment step is applied, the stripped elemental mercury is concentrated on an adsorbent suitable for amalgamation (e.g. a gold-platinum gauze) and subsequently desorbed by rapid heating before being measured with AAS [206, CEN 2012]. EN ISO 17852:2008 is based on atomic fluorescence spectrometry (AFS). Similarly to EN ISO 12846:2012, mercury compounds are first oxidised with potassium bromate/potassium bromide and then reduced with tin(II) chloride, followed by stripping of the generated elemental mercury. The latter is then excited with UV light and the emitted radiation is measured [207, CEN 2008].
Mercury can also be measured with inductively coupled plasma mass spectrometry (ICP-MS) according to EN ISO 17294-2:2016 (see Section 5.3.5.8.10).

5.3.5.8.10 Metals and other elements

In 2016, several EN standards for the measurement of metals and other elements were available.

EN ISO 17294-2:2016 describes the determination of selected elements with inductively coupled plasma mass spectrometry (ICP-MS). For the measurement, the sample is introduced into a radio-frequency plasma where energy transfer processes from the plasma cause desolvation, decomposition, atomisation, and ionisation of elements. The generated ions are subsequently extracted through a differentially pumped vacuum interface with integrated ion optics, separated on the basis of their mass-to-charge ratio by a mass spectrometer, and detected, usually by a continuous dynode electron multiplier assembly [208, CEN 2016]. In general terms, ICP-MS is the most versatile and sensitive multi-element measurement method, but it is also the most expensive one.

EN ISO 11885:2009 can be used to measure elements with inductively coupled plasma optical emission spectrometry (ICP-OES). As for ICP-MS, samples are introduced into a radio-frequency plasma where excitation of the generated atoms and ions occurs. The generated characteristic emission spectra are dispersed by a grating spectrometer and the light intensities at specific wavelengths are measured by a detector [187, CEN 2009]. Mercury is usually not measured with ICP-OES, as it is usually not sensitive enough (see Section 5.3.5.8.9).

An example of an inductively coupled plasma optical emission spectrometer is shown in Figure 5.6.

Source: [243, DE UBA 2016]

Figure 5.6: Example of an inductively coupled plasma optical emission spectrometer

EN ISO 15586:2003 describes a method for measuring 17 trace elements using atomic absorption spectrometry (AAS) with electrothermal atomisation using a graphite furnace. For the measurement, the sample solution is injected into an electrically heated graphite furnace where it is dried, pyrolised, and atomised. The atoms thus generated are measured spectrophotometrically using light sources specific for a certain element (or elements) [209, CEN 2003]. Other AAS standards based on flame atomisation or electrothermal atomisation are available for specific elements, e. g. for the measurement of Al, Ca, Cd, Cr, and Mg [121, CEN 2016]. In the past, the disadvantage of AAS compared to ICP-MS and ICP-OES was that only one element could be measured at a time. However, high-resolution continuum source AAS instruments became commercially available some years ago (in 2003 for flame atomisation and in 2007 for electrothermal atomisation) which allow the sequential and also, depending on the conditions, simultaneous determination of multiple elements [213, Resano et al. 2013].

Common alkali and alkaline earth metal cations (i.e. Li^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, Sr^{2+}, and Ba^{2+}) can also be measured with ion chromatography according to EN ISO 14911:1999 [210, CEN 1999].

The aforementioned methods generally measure the dissolved fraction of the elements. When the total concentration of an element needs to be determined, a sample digestion step is carried out prior to analysis, typically using *aqua regia* according to EN ISO 15587-1:2002 or nitric acid according to EN ISO 15587-2:2002. These digestion methods are empirical and might not release all elements completely. However, for most environmental applications, the results are fit for purpose [214, CEN 2002], [215, CEN 2002]. EN ISO 11885:2009 and EN ISO 17294-2:2016 describe some specific digestion methods for certain elements (i.e. Sn, Ti) [187, CEN 2009], [208, CEN 2016].

5.3.5.8.11 Phenol index

The phenol index may be determined with EN ISO 14402:1999. It is an analytical convention that represents a group of aromatic compounds which under the specific reaction conditions form coloured condensation products. The analytical result is expressed in terms of phenol concentration. EN ISO 14402:1999 describes two methods, both based on flow analysis: the determination of the phenol index (without distillation) after extraction and the determination of the phenol index (without extraction) after distillation. For the first method, the sample is fed into a carrier stream where phenolic compounds are oxidised by potassium permanganate, and the resulting quinones react with 4-aminoantipyrine to form coloured condensation products. These are extracted into chloroform and measured spectrophotometrically at 470–475 nm.

Aromatic amines also form condensation products leading to positive bias. For the second method, the sample is fed into a carrier stream, acidified with phosphoric acid to pH 1.4, and distilled. The distillate contains the steam-volatile fraction of the phenolic compounds. These are oxidised with potassium hexacyanoferrate(III), and the resulting quinones react with 4-aminoantipyrine to form yellow condensation products that are measured spectrophotometrically at 505–515 nm [98, CEN 1999].

ISO 6439:1990 describes a similar, manual method of determining the phenol index based on the same chemical reaction principles [203, ISO 1990].

When measuring the phenol index, the recovery of individual phenolic compounds varies considerably [154, COM 2016]. For example, ISO 6439:1990 stipulates that some phenolic compounds with alkyl, aryl, and nitro substituents in the *para* position do not produce colour and are thus not measured [203, ISO 1990]. Therefore, the comparability of the results obtained using EN ISO 14402:1999 with those obtained using other methods cannot be taken for granted.

In addition to the phenol index, several EN standards for the measurement of individual phenolic compounds are available, e.g. for chlorophenols, nitrophenols, and alkylphenols [121, CEN 2016].

5.3.5.8.12 Sulphide

BAT-AELs for emissions of sulphide to water were defined in some BAT conclusions (e.g. for easily released sulphide in the BREF for Iron and Steel Production (IS BREF) [142, COM 2013] and for sulphide in the BREF for Tanning of Hides and Skins (TAN BREF) [179, COM 2013]. In 2016, there were only two ISO standards available, but no EN standard [121, CEN 2016], [122, ISO 2016].

ISO 10530:1992 describes the determination of dissolved sulphide. For the measurement, the sample is filtered followed by sulphide stripping and absorption in a zinc acetate solution. Subsequently, reagents are added with which sulphide reacts to give methylene blue which is measured spectrophotometrically at 665 nm [204, ISO 1992]. The determination of easily released sulphide according to ISO 13358:1997 follows the same principle except that stripping is carried out at pH 4. Easily released sulphide includes dissolved sulphide and, to various degrees, some undissolved sulphides, depending on their solubility and ageing properties. Examples of the latter are sulphides of zinc, iron, and manganese. Other undissolved sulphides such as mercury sulphide are not included [205, ISO 1997].

5.3.5.8.13 Total nitrogen (TN)/Total inorganic nitrogen (N_{inorg})/Total Kjeldahl nitrogen (TKN)

When using EN standards, there are three general approaches to determine total nitrogen:

- The measurement of total nitrogen as total nitrogen bound (TN_b) by thermal oxidation with subsequent chemiluminescence detection of nitrogen oxides according to EN 12260:2003 [99, CEN 2003].
- The measurement of total nitrogen by wet chemical oxidation with peroxodisulphate and subsequent measurement of nitrate according to EN ISO 11905-1:1998 (Koroleff method) [100, CEN 1998].
- The measurement of total nitrogen as the sum of total Kjeldahl nitrogen [101, CEN 1993], nitrate nitrogen (NO_3-N) and nitrite nitrogen (NO_2-N) (various standards available) [121, CEN 2016].

Depending on the characteristics of the sample, these three approaches for determining total nitrogen can lead to different results, as some organic compounds are oxidised to different extents. Dissolved nitrogen gas is not covered by any of these methods.

Instead of TN, the parameters N_{inorg} or TKN are sometimes used in legislation or permits. From the aforementioned definitions (see Section 5.2), it is apparent that the parameters are not equivalent; **therefore, analytical results are not comparable**. By definition, the following applies: $TN \geq N_{inorg}$ and $TN \geq TKN$.

When collecting and assessing data for BREF reviews, it is important that they are in the same format, as concentrations for inorganic nitrogen species may be expressed for the ions (i.e. the concentration of the NH_4^+, NO_2^- or NO_3^- ions) or for the nitrogen concentration that is present in the form of these ions (i.e. NH_4-N, NO_2-N or NO_3-N).

TN is often considered a more pertinent parameter as all forms of organic and inorganic nitrogen can contribute to eutrophication. TN reflects the performance of the whole waste water treatment, including the pretreatment of poorly biodegradable organic nitrogen compounds and the removal of solids containing nitrogen. TN can be measured simultaneously with TOC. In contrast, the parameter N_{inorg} reflects the performance of biological nitrification and denitrification. Literature suggests that TN potentially overestimates the bioavailable nitrogen while N_{inorg} potentially underestimates it [148, Seitzinger et al. 1997].

The aforementioned COD/TOC study carried out in Germany at the end of the 1990s also examined the N_{inorg}/TN ratio in the final effluents of a number of industry sectors. On average, approximately 20 % of TN was made up of organically bound nitrogen [88, Braun et al. 1999].

5.3.5.8.14 Total phosphorus (TP)

The parameter total phosphorus includes all organic and inorganic phosphorus compounds, dissolved or bound to particles. The inorganic forms of phosphorus include orthophosphate (i.e. $HPO_4^{2-}/H_2PO_4^-$), diphosphate (i.e. $HP_2O_7^{3-}/H_2P_2O_7^{2-}$), and oligo/polyphosphates. Organically bound phosphorus can for example be found in biomass (e.g. in adenosine triphosphate) or in phosphonates (e.g. used as anti-scaling agents for the treatment of cooling water).

Several EN standards for the determination of TP exist:

- EN ISO 6878:2004 specifies methods for the determination of different types of phosphates by spectrophotometry using ammonium molybdate. The measurement of TP requires prior sample digestion with peroxodisulphate or nitric acid. The digestion with peroxodisulphate is not effective in the presence of high TOC/COD concentrations (e.g. COD > 270 mg/l) [184, CEN 2004], [189, Kullwatz et al. 2008].
- EN ISO 15681-1:2004 and EN ISO 15681-2:2004 specify flow analysis methods (i.e. flow injection analysis (FIA) or continuous flow analysis (CFA)) [185, CEN 2004], [186, CEN 2004].
- Another possibility is to use inductively coupled plasma optical emission spectrometry (ICP-OES) according to EN ISO 11885:2009 (see Section 5.3.5.8.10) [187, CEN 2009].

Compared to the spectrophotometric method described in EN ISO 6878:2004, the use of ICP-OES as described in EN ISO 11885:2009 allows a higher automation and the simultaneous measurement of other elements (e.g. metals), but a higher investment for the equipment is needed. The aforementioned German COD/TOC study also compared the results of the spectrophotometric method with those of ICP-OES for the final effluents of a number of industry sectors. On average, the ratio of TP(spectrophotometry)/TP(ICP-OES) was 0.96 indicating that the two methods provide largely comparable results [88, Braun et al. 1999].

5.3.5.8.15 Total suspended solids (TSS)

The parameter TSS includes both organic and inorganic suspended solids. It is usually measured according to EN 872:2005 which is based on sample filtration through a glass fibre using vacuum or pressure. The filter is then dried at 105 °C ± 2 °C and the mass of the residue retained on the filter is determined by weighing [188, CEN 2005].

TSS can be used to describe the performance of solids removal techniques during waste water treatment. In some cases, TSS levels correlate with levels of other parameters, namely BOD, COD/TOC, total phosphorous, total nitrogen, and metals [154, COM 2016].

Settleable solids need to be distinguished from TSS, as they represent the TSS subfraction that settles under specified conditions (e.g. after a certain settling time). Settleable solids may be determined volumetrically with an Imhoff cone or gravimetrically [149, CEN 2007] [259, APHA 1999].

Turbidity might be measured as a qualitative surrogate parameter for suspended solids (see Section 5.4.1). EN ISO 7027-1:2016 describes two quantitative methods which rely on the measurement of monochromatic infrared light scattering or attenuation, both induced by particles. Instruments are calibrated with standardised solutions of formazin, preferably obtained commercially or prepared by mixing solutions of hexamethylenetetramine and hydrazine. For water samples with low turbidity (e.g. drinking water), light scattering is measured (i.e. nephelometry), while for water samples with high turbidity (e.g. waste water), light attenuation is measured (i.e. turbidimetry). Turbidity measurements are easier to automatise than TSS measurements, but the result depends on the size and shape of the particles and not only on their mass concentration [191, CEN 2016]. In 2016, another standard on semi-quantitative methods for the measurement of turbidity was in preparation (i.e. ISO 7027-2) [122, ISO 2016].

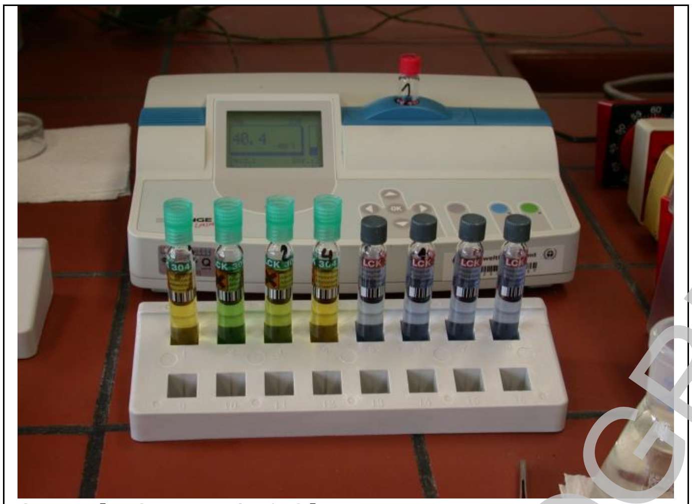
5.3.5.8.16 Test kits

Test kits or rapid tests are an alternative to more traditional analytical methods for measuring pollutants and sum parameters in waste water. The majority of test kits involve colorimetric methods. They come in two main formats, those using visual comparators and those using portable or benchtop spectrophotometers [103, MCERTS 2015].

Generally, the use of visual comparators is not recommended, as these systems are very dependent on the user and the environmental conditions [103, MCERTS 2015]. They often lack the accuracy required for assessing compliance with permit conditions and for the definition of BAT-AEPLs, but they may help the operator of a waste water treatment plant to collect actual performance data.

Test kits using spectrophotometers have increased in sophistication and quality in the past years, and many are based on standard laboratory methods. Measurement results can be stored electronically to ensure traceability. Test kits are available for many parameters, such as COD, ammonia, phosphate and iron [103, MCERTS 2015].

An example of a test kit with a spectrophotometer is shown in Figure 5.7.



Source: [243, DE UBA 2016]

Figure 5.7: Example of a test kit with a spectrophotometer

Test kits offer advantages such as ease of use (e.g. prepackaged reagents, built-in calibrations) and low costs when few analyses are carried out [88, Braun et al. 1999], [103, MCERTS 2015]. However, they should undergo a full evaluation before use, ensuring appropriate performance characteristics and matrix suitability, and be treated in the same way as a standard method in terms of documentation and quality assurance/control procedures [103, MCERTS 2015].

Generally, proof is needed to show that the analytical results of test kits are of an equivalent scientific quality to the ones obtained by EN standards or, if EN standards are not available, by ISO, national or other international standards before they can be used to assess compliance with permit conditions or as references in BAT conclusions; in addition, the equivalent scientific quality needs to be checked regularly.

5.3.6 Data treatment

Measurement results can be obtained by continuous or periodic measurements, and this will lead to different data treatment steps.

In the case of **continuous measurements**, average levels may refer to different time periods. Common averaging periods are one hour, two hours or 24 hours, depending on the measurement objective. If the task is to derive a daily average, 24 hours may be the right averaging period. If the performance of a plant over the day is of interest, averages for shorter periods, e.g. one hour, may be calculated. The same time period is used for averaging the results of the flow measurements.

In the case of **periodic measurements** with flow-proportional composite samples, no additional calculations are required to derive representative averages as the sampling method already considers the waste water flow. Other samples such as time-proportional composite samples may require additional calculations to be representative of the discharge of a pollutant for the entire day for example.

To calculate a **representative average concentration over a longer time period,** the individual measurement results need to be averaged and weighted by the related waste water flow, as given in the following equation:

Equation 5.1

$$c_w = \frac{\sum_{i=1}^{n} c_i q_i}{\sum_{i=1}^{n} q_i}$$

where c_w = flow-weighted average concentration of the parameter;
n = number of measurement periods;
c_i = average concentration of the parameter during ith measurement period;
q_i = average flow rate during ith measurement period.

In the case of a BAT-AEPL or an ELV given as a yearly average concentration based on 24-hour flow-proportional composite samples, this means that the measurement result of each 24-hour flow-proportional composite sample obtained during the observed year has to be multiplied by the corresponding daily average flow, summed up and divided by the sum of all daily average flows. The result is a flow-weighted yearly average concentration. Some example calculations are given in Annex A.6.

The **calculation of the average specific load** (e.g. as a monthly or yearly average) can be carried out according to Equation 5.2:

Equation 5.2

$$l_{specific} = \frac{\sum_{i=1}^{n} \frac{c_i q_i}{p_i}}{n}$$

where $l_{specific}$ = average specific load of the parameter;
n = number of measurement periods;
c_i = average concentration of the parameter during ith measurement period;
q_i = average flow rate during ith measurement period;
p_i = production output during ith measurement period.

Depending on the industrial sector, it might be appropriate to use the raw material consumption instead of the production output for example.

In the case of a BAT-AEPL or ELV given as a yearly average specific load based on 24-hour flow-proportional composite samples, this means that the measurement result of each 24-hour flow-proportional composite sample obtained during one year is multiplied by the corresponding daily average flow and then divided by the daily production output to calculate the **daily specific load**. The daily specific loads are summed up and divided by the number of measurement periods to calculate the **yearly average specific load**. Some example calculations are given in Annex A.6.

When the daily production output is more or less stable over the year, the yearly average specific load can by calculated by summing up all daily specific loads and dividing them by the yearly production output.

The calculation of specific loads based on a measurement frequency less than daily can be carried out in a similar way, but it needs to be ensured that the measurement results are representative of the examined time period. In this case, it seems more appropriate to refer to an average over the given time period (e.g. over one year or month), to avoid any confusion with averages based on a daily measurement frequency (see Section 3.4.4.2).

If some concentration values of the parameter are below the limit of quantification, assumptions are needed on how to treat these data and how to calculate the load. For further information see Section 3.4.4.4.

There might be cases where daily measurement results are not available (e.g. in the case of batch or seasonal production). To estimate the load, a particular day or number of days might be considered as being representative of a particular period and the calculation could then be based on this/these day(s).

5.3.7 Reporting

Each standard specifying the determination of a single substance or sum parameter contains provisions on reporting and on the expression of results (see the list of standards in Annex A.2). The measurement report transparently describes where and how the measurements were carried out, and provides sufficient detail to trace the results back through the calculations to the collected raw data and operating conditions. In general, the measurement report contains information on at least:

- the EN standard(s) applied;
- the sample identity;
- the results, expressed as indicated in the EN standard(s);
- the sampling method and the sample pretreatment, if appropriate;
- any deviations from the standardised method; and
- any details of all circumstances which could have affected the results.

Further information might be needed to ensure a sound interpretation of the results, in particular for assessing compliance with permit conditions or for the definition of BAT-AEPLs, e.g.:

- name and address of the laboratory carrying out the sampling and the analysis;
- reference to the sampling plan indicating deviations, if any occurred;
- identification of the sampling site(s) and sampling point(s);
- sampling date and time (for composite samples start/stop dates and times);
- information on operating conditions before and during sampling;
- further sampling details and observations necessary to evaluate the measurement results;
- sample preservation;
- waste water flow, at least during the sampling period if not required continuously;
- quality control results for sampling and analysis;
- description of the applied chain of custody for sampling and analysis;
- limit of detection and/or limit of quantification;
- measurement uncertainty.

Under certain conditions, measurement results/reports are made publicly available, for example according to IED Article 24(3)(b) [24, Directive 2010/75/EU 2010].

5.3.8 Drawing up or review of BREFs

The provided data are the basis for defining BAT and BAT-AEPLs, where appropriate. In association with BAT-AEPLs, the monitoring regime needs to be established. The waste water samples predominantly taken in Europe are **24-hour flow-proportional composite samples.** These samples guarantee, to a great extent, representative daily measurement results, even if the concentrations and the flows vary. Therefore, BAT conclusions generally refer to this sample type even though under certain specific conditions other sample types might also be appropriate or even better suited (see Section 5.3.5.4).

For the definition of BAT and BAT-AEPLs, it is often very useful to report time series of measurement results and not only averages, in order to understand emission patterns. Furthermore, it is necessary to report all relevant **reference conditions** such as sampling and measurement methods, measurement frequencies, limits of quantification and detection, measurement uncertainties, complementary parameters (e.g. flow, temperature, pH), and operating conditions (e.g. normal or other than normal operating conditions). Usually, complete measurement reports are not provided, but it might be useful in certain cases.

Measurement frequencies in BAT conclusions are based on the data provided and on the relevance of the parameter for the specific industrial sector. They reflect an adequate minimum frequency for the determination of the parameter, even though other frequencies, e.g. lower or higher, might be applied in special cases, taking into account local conditions for example. For the sake of clarity, it is advisable to use the terms mentioned in Section 5.3.5.6, such as once every week, month, or year.

Data of waste water flows are essential for defining BAT and BAT-AEPLs, independently of whether they are expressed as concentrations or as loads.

As already mentioned, BAT-AEPLs are generally based on 24-hour flow-proportional composite samples and often expressed as daily, weighted monthly or weighted yearly average **concentrations** or as daily, monthly or yearly average **specific loads,** e.g. per unit of product.

Generally, it seems appropriate to express BAT-AEPLs as **concentrations**, if:

- the emission levels can be effectively controlled by the design and operation of the waste water treatment plant;
- water- or energy-saving techniques do not significantly affect the emission levels.

For example, the achieved emission levels of the parameters TSS, BOD_n and TP essentially depend on the design and operation of the final waste water treatment plant. Expressing BAT-AEPLs as specific loads in these cases may lead to very wide ranges due to varying flows, even though the concentration values are similar.

BAT-AEPLs are most commonly expressed as concentrations [39, EU 2012]. In specific cases, they may be combined with abatement efficiencies or a minimum mass flow (e.g. in the BREF for Common Waste Water and Waste Gas Treatment/Management Systems in the Chemical Sector (CWW BREF) [154, COM 2016]).

Arguably, it might be appropriate to express BAT-AEPLs as **specific loads,** if:

- the emission levels mainly depend on the production process and applied process-integrated techniques;
- the emission levels correlate with a production-specific parameter (e.g. the mass of product manufactured or raw material used);
- water- or energy-saving techniques lead to increased emission levels (e.g. for COD and AOX).

In the case of some industrial sectors, certain BAT-AEPLs are expressed as specific loads (e.g. in the BREF for the Production of Pulp, Paper and Board (PP BREF) [160, COM 2015]).

For further information on data gathering and reference information accompanying emission data, see the 'BREF guidance' [39, EU 2012].

5.4 Surrogate parameters

5.4.1 Examples of surrogate parameters

General aspects of surrogate parameters including the distinction between quantitative, qualitative, and indicative surrogate parameters are described in Section 3.3.3.3.1.

The determination of emissions to water is covered to a large extent by the measurement of sum parameters which are **quantitative surrogate parameters**. They represent a group of substances [3, COM 2003]:

1. containing the same chemical element or the same chemical element in certain bond types;
2. showing similar characteristics.

Examples of the first type of sum parameters include the following:

- total organic carbon (TOC) instead of the individual organic compounds (see Section 5.3.5.8.5);
- total nitrogen (TN) instead of the individual nitrogen compounds (see Section 5.3.5.8.13);
- adsorbable organically bound halogens (AOX) instead of the individual halogenated organic compounds (see Section 5.3.5.8.2);
- hydrocarbon oil index (HOI) instead of the individual hydrocarbon compounds (see Section 5.3.5.8.8);
- phenol index instead of the individual phenolic compounds (see Section 5.3.5.8.11).

Examples of the second type of sum parameters include the following:

- in the case of chemical oxygen demand (COD), the oxidisability by dichromate instead of the individual organic compounds (see Section 5.3.5.8.5);
- in the case of biochemical oxygen demand (BOD_n), the mass of oxygen consumed by a seed of aerobic microorganisms (see Section 5.3.5.8.4);
- in the case of toxicity tests, the effect of all substances present in the sample on a specific organism (see Section 5.5).

Examples of **qualitative surrogate parameters** include the following [3, COM 2003]:

- conductivity, instead of the individual metal compounds in precipitation and sedimentation processes;
- turbidity, instead of the individual metal compounds or suspended solids in precipitation, sedimentation and flotation processes.

Examples of **indicative surrogate parameters** include the following [3, COM 2003]:

- pH, for precipitation and sedimentation processes;
- pH, for the discharge of acidic or alkaline substances;
- changes in perceived odours on site, as an indication of unexpected stripping processes.

Combinations of surrogate parameters may result in a stronger correlation between controlled parameters and expected emissions.

5.4.2 Drawing up or review of BREFs

Whenever emissions to water are addressed in BAT conclusions and BAT-AEPLs are defined, sum parameters are frequently used to quantify the emission, since it is often not possible to specify all the substances that will occur in the waste water discharge throughout a complete industrial sector.

For further information on data gathering and reference information accompanying emission data, see the 'BREF guidance' [39, EU 2012].

5.5 Toxicity tests and whole effluent assessment

5.5.1 Toxicity tests

5.5.1.1 Overview

Toxicity tests, also referred to as biotests or bioassays, involve exposing test organisms to an environment (e.g. an original or diluted waste water sample) to determine the effects on their physiological properties, survival, growth, or reproduction. Different organisms representing distinct trophic levels are used, including bacteria, algae, higher plants, invertebrates, fish eggs and fish. The selection of the test organism depends on the type of receiving water body (fresh or salt water). Toxicity tests are quantitative surrogate parameters (see Section 5.4.1). They are an integral part of any whole effluent assessment (see Section 5.5.2).

Acute toxicity tests measure the injurious effects of a substance or waste water during a short-term exposure. Chronic toxicity tests measure the injurious effects resulting from a longer exposure in relation to the life cycle of the organism [173, Regulation EC/1272/2008 2008]. Chronic toxicity tests are less widespread than acute toxicity tests and short-term chronic tests are to be preferred in order to avoid any possible change in the characteristics of the effluent during the test [116, TOTAL 2009].

Toxicity tests are carried out by (accredited) laboratories, where test organisms (mainly from standardised cultures) are exposed to waste water that has been transferred to the testing laboratory. Toxicity tests are rarely carried out on-line. The time needed to obtain the results, typically between 24 and 96 hours, does not allow the direct control of the waste water treatment. The application of toxicity tests requires specific skills that are different from those required for physico-chemical analyses as described in Sections 5.3 and 5.4. Experienced testing laboratories were not necessarily available in all EU Member States at the time of writing this document (2016).

The use of toxicity tests offers a number of (potential) advantages [113, OSPAR 2007] [154, COM 2016]:

- Toxicity tests allow for an integrated assessment of the potential environmental impact of a waste water stream (including synergistic/antagonistic effects of compounds) that cannot be achieved by analysing single substances or other chemical sum parameters.
- The test results reflect the effect of all compounds present in the waste water, regardless of their origin and nature (e.g. including side products and metabolites). The compounds do not necessarily need to be identified.
- The sources of hazardous effluents (production steps or hot spots) inside industrial areas can often be identified by backtracking, provided that unknown combined or synergistic effects of pollutants are negligible.
- Toxicity tests might be quicker and less expensive than the quantification of (several) single substances with toxic properties.

Toxicity tests are particularly useful in the case of effluents that contain complex mixtures of known and unknown substances and where the industrial activities potentially lead to emissions of toxic substances [113, OSPAR 2007].

Toxicity tests are frequently used in permits in at least five EU Member States:

- In Austria, ELVs are set in a number of industry sectors. Up to four toxicity tests are used in combination (fish, daphnia, algae, and luminescent bacteria), e.g. for some effluents from the chemical industry [170, AT 2015].
- Germany has mandatory ELVs in several industry sectors. The most comprehensive set of toxicity tests has been in use for effluents from the chemical industry since 1999. It

covers five trophic levels (i.e. fish eggs, daphnia, algae, luminescent bacteria, and genotoxicity). Toxicity tests with fish date back to the late 1980s [29, DE 2014].

- In Ireland, ELVs are set for discharges that are deemed non-simple (complex). Toxicity tests have been used in permits since 1993. An initial screening is carried out for at least four aquatic species from different trophic levels (i.e. fish, crustacean, algae, and luminescent bacteria) and subsequent compliance monitoring for the two most sensitive species [171, Enterprise Ireland 2012].
- Italy has obligatory acute toxicity tests for discharges to surface water and sewers (e.g. for daphnia, algae or luminescent bacteria). The legal consequences of exceeding an ELV are, however, less stringent than for other parameters [172, IT 2006].
- Lithuania requires effluents entering surface waters to pass acute daphnia tests [117, COHIBA 2010].

Furthermore, other EU Member States sometimes use toxicity tests in permits: Belgium (Flanders), Denmark, Finland and Sweden [117, COHIBA 2010], [154, COM 2016].

Toxicity tests can also be used to assess the impact of waste water streams on biological waste water treatment plants, but the tests/organisms used for that purpose are usually different from those used for final effluents (e.g. the inhibition of activated sludge is measured [174, CEN 2007], [175, CEN 2006]).

When using test organisms falling under the scope of Directive 2010/63/EU on the protection of animals used for scientific purposes (e.g. live non-human vertebrate animals including independently feeding larval forms), adherence to the 'Three R' principle (replacement, reduction, refinement) has to be ensured [114, EU 2010].

5.5.1.2 EN standards

A large number of EN, ISO, and national standards for **waste water** toxicity tests are available (see Annex A.2) [121, CEN 2016], [122, ISO 2016]. The OECD also provides in its 'OECD Guidelines for the Testing of Chemicals' tests to assess the effects of **single substances** on biotic systems, including toxicity tests [118, OECD 2013].

Table 5.5 lists EN standards for toxicity tests following an ascending order of the trophic levels.

Table 5.5: EN standards for toxicity tests

Standard	Title
EN ISO 5667-16:2017	Water quality - Sampling - Part 16: Guidance on biotesting of samples (ISO 5667-16:2017)
EN ISO 21427-2:2009	Water quality - Evaluation of genotoxicity by measurement of the induction of micronuclei - Part 2: Mixed population method using the cell line V79 (ISO 21427-2:2006)
EN ISO 11348:2008, Parts 1 to 3	Water quality - Determination of the inhibitory effect of water samples on the light emission of *Vibrio fischeri* (Luminescent bacteria test) Part 1: Method using freshly prepared bacteria (ISO 11348-1:2007) Part 2: Method using liquid-dried bacteria (ISO 11348-2:2007) Part 3: Method using freeze-dried bacteria (ISO 11348-3:2007)
EN ISO 10712:1995	Water quality - *Pseudomonas putida* growth inhibition test (pseudomonas cell multiplication inhibition test) (ISO 10712:1995)
EN ISO 8692:2012	Water quality - Fresh water algal growth inhibition test with unicellular green algae (ISO 8692:2012)
EN ISO 10253:2016	Water quality - Marine algal growth inhibition test with *Skeletonema sp.* and *Phaeodactylum tricornutum* (ISO 10253:2016)
EN ISO 10710:2013	Water quality - Growth inhibition test with the marine and brackish water macroalga *Ceramium tenuicorne* (ISO 10710:2010)
EN ISO 20079:2006	Water quality - Determination of the toxic effect of water constituents and waste water on duckweed (*Lemna minor*) - Duckweed growth inhibition test (ISO 20079:2005)
EN ISO 6341:2012	Water quality - Determination of the inhibition of the mobility of *Daphnia magna* Straus (Cladocera, Crustacea) - Acute toxicity test (ISO 6341:2012)
EN ISO 15088:2008	Water quality - Determination of the acute toxicity of waste water to zebrafish eggs (*Danio rerio*) (ISO 15088:2007)
EN ISO 7346:1997, Parts 1 to 3	Water quality - Determination of the acute lethal toxicity of substances to a freshwater fish [*Brachydanio rerio* Hamilton-Buchanan (Teleostei, Cyprinidae)] Part 1: Static method (ISO 7346-1:1996) Part 2: Semi-static method (ISO 7346-2:1996) Part 3: Flow-through method (ISO 7346-3:1996)

EN ISO 5667-16:2017 describes special sampling and pretreatment provisions relevant for toxicity tests [150, CEN 2017].

EN ISO 21427-2:2009 specifies a method for the determination of **genotoxicity** of water and waste water using a mammalian in vitro test which detects damage, induced by water-soluble substances, to the chromosomes or the mitotic apparatus of V79 cells from the Chinese hamster. V79 cells are exposed for 24 hours (4 hours with the S9 mix) to a range of concentrations of a test sample. Thereafter, slides are prepared, and cells are stained and evaluated for the presence of micronucleated cells. An increased incidence of these micronucleated cells in comparison to the control samples indicates that the test item may cause chromosome breaks or spindle disorders in V79 cells in vitro [163, CEN 2009].

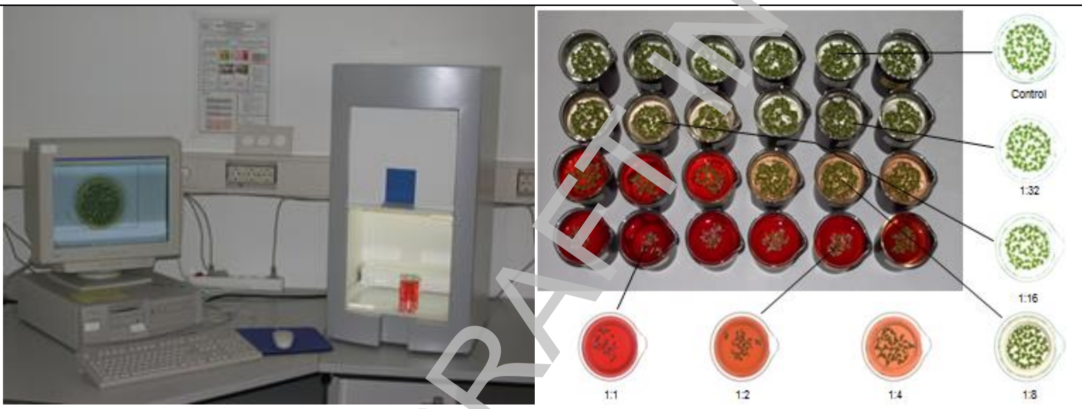
EN ISO 11348:2008, Parts 1 to 3 specify methods for the determination of the inhibitory effect of water samples on the light emission of a marine **bacterium** (luminescent bacteria test). Specified volumes of the (diluted) sample are mixed with the luminescent bacteria suspension in a test tube. The test criterion is the luminescence, measured after a defined contact time (i.e. 5, 15, or 30 minutes) taking into account a correction factor for the intensity changes of control samples during the exposure time. EN ISO 11348-1:2008 uses freshly prepared bacteria, EN ISO 11348-2:2008 liquid-dried bacteria, and EN ISO 11348-3:2008 freeze-dried bacteria [155, CEN 2008], [156, CEN 2008], [157, CEN 2008].

EN ISO 10712:1995 also uses a bacterium as a test organism, but for a growth inhibition test, measured via turbidity [158, CEN 1995].

EN ISO 8692:2012 and **EN ISO 10253:2016** specify growth inhibition tests with fresh water or marine **unicellular algae**. An inoculum of exponentially growing monospecies algal strains is cultured for several generations in defined media containing a range of concentrations of the test sample. Inhibition is measured over three days as a reduction in specific growth rate, relative to control cultures grown under identical conditions. The measurement is usually carried out with a particle counter, or with a microscope and a counting chamber [159, CEN 2012], [161, CEN 2016].

EN ISO 10710:2013 specifies a method for the determination of the growth inhibition of a marine and brackish water **macroalga**. Algal tips are grown under defined test conditions and in a defined medium containing a range of concentrations of the test sample. After seven days, the increase in length is measured and the inhibition of growth is determined as a reduction in growth rate, relative to control cultures grown under identical conditions [162, CEN 2013].

EN ISO 20079:2006 uses the duckweed species *Lemna minor* as a model organism for **higher plants** in fresh water. The standard specifies a method for the determination of the growth-inhibiting response of duckweed to substances and mixtures contained in waste water. The plants are allowed to grow as monocultures in different concentrations of the test sample over a period of seven days. To quantify substance-related effects, the growth rate in the test solutions is calculated from the observation parameters (frond number, frond area, chlorophyll, dry weight) and compared with that of the control samples (Figure 5.8) [164, CEN 2006].



NB: Left: example of a duckweed toxicity test analyser; right: duckweed samples after seven days of incubation at various dilution levels.

Source: [243, DE UBA 2016]

Figure 5.8: Duckweed toxicity test

EN ISO 6341:2012 uses the water flea *Daphnia magna* Straus, a crustacean representing a primary consumer, an **invertebrate**, and a major component of the zooplankton in aquatic ecosystems. The test specifies the determination of the immobilisation of the water flea after 24 hours or 48 hours of exposure to the test sample under specified conditions (Figure 5.9) [165, CEN 2012].

NB: Left: simple daphnia hatching equipment; right: *Daphnia magna* Straus.

Source: [243, DE UBA 2016]

Figure 5.9: Daphnia toxicity test

EN ISO 15088:2008 uses the eggs of the zebrafish (*Danio rerio* Hamilton-Buchanan, former *Brachydanio rerio*) as the test organism. The standard specifies a method for the determination of the degrees of dilution or of concentration, as a measure of the acute toxic effect of waste water to **fish eggs** within 48 hours. A microscope or binocular is used to determine the toxicological endpoint (i.e. egg coagulation, tail detachment, or heartbeat) (Figure 5.10). Fish, as high-order consumers, are a confirmed part within test concepts regarding aquatic organisms from different trophic levels. EN ISO 15088:2008 was developed as a substitute for the acute fish toxicity test. Applied to waste water, it gives the same or similar results as those achieved from the acute fish toxicity test according to EN ISO 7346, Part 1 or 2 [166, CEN 2008].

NB: Top: breeding of zebrafish in an aquarium; bottom: toxicological end points: left: coagulated egg, middle: no tail detachment, right: no heartbeat.

Source: [243, DE UBA 2016]

Figure 5.10: Zebrafish egg toxicity test

EN ISO 7346:1997, Parts 1 to 3 describe the determination of the acute lethal toxicity of substances under specified conditions to a fresh water **fish** (zebrafish *Danio rerio* Hamilton-Buchanan). The fish are exposed to the test substance by means of a serial dilution for a period of 96 hours. After 24, 48, 72, and 96 hours, the mortalities and the test conditions (temperature, pH, and oxygen content) are recorded. The LC_{50} (lethal concentration for 50 % of the test fish) is calculated from the concentration-effect relationship. EN ISO 7346-1:1997 describes a static method, EN ISO 7346-2:1997 a semi-static method, and EN ISO 7346-3:1997 a flow-through method [167, CEN 1997], [168, CEN 1997], [169, CEN 1997]. Even though the standards address single substances, they have also been used to assess the toxicity of waste water [166, CEN 2008]. In some Member States, fish tests are replaced by other methods for ethical reasons (e.g. by EN ISO 15088:2008).

5.5.1.3 Data treatment and reporting

The results of toxicity tests may be expressed in different ways, the most common being the following [117, COHIBA 2010]:

- **Effective concentration (EC_X):** The X in EC_X stands for the given percentage of the test organisms exhibiting the end point in question. The end point considered depends on the test. For example, an EC_{50} of 20 % means that 50 % of the test organisms were affected when the concentration was 20 %. The smaller the effective concentration, the more toxic the substance is. The EC values are point estimates and are based on concentration-response relationships. They can be determined statistically (concentration-response modelling) or graphically with at least five concentration-response data pairs and responses ranging from 0 to 100 %. On the basis of the EC data, error terms can be calculated, but, for moderately toxic samples, statistical requirements for the calculation of EC values are often not met. Lethal concentration (LC_X) and inhibition concentration (IC_X) follow the same logic.

  EC values are the most commonly used units for toxicity and all EN standards given in Annex A.2 use this unit.
  The EC_X methodology is usually applied to single substances, and results are expressed as concentration values (e.g. in mg/l). However, for a waste water sample, dilution series may also be used to determine EC_{50} values as percentages of waste water (see LID below).
- **No Observed Effect Concentration (NOEC):** NOEC is the highest concentration of the substance where no observable adverse effects are detected. NOECs are used in many countries, especially when determining chronic toxicity. NOEC is based on hypothesis testing and has been criticised for various reasons. First of all, it is an unsound idea to measure something that is not observable. Second, the selection of the concentration series can affect the NOEC values, which reduces their comparability. Third, error terms cannot be calculated on the basis of NOEC data.
- **Lowest Ineffective Dilution (LID):** The LID approach is used to measure the toxicity of the waste water by means of dilution series. The sample is diluted with defined ratios of dilution water until the defined effect is no longer observed. A statistical evaluation of the concentration-response relationship is not necessary, because a yes/no-type decision is made with regards to the defined effect level described in the respective standard (usually 10 % or 20 % effect in comparison to control samples).

  Procedures on how to calculate LID values are given in all the EN standards listed in Annex A.2.
  The LID value gives the ratio of the volume of the diluted sample in relation to the original sample; the higher the LID value, and therefore the necessary dilution, the higher the toxicity of the original sample.
- **Toxicity Unit (TU):** TUs represent the result of different calculations based on some of the units mentioned above. The rationale for the use of TUs is that they are easier to

comprehend than EC values for the whole effluent: the higher the TU, the more toxic the effluent. There are separate TUs for acute and chronic toxicity: acute toxicity TU_A = $100/EC_{50}$ and chronic toxicity TU_C = 100/NOEC. However, other definitions for TU are also used (e.g. $TU_C = EC_{10}$ [113, OSPAR 2007]), which makes the comparison between TUs difficult.

Given the importance of data treatment and statistical analyses, it is good practice to include their description in the measurement report (see Section 5.3.7).

5.5.2 Whole effluent assessment

In addition to testing the toxicity, whole effluent assessment (WEA) also aims at estimating the persistence (degradability) and bioaccumulation potential. By applying the so-called PBT criteria (**P**ersistence, **B**ioaccumulation, and **T**oxicity), the possible hazardous character of effluents is assessed, which could otherwise be insufficiently controlled when relying only on physico-chemical waste water parameters [115, OSPAR 2005].

WEA refers to persistence, but actually biodegradability is measured. In the case of biologically treated waste water, biodegradability tests give information on whether the treatment is adequate. In the case of untreated waste water, such tests indicate whether biological treatment should be considered. If biodegradability tests are followed by toxicity tests, an indication of the potential for the reduction of toxicity can be given. Biodegradability can for example be quantified by measurements of dissolved organic carbon (DOC) reduction or CO_2 evolution [115, OSPAR 2005]. Several EN and ISO standards are available [121, CEN 2016], [122, ISO 2016]. CEN ISO/TR 15462:2009 provides guidance on the selection of tests for biodegradability [176, CEN 2009].

Bioaccumulation is measured (both before and after biodegradation) by directly extracting the sample with a solid phase polymer (Solid Phase Micro Extraction, SPME), or alternatively by liquid/liquid extraction. Quantification is carried out by gas or liquid chromatography [115, OSPAR 2005].

The toxicity in WEA is measured with standard toxicity tests (see Section 5.5.1). Additionally, genotoxicity and endocrine disruption may be studied using WEA protocols, but, so far, these are less common [115, OSPAR 2005].

The advantages of WEA are basically the same as those of toxicity tests, namely an integrated assessment of the potential environmental impact of the effluent, the consideration of all compounds present in the effluent, the potential to identify sources of pollution, and the potential reduction of analytical efforts and costs (see Section 5.5.1.1).

Similarly to toxicity tests, WEA is particularly useful in the case of effluents that contain complex mixtures of known and unknown substances [113, OSPAR 2007].

However, the application of WEA presents some difficulties, including the following:

- No EN or ISO standards for persistence were available in 2016 [121, CEN 2016] [122, ISO 2016].
- It might be difficult to find competent laboratories to routinely run WEA tests. The availability of the laboratory may also be an issue, because the effluent samples refrigerated for 24 hours must be tested as soon as they arrive at the laboratory [116, TOTAL 2009].

Examples of the application of WEA or toxicity tests, if applied alone, include the following:

- ranking the environmental risk of waste water discharges;
- toxicity identification/reduction evaluations;
- prioritisation of waste water treatment techniques;
- judging effectiveness of treatment improvements;
- identifying sources for effects observed in receiving water bodies.

5.5.3 Drawing up or review of BREFs

Toxicity tests represent a valuable tool for the assessment of the potential environmental impacts of waste water discharges, in particular in the case of complex effluents. If sufficient data are available, they can also provide the basis for the design and operation of techniques to control pollution and to assess their performance. BAT and BAT-AEPLs normally address specific substances and sum parameters. In specific industrial sectors, in particular where complex waste water effluents can be expected and where the sole analysis of specific substances or sum parameters is insufficient to control pollution, it may be appropriate to derive BAT and BAT-AEPLs for toxicity, and potentially also for WEA. In 2005, OSPAR argued that, as the complexity of substances in effluents was increasing and the methods for assessing the effects were improving at the same time, it seemed obvious that WEA parameters would be used regularly for the benchmarking of BAT performance [115, OSPAR 2005].

In 2016, a number of BREFs addressed toxicity tests and WEA, including the following:

- BREF for Common Waste Water and Waste Gas Treatment/Management Systems in the Chemical Sector (CWW BREF): The BREF describes toxicity tests and WEA in detail. Furthermore, toxicity data from several installations are included. The BAT conclusions stipulate that it is BAT to use an appropriate combination of toxicity tests on different trophic levels (i.e. fish eggs, daphnia, duckweed, algae, luminescent bacteria) to monitor emissions to water. The monitoring frequency is to be decided based on a risk assessment, after an initial characterisation. No BAT-AEPLs are set for toxicity [154, COM 2016].
- BREF for the Manufacture of Organic Fine Chemicals (OFC BREF): The adopted BREF from 2006 describes techniques to reduce the toxicity of aqueous effluents and contains toxicity data from several installations. The BAT chapter stipulates that it is BAT to carry out regular toxicity tests of the total effluent after the biological waste water treatment plant if substances with ecotoxicological potential are handled or produced intentionally or by accident. Moreover, it is BAT to use on-line toxicity tests with on-line TOC measurements if residual acute toxicity is identified as a concern. BAT-AELs after the biological waste water treatment are set and expressed as LID values for fish, daphnia, algae, luminescent bacteria, and genotoxicity [119, COM 2006].
- BREF for the Production of Pulp, Paper, and Board (PP BREF): The revised BREF from 2015 mentions that toxicity tests have been used in the paper sector to characterise waste water (e.g. in Germany: toxicity to duckweed) and to set permit conditions (e.g. in Austria: toxicity to fish), due to the complexity of the effluents [160, COM 2015].
- BREFs for Industrial Cooling Systems (ICS BREF) [178, COM 2001], Iron and Steel Production (IS BREF) [142, COM 2013], and Large Volume Organic Chemical Industry (LVOC BREF) [177, COM 2017]: Data on toxicity were collected for some subsectors and are included in the related sections.
- BREF for the Tanning of Hides and Skins (TAN BREF): The revised BREF from 2013 contains a recommendation that the exchange of information on toxicity and WEA would be beneficial for the next review of the BREF and for all regulatory authorities [179, COM 2013].

The collection and analysis of toxicity data for the definition of BAT and BAT-AEPLs requires some specific considerations in addition to those of physico-chemical measurements (see Section 5.3.8). These include the following:

- The data treatment influences the final result (see Section 5.5.1.3).
- Inorganic ions above certain concentrations show toxic effects, depending on the organism (e.g. chloride and sulphate) [29, DE 2014]. This effect needs to be considered if the aim is to address the toxicity of organic compounds.

5.6 Costs

Qualitative information on the costs of monitoring emissions to water is given in several sections of this chapter, for example in relation to different monitoring regimes (see Sections 5.3.2 and 5.3.3) and different sampling frequencies (see Section 5.3.5.6). However, no cost data were provided during the drawing up of this document. Therefore, quantitative information cannot be provided for sampling or analysis.

Some very general information is available in a report provided by CONCAWE, which serves as guidance for their members on analytical methods that could be used to monitor oil refinery effluents. In this report, a method assessment programme is presented, whereby the performance of analytical methods can be compared and prioritised in order of their analytical performance capabilities and their overall quality. The report also takes into account indicative costs, placing them in one of three categories, based on sample preparation, pretreatment and analysis. Usually, the more complex the analysis, the higher the costs and the ranking score. The determination of almost all water parameters is categorised as 'high cost', including of sum parameters such as COD, TOC, and AOX [120, CONCAWE 2013].

6 CONCLUDING REMARKS AND RECOMMENDATIONS FOR FUTURE WORK

Timing of the drafting process

The key milestones of the drafting process for this document are summarised in Table 6.1.

Table 6.1: Key milestones of the drafting process for the JRC Reference Report on Monitoring of emissions to air and water from IED installations (ROM)

Key milestone	Date
Reactivation of the TWG for the review of the MON REF	22 December 2009
Call for wishes	7 April 2010
Discussion on the work programme and the MON REF at the IED Article 13 forum	12-13 September 2011
Decision of the European Commission to draft a JRC Reference Report on Monitoring (ROM) and conversion of the TWG to the MEG	12 March 2012
Draft structure	9 April 2012
End of commenting period on structure (97 comments)	25 April 2012
Draft scope	21 June 2012
End of commenting period on scope (14 comments)	13 July 2012
Draft chapter on general aspects of monitoring	13 February 2013
End of commenting period on generic chapter (126 comments received)	8 March 2013
Draft chapter on emissions to air	15 May 2013
End of commenting period on air chapter (363 comments received)	14 June 2013
Draft chapter on emissions to water	1 August 2013
End of commenting period on water chapter (123 comments received)	13 September 2013
Final draft	24 October 2013
End of commenting period on final draft (377 comments received)	15 November 2013
First working document after final draft	16 February 2015
Second working document after final draft	23 July 2015
Third working document after final draft	22 July 2016
Revised final draft	05 June 2017

Sources of information

The ROM summarises general and commonly available information collected by the European IPPC Bureau from various sources, such as international and national standards, as well as scientific publications. Some Member States also provided special contributions summarising their monitoring practices. Altogether, more than 240 references are included in the ROM. All the information gathered was made available to the MEG, unless protected by copyright law.

Furthermore, the Technical Committees CEN/TC 230 'Water analysis' and CEN/TC 264 'Air quality' of the European Committee for Standardization provided information to draft the Annexes on standards for the measurement of emissions to air (A.1) and water (A.2), respectively. Information for Annex A.5 'Monitoring costs of emissions to air' was provided by the Source Testing Association of the United Kingdom.

Recommendations for future work

The current document only covers the monitoring of emissions to air and to water. Monitoring is also of interest for other environmental issues, such as noise, emissions to soil and groundwater, waste generation, and energy efficiency. This may warrant further information gathering and an expansion of the ROM scope in the future.

Another idea is to add information on analytical methods for further pollutants/parameters (e.g. for those for which BAT-AEPLs have been set in BAT conclusions).

7 ANNEXES

A.1. Standards and methods for the measurement of emissions to air

Table 7.1: Specific standards for the periodic measurement of emissions to air

Parameter/ Substance(s) (1)	EN or ISO standard (1)	Monitoring methods	Measurement ranges and/or measurement limits (2)	Remarks
Ammonia (NH_3)	No EN or ISO standard available	NA	NA	Several national/industry standards are available, e.g. IS 11255- 6; NF X43-303; SCAQMD 207.1; UNICHIM 632; US EPA CTM-027; VDI 3878
Carbon monoxide (CO)	EN 15058:2017	Extraction, filtration and conditioning followed by non-dispersive infrared spectrometry	Up to 400 mg/m^3 at large combustion plants (sampling duration of 30 min); Up to 740 mg/m^3 at waste (co-)incineration plants (sampling duration of 30 min)	—
Dinitrogen monoxide (N_2O)	EN ISO 21258:2010	Extraction, filtration and conditioning followed by non-dispersive infrared spectrometry	Up to 200 mg/m^3 (3)	—
Dust	EN 13284-1:2001	Extraction and filtration followed by gravimetry	Up to 50 mg/m^3, measurements typically at 5 mg/m^3; LoD: ~ 0.3 mg/m^3 (dry gases, sampling duration of 30 min), ~ 2 mg/m^3 (vapour-saturated gases, sampling duration of 30 min) (3)	—
Flow rate	EN ISO 16911-1:2013	- Differential pressure (Pitot tube) - Vane anemometer - Tracer dilution - Tracer transit time - Calculation from energy consumption	NS	CEN/TR 17078:2017 provides guidance on the application of EN ISO 16911-1:2013
Formaldehyde (CH_2O)	No EN or ISO standard available	NA	NA	Several national/industry standards are available, e.g. CARB M 430; FD X43-319; NCASI CI/WP-98.01; US EPA M 0011 and M 316; VDI 3862-2 and -6

Parameter/ Substance(s) (1)	EN or ISO standard (1)	Monitoring methods	Measurement ranges and/or measurement limits (2)	Remarks
Gaseous chlorides	EN 1911:2010	Extraction and filtration, followed by absorption in water with subsequent silver potentiometric titration (method A), mercuric-thiocyanate spectrophotometry (method B), or ion chromatography (method C)	1 mg/m^3 to 5 000 mg/m^3 (3); LoD: ~ 0.2 mg/m^3 (sample gas volume of 0.4–0.5 m^3, sampling duration of 2 h, method A) For water analysis: - Method A: LoD: 0.5–1 mg/l - Methods B and C: LoD: 0.05–0.1 mg/l	—
Gaseous fluorides	ISO 15713:2006	Extraction and filtration, followed by absorption in liquid phase with subsequent use of an ion-selective electrode	Up to 200 mg/m^3; LoD: ~ 0.1 mg/m^3 (sample gas volume of 0.1 m^3)	—
Gaseous organic compounds	No EN or ISO standard available	NA	NA	CEN/TS 13649:2014 describes the determination of the mass concentration of individual gaseous organic compounds
Mercury (Hg)	EN 13211:2001	Extraction and filtration followed by absorption in liquid phase (solution of $KMnO_4/H_2SO_4$ or $K_2Cr_2O_7/HNO_3$); subsequent digestion of the filter; final analysis of the aqueous samples by AAS	1 $\mu g/m^3$ to 500 $\mu g/m^3$ (3); LoD: 2.6 $\mu g/m^3$ (sample gas volume of 0.05 m^3)	AC:2005 (Technical corrigendum)
Metals (As, Cd, Tl, Sb, Pb, Cr, Co, Cu, Mn, Ni, V)	EN 14385:2004	Extraction and filtration followed by absorption in liquid phase (solution of H_2O_2/HNO_3); subsequent digestion of the filter; final analysis of the aqueous samples by AAS, ICP-OES or ICP-MS	5 $\mu g/m^3$ to 500 $\mu g/m^3$ (for each element) (3); Required LoD: ≤ 1 $\mu g/m^3$ for each element and sampling train; Resulting LoD: 5 $\mu g/m^3$ for the whole sampling train	—
Methane (CH_4)	EN ISO 25139:2011	Extraction, filtration and conditioning followed by gas chromatography with flame ionisation detection	Up to 1 500 mg/m^3	—
Nitrogen oxides (NO_X)	EN 14792:2017	Extraction, filtration and conditioning followed by chemiluminescence (after conversion to NO and reaction with ozone)	Up to 1 300 mg/m^3 at large combustion plants; Up to 400 mg/m^3 at waste (co-)incineration plants	—
Odour	EN 13725:2003	Dynamic olfactometry	Measurements typically from 10^1 ou_E/m^3 to 10^7 ou_E/m^3 (including predilution); Detection threshold: 1 ou_E/m^3	AC:2006 (Technical corrigendum)
Oxygen (O_2)	EN 14789:2017	Extraction, filtration and conditioning followed by paramagnetism	3 vol-% to 21 vol-% (sampling duration of 30 min) (3) (4) (5)	—
$PM_{10}/PM_{2.5}$	EN ISO 23210:2009	Impactors followed by gravimetry	LoD: PM_{10}: 0.4 mg/m^3 (sample gas volume: 1 m^3, sampling duration of ~ 30 min) LoD: $PM_{2.5}$: 0.3 mg/m^3 (sample gas volume: 1 m^3, sampling duration of ~ 30 min)	—

Parameter/ Substance(s) (1)	EN or ISO standard (1)	Monitoring methods	Measurement ranges and/or measurement limits (2)	Remarks
Dioxin-like PCBs	EN 1948-4:2010	Sampling according to EN 1948-1, followed by extraction and clean-up according to EN 1948-2 and subsequent identification and quantification using isotope dilution gas chromatography with mass spectrometry	LoD: 0.11–0.57 pg WHO-TEQ/m^3, LoQ: 0.20–1.37 pg WHO-TEQ/m^3 (depending on sampling method) (3)	A1:2013 (Amendment 1)
PCDDs/PCDFs	EN 1948-1:2006 EN 1948-2:2006 EN 1948-3:2006	EN 1948-1: Sampling by filter/condenser method, dilution method, or cooled probe method EN 1948-2: Extraction and clean-up EN 1948-3: Identification and quantification using isotope dilution gas chromatography with mass spectrometry	Measurements typically at 0.1 ng I-TEQ/m^3; LoQ: 0.1–8.8 pg/m^3 for individual congeners (3) (corresponds to a LoQ of 1.2–3.7 pg I-TEQ/m^3)	CEN/TS 1948-5:2015 describes the long-term sampling of PCDDs/PCDFs and PCBs
Polycyclic aromatic hydrocarbons (PAHs)	ISO 11338-1:2003 ISO 11338-2:2003	ISO 11338-1: Sampling by the dilution method, the heated filter/condenser/adsorber method, or the cooled probe/adsorber method ISO 11338-2: Sample preparation, clean-up and determination by high-performance liquid chromatography (HPLC) or gas chromatography mass spectrometry (GC-MS)	NI	—
Sulphur oxides (SO_X)	EN 14791:2017	Extraction and filtration followed by absorption in aqueous H_2O_2 solution with subsequent sulphate determination via ion chromatography or titration	- Ion chromatography: 0.5 mg/m^3 to 2 000 mg/m^3 (sampling duration of 30 min) (3) (4); LoQ: ≥ 0.1 mg/m^3 (flow rate of 1 l/min, 100 ml of absorption solution, sampling duration of 30 min) - Titration: 5 mg/m^3 to 2 000 mg/m^3 (sampling duration of 30 min) (3) (4); LoQ ≥ 2.2 mg/m^3 (flow rate of 1 l/min, 100 ml of absorption solution, sampling duration of 30 min)	—
Temperature	No EN or ISO standard available	NA	NA	—
Total volatile organic carbon (TVOC)	EN 12619:2013	Extraction and filtration followed by flame ionisation detection	Up to 1 000 mg/m^3	—
	EN ISO 13199:2012	Extraction and filtration followed by catalytic conversion and NDIR	From about 70 mg/m^3 to 600 mg/m^3	Not applicable to combustion processes
Water vapour	EN 14790:2017	- Extraction and filtration followed by adsorption or condensation/adsorption with subsequent gravimetry - Temperature method for vapour-saturated gases	4 vol-% to 40 vol-%	—

Parameter/ Substance(s) (1)	EN or ISO standard (1)	Monitoring methods	Measurement ranges and/or measurement limits (2)	Remarks

(1) Non-exhaustive list.
(2) Under standard conditions, i.e. dry gas, 273.15 K, 101.3 kPa, at the reference O_2 concentration.
(3) Validated during field trials at waste (co-)incineration plants.
(4) Validated during field trials at large combustion plants.
(5) Validated on a recognised test bench.

NB: AAS = atomic absorption spectrometry; GC-MS = gas chromatography mass spectrometry; HPLC = high-performance liquid chromatography; ICP-OES = inductively coupled plasma optical emission spectrometry; ICP-MS = inductively coupled plasma mass spectrometry; I-TEQ = international toxic equivalent; LoD = limit of detection; LoQ = limit of quantification; NA = not applicable; NDIR = non-dispersive infrared spectrometry; NI = no information provided; NS = not specified.

Source: [59, CEN 2016], [112, ISO 2016]

Table 7.2: Methods of certified AMS for emissions to air

Parameter/ Substance(s)	Monitoring methods	Certified measurement ranges and measurement limits (1) (2) (3)	Certification and calibration standards	EN or ISO standard for SRM
Ammonia (NH_3)	FTIR, NDIR with GFC, TDL	Lowest range: ≤ 0.8 mg/m^3 (LoQ req.) to 10 mg/m^3 Highest range: up to 500 mg/m^3	Generic standards (4)	No EN or ISO standard available
Carbon monoxide (CO)	FTIR, NDIR	Lowest range: ≤ 2.5 mg/m^3 (LoQ req.) to 31 mg/m^3 Highest range: up to 4.4 g/m^3	Generic standards (4)	EN 15058:2017
Dinitrogen monoxide (N_2O)	FTIR, NDIR	Lowest range: ≤ 1.6 mg/m^3 (LoQ req.) to 20 mg/m^3 Highest range: up to 9.8 g/m^3	Generic standards (4)	EN ISO 21258:2010
Dust	Light attenuation or scattering, triboelectric	Lowest range: ≤ 0.24 mg/m^3 (LoQ req.) to 3 mg/m^3 Highest range: up to 200 mg/m^3	Generic standards (4) and EN 13284-2:2004	EN 13284-1:2001
Flow rate	Ultrasound, differential pressure (Pitot tube), IR cross-correlation of turbulence, thermal mass flow	Lowest range: ≤ 0.96 m/s (LoQ req.) to 12 m/s Highest range: up to 60 m/s	Generic standards (4) and EN ISO 16911-2:2013	EN ISO 16911-1:2013
Hydrogen chloride (HCl)	FTIR, NDIR with GFC, TDL	Lowest range: ≤ 0.8 mg/m^3 (LoQ req.) to 10 mg/m^3 Highest range: up to 5.0 g/m^3	Generic standards (4)	EN 1911:2010
Hydrogen fluoride (HF)	FTIR, TDL	Lowest range: ≤ 0.08 mg/m^3 (LoQ req.) to 1 mg/m^3 Highest range: up to 50 mg/m^3	Generic standards (4)	ISO 15713:2006
Methane (CH_4)	FID, FTIR, NDIR	Lowest range: ≤ 0.8 mg/m^3 (LoQ req.) to 10 mg/m^3 Highest range: up to 500 mg/m^3	Generic standards (4) and EN ISO 25140:2010	EN ISO 25139:2011
Mercury (Hg)	AAS, DOAS	Lowest range: ≤ 0.8 µg/m^3 (LoQ req.) to 10 µg/m^3 (5) Highest range: up to 1 mg/m^3	Generic standards (4) and EN 14884:2005	EN 13211:2001
Nitrogen oxides (NO_X) (6)	Chemiluminescence, FTIR, NDIR, NDUV, DOAS	Lowest range: ≤ 1.6 mg/m^3 (LoQ req.) to 20 mg/m^3 Highest range: up to 7.5 g/m^3	Generic standards (4)	EN 14792:2017
Oxygen (O_2)	Paramagnetism, electrochemical cell, zirconia (ZrO_2)	Lowest range: ≤ 0.8 vol-% (LoQ req.) to 5 vol-% Highest range: up to 25 vol-%	Generic standards (4)	EN 14789:2017
Sulphur dioxide (SO_2)	FTIR, NDIR, NDUV, DOAS	Lowest range: ≤ 0.8 mg/m^3 (LoQ req.) to 10 mg/m^3	Generic standards (4)	EN 14791:2017

Parameter/ Substance(s)	Monitoring methods	Certified measurement ranges and measurement limits (1) (2) (3)	Certification and calibration standards	EN or ISO standard for SRM
		Highest range: up to 8.0 g/m^3		
Temperature	Thermocouples, pyrometry	400 °C to 1 300 °C (one certified AMS)	Generic standards (4)	No specific EN or ISO standard for measurements in air available
Total volatile organic carbon (TVOC)	FID	Lowest range: ≤ 1.2 mg/m^3 (LoQ req.) to 15 mg/m^3 Highest range: up to 2.0 g/m^3	Generic standards (4)	EN 12619:2013
Water vapour	FTIR, NDIR with GFC, TDL	Lowest range: ≤ 2 vol-% (LoQ req.) to 25 vol-% Highest range: up to 50 vol-%	Generic standards (4)	EN 14790:2017

(1) The certification process is described in Section 4.3.2.2.1.

(2) Under standard conditions, i.e. dry gas, 273.15 K, 101.3 kPa, at the reference O_2 concentration.

(3) LoQs are specified as performance criteria and are derived from four times the performance criterion for the repeatability standard deviation (RSD) at zero in laboratory tests according to EN 15267-3:2007. For the flow rate, particulate matter, and gaseous compounds except oxygen, the performance criterion for RSD is ≤ 2.0 % of the upper limit of the certification range. For oxygen, the performance criterion for the RSD is ≤ 0.20 vol-%. For the flow rate, the RSD applies at the lower reference point (instead of applying at zero). Actual LoQs may be (much) lower than the required performance.

(4) EN15267-1:2009, EN15267-2:2009, EN15267-3:2007, and EN 14181:2014.

(5) In 2016, this measurement range was certified for one AMS. The other AMS showed ranges of ≤ 3.2 µg/m^3 (LoQ req.) to 30 µg/m^3 or of ≤ 6 µg/m^3 (LoQ req.) to 75 µg/m^3.

(6) AMS for measuring NO and NO_2 separately are also available.

NB: AAS = atomic absorption spectrometry; DOAS = differential optical absorption spectroscopy; FID = flame ionisation detection; FTIR = Fourier transform infrared spectrometry; GFC = gas filter correlation; LoQ = limit of quantification; NDIR = non-dispersive infrared spectrometry; NDUV = non-dispersive UV spectrometry; req. = requirement; SRM = standard reference method; TDL = tunable diode laser absorption spectrometry.

Source: [59, CEN 2016], [104, MCERTS 2017], [112, ISO 2016], [129, DE UBA and TÜV 2016]

A.2. Standards for the measurement of emissions to water

Table 7.3: Specific standards for the measurement of emissions to water

Parameter/ Substance(s) (1)	EN or ISO standard (1)	Monitoring frequency	Monitoring methods	Measurement ranges and/or measurement limits (2)	Remarks
Adsorbable organically bound halogens (AOX)	EN ISO 9562:2004	Periodic	Determination of organically bound chlorine, bromine and iodine (expressed as chloride) adsorbable on activated carbon	10 µg/l to 300 µg/l	—
Ammonium	ISO 15923-1:2013	Periodic	Discrete analysis system with spectrophotometric and turbidimetric detection	NI	—
Ammonium nitrogen (NH_4-N)	EN ISO 11732:2005	Periodic	Flow analysis (FIA and CFA) and spectrophotometric detection	0.1 to 10 mg/l	—
	ISO 5664:1984	Periodic	Distillation and titration	Up to 10 mg in the test portion	
	ISO 6778:1984	Periodic	Potentiometric method using an ammonia-sensing membrane probe	~ 0.2 mg/l (LoD) to 50 mg/l	
	ISO 7150-1:1984	Periodic	Manual spectrophotometry	Up to 1 mg/l using the maximum test portion of 40 ml	
Anions	EN ISO 10304-1:2009	Periodic	Ion chromatography: bromide, chloride, fluoride, nitrate, nitrite, orthophosphate and sulphate	LLoA: Br^-, NO_2^-: ≥ 0.05 mg/l Cl^-, F^-, NO_3^-, PO_4^{3-}, SO_4^{2-}: ≥ 0.1 mg/l (for Br^-, NO_2^-, and NO_3^-, the LLoA may be reduced by using a special pretreatment and/or a UV detector)	AC:2012 (Technical corrigendum)
	EN ISO 10304-3:1997	Periodic	Ion chromatography: chromate, iodide, sulphite, thiocyanate and thiosulfate	≥ 0.05 mg/l to 50 mg/l (depending on the ion and the detector)	—
	EN ISO 10304-4:1999	Periodic	Ion chromatography: chlorate, chloride and chlorite	≥ 0.01 mg/l to 50 mg/l (depending on the ion and the detector)	—
	ISO 15923-1:2013	Periodic	Discrete analysis system with spectrophotometric and turbidimetric detection: chloride, nitrate, nitrite, orthophosphate, silicate and sulphate	NI	—
Biochemical oxygen demand (BOD_n)	EN 1899-1:1998 ISO 5815-1:2003	Periodic	Dilution and seeding method with allylthiourea addition	3 mg/l (LoQ) to 6 000 mg/l	In Europe, EN 1899-1 is applied
	EN 1899-2:1998 ISO 5815-2:2003	Periodic	Method for undiluted samples	0.5 mg/l (LoQ) to 6 mg/l	In Europe, EN 1899-2 is applied

Parameter/ Substance(s) (1)	EN or ISO standard (1)	Monitoring frequency	Monitoring methods	Measurement ranges and/or measurement limits (2)	Remarks
Cations	EN ISO 14911:1999	Periodic	Ion chromatography: ammonium, barium, calcium, lithium, magnesium, manganese, potassium, sodium, and strontium	Li^+: 0.01 mg/l to 1 mg/l Na^+, NH_4^+, K^+: 0.1 mg/l to 10 mg/l Ca^{2+}, Mg^{2+}, Mn^{2+}, Sr^{2+}: 0.5 mg/l to 50 mg/l Ba^{2+}: 1 mg/l to 100 mg/l (lower measurement ranges possible with larger sample injection)	—
Chemical oxygen demand (COD)	ISO 15705:2002	Periodic	Oxidation with dichromate via small-scale sealed-tube method followed by: a) spectrophotometric detection b) titrimetric detection	a) 6 mg/l (LoD) to 1 000 mg/l b) 15 mg/l (LoD) to 1 000 mg/l	No EN standard; several Member States use national standards for regulatory purposes (e.g. DIN 38409-41 in DE, SFS 5504 in FI, NF T90-101 in FR, APAT 5130 in IT or NEN 6633 in NL)
	ISO 6060:1989	Periodic	Oxidation with dichromate via open reflux method followed by titration	30 mg/l to 700 mg/l	
Chlorine	EN ISO 7393-1:2000	Periodic	Titrimetric method using *N*,*N*-diethyl-1.4-phenylenediamine	0.03 mg/l to 5 mg/l	—
	EN ISO 7393-2:2000	Periodic	Colorimetric method using *N*,*N*-diethyl-1, 4-phenylenediamine, for routine control purposes	0.03 mg/l to 5 mg/l	—
	EN ISO 7393-3:2000	Periodic	Iodometric titration	0.71 mg/l to 15 mg/l	—
Chloride	EN ISO 15682:2001	Periodic	Flow analysis (CFA and FIA) and spectrophotometric or potentiometric detection	1 mg/l to 1 000 mg/l	—
	ISO 9297:1989	Periodic	Silver nitrate titration with chromate indicator (Mohr)	5 mg/l to 150 mg/l	—
Chromium(VI)	EN ISO 23913:2009	Periodic	Flow analysis (FIA and CFA) and spectrophotometric detection	FIA: 20 µg/l to 2000 µg/l CFA: 2 µg/l to 200 µg/l	—
	EN ISO 18412:2006	Periodic	Spectrophotometric method using 1,5-diphenylcarbazide	2 µg/l to 50 µg/l	For weakly contaminated water
	ISO 11083:1994	Periodic	Spectrophotometric method using 1,5-diphenylcarbazide	NI	—
Conductivity	EN 27888:1993 ISO 7888:1985	Continuous/periodic	Measurement of electrical conductivity	NS	In Europe, EN 27888 is applied

Parameter/ Substance(s) ([1])	EN or ISO standard ([1])	Monitoring frequency	Monitoring methods	Measurement ranges and/or measurement limits ([2])	Remarks
Cyanide	EN ISO 14403-1:2012	Periodic	Total cyanide: FIA with in-line UV digestion, distillation/gas diffusion at pH 3.8 and spectrophotometric detection Free cyanide: FIA with distillation/gas diffusion at pH 3.8 and spectrophotometric detection	2 µg/l to 500 µg/l	—
	EN ISO 14403-2:2012	Periodic	Total cyanide: CFA with in-line UV digestion, distillation/gas diffusion at pH 3.8 and spectrophotometric detection Free cyanide: CFA with distillation/gas diffusion at pH 3.8 and spectrophotometric detection	2 µg/l to 500 µg/l	—
	ISO 6703-1:1984 ISO 6703-2:1984	Periodic	Part 1: Total cyanide Part 2: Easily liberatable cyanide Methods based on liberation of hydrogen cyanide under different conditions followed by absorption and: a) spectrophotometric detection using pyridine/barbituric acid b) titrimetric detection using the Tyndall effect c) titrimetric detection using an indicator	a) 2 to 25 µg (absolute) b) > 5 µg (absolute) c) > 50 µg (absolute)	—
	ISO 6703-3:1984	Periodic	Part 3: Cyanogen chloride	0.02 mg/l to 15 mg/l	—
	ISO 17690:2015	Periodic	Free cyanide (pH 6): FIA with gas diffusion and amperometric detection	5 µg/l to 500 µg/l	—
Extractable organically bound halogens (EOX)	No EN or ISO standard available	Periodic	Liquid-liquid extraction with non-polar solvent (e.g. hexane) followed by combustion in oxyhydrogen torch, absorption of combustion gases and argentometry	NA	Some Member States use national standards (e.g. OENORM M 6614 in AT, NEN 6402 in NL)
Flow rate	Several EN and ISO standards available	Continuous/periodic	Various	NA	In addition to EN and ISO standards, several Member States use national standards for regulatory purposes
Hydrocarbon oil index	EN ISO 9377-2:2000	Periodic	Solvent extraction and gas chromatography	LLoA: 0.1 mg/l	—

Parameter/ Substance(s) (1)	EN or ISO standard (1)	Monitoring frequency	Monitoring methods	Measurement ranges and/or measurement limits (2)	Remarks
Metals and metalloids	EN ISO 11885:2009	Periodic	Inductively coupled plasma optical emission spectrometry (ICP-OES)	LoQ: As: ~ 5 µg/l; Cd: ~ 0.2 µg/l; Cr: ~ 2 µg/l; Cu: ~ 2 µg/l; Ni: ~ 2 µg/l; Pb: ~ 5 µg/l; Zn: ~ 1 µg/l	—
	EN ISO 15586:2003	Periodic	Atomic absorption spectrometry (AAS) with graphite furnace	LoD: As: ~ 1 µg/l; Cd: ~ 0.1 µg/l; Cr: ~ 0.5 µg/l; Cu: ~ 0.5 µg/l; Ni: ~ 1 µg/l; Pb: ~ 1 µg/l; Zn: ~ 0.5 µg/l	—
	EN ISO 17294-2:2016	Periodic	Inductively coupled plasma mass spectrometry (ICP-MS)	LLoQ: As: ~ 0.1 µg/l; Cd: ~ 0.1 µg/l; Cr: ~ 0.1 µg/l; Cu: ~ 0.1 µg/l; Ni: ~ 0.1 µg/l; Pb: ~ 0.1 µg/l; Zn: ~ 1 µg/l	—
Mercury (Hg)	EN ISO 12846:2012	Periodic	Atomic absorption spectrometry (AAS)	With enrichment: 0.01 µg/l to 1 µg/l; LoQ 0.008 µg/l Without enrichment: LLoA: ~ 0.05 µg/l; LoQ: 0.024 µg/l	—
	EN ISO 17852:2008	Periodic	Atomic fluorescence spectrometry (AFS) without enrichment	~ 1 ng/l to 100 µg/l; LoQ: < 1 ng/l	—
	EN ISO 17294-2:2016	Periodic	Inductively coupled plasma mass spectrometry (ICP-MS)	LLoQ: ~ 0.05 µg/l	—
Nitrite nitrogen (NO_2-N)	EN 26777:1993 ISO 6777:1984	Periodic	Molecular absorption spectrometry	NI	—
Nitrite nitrogen (NO_2-N), nitrate nitrogen (NO_3-N)	EN ISO 13395:1996	Periodic	Flow analysis (FIA and CFA) and spectrophotometric detection	NO_2-N: 0.01 mg/l to 1 mg/l NO_3-N: 0.2 mg/l to 20 mg/l	—
Nitrate nitrogen (NO_3-N)	ISO 7890-3:1988	Periodic	Spectrophotometry using sulphosalicylic acid	LoD: 3 µg/l to 13 µg/l using cells with a path length of 40 mm and the maximum test portion of 25 ml	—
Orthophosphate (PO_4-P)	EN ISO 6878:2004	Periodic	Spectrophotometry using ammonium molybdate	0.005 mg/l to 0.8 mg/l	—
	EN ISO 15681-1:2004 EN ISO 15681-2:2004	Periodic	Flow analysis (FIA and CFA)	0.01 mg/l to 1.0 mg/l	—
Oxygen	EN ISO 5814:2012	Continuous/periodic	Determination by means of an electrochemical cell	1 % to 100 % oxygen saturation	—
	EN 25813:1992 ISO 5813:1992	Periodic	Iodometric titration (Winkler method)	0.2 mg/l to double saturation	In Europe, EN 25813 is applied
	ISO 17289:2014	Continuous/periodic	Determination with an optical sensor based on fluorescence quenching	~ 0.1/0.2 mg/l (LoD) to > 100 % (supersaturation)	—

Parameter/ Substance(s) (1)	EN or ISO standard (1)	Monitoring frequency	Monitoring methods	Measurement ranges and/or measurement limits (2)	Remarks
pH	EN ISO 10523:2012	Continuous/periodic	Measurement of the potential difference of an electrochemical cell	pH 2 to pH 12	—
Phenol index	EN ISO 14402:1999	Periodic	Flow analysis (FIA and CFA)	0.01 mg/l to 1.0 mg/l	—
	ISO 6439:1990	Periodic	Distillation followed by: a) reaction with 4-aminoantipyrine and spectrophotometry b) reaction with 4-aminoantipyrine followed by chloroform extraction and spectrophotometry	a) LLoA: 0.1 mg/l b) LLoA: ~ 0.002 mg/l to ~ 0.1 mg/l	—
Sulphide, dissolved	ISO 10530:1992	Periodic	Filtration, stripping, and absorption in zinc acetate solution followed by formation of methylene blue and spectrophotometric detection	0.04 mg/l to 1.5 mg/l	—
Sulphide, easily released	ISO 13358:1997	Periodic	Stripping at pH 4 and absorption in zinc acetate solution followed by formation of methylene blue and spectrophotometric detection	0.04 mg/l to 1.5 mg/l	—
Temperature	No specific EN or ISO standard for measurements in water available	Continuous/periodic	NA	NA	—
Total Kjeldahl nitrogen	EN 25663:1993 ISO 5663:1984	Periodic	Selenium-catalysed digestion with concentrated sulphuric acid followed by ammonia stripping and absorption with subsequent titration or spectrophotometric detection	LoD: 1 mg/l	In Europe, EN 25663 is applied
Total nitrogen (TN)	EN 12260:2003	Periodic	Total nitrogen bound (TN_b): Oxidation by catalytic combustion followed by determination of nitrogen oxides using chemiluminescence (after conversion to NO and reaction with ozone)	~ 1 mg/l to 200 mg/l; LoD: ~ 0.5 mg/l	—
	EN ISO 11905-1:1998	Periodic	Oxidation with peroxodisulphate followed by reduction of nitrate to nitrite on copperised cadmium and subsequent flow analysis with spectrophotometric detection	LoD: 0.02 mg/l	—
	ISO 29441:2010	Periodic	In-line UV digestion with subsequent flow analysis (CFA and FIA) and spectrophotometric detection	2 mg/l to 20 mg/l; (0.2 mg/l to 2 mg/l is possible)	—

Parameter/ Substance(s) (1)	EN or ISO standard (1)	Monitoring frequency	Monitoring methods	Measurement ranges and/or measurement limits (2)	Remarks
Total organic carbon (TOC)	EN 1484:1997 ISO 8245:1999	Periodic	Oxidation of organic carbon by combustion, by addition of oxidants, by UV radiation or by any other high-energy radiation followed by determination of carbon dioxide (e.g. by IR spectrometry)	0.3 mg/l to 1 000 mg/l (lower end is for special cases, e.g. drinking water)	In Europe, EN 1484 is applied
Total phosphorus (TP)	EN ISO 6878:2004	Periodic	Spectrophotometry using ammonium molybdate after digestion with peroxodisulphate or nitric acid	0.005 mg/l to 0.8 mg/l	—
	EN ISO 15681-1:2004 EN ISO 15681-2:2004	Periodic	Flow analysis (FIA and CFA) after manual digestion with peroxodisulphate	0.1 mg/l to 10 mg/l	—
	EN ISO 11885:2009	Periodic	Inductively coupled plasma optical emission spectrometry (ICP-OES)	LoQ: ~ 0.013 mg/l	—
Total suspended solids (TSS)	EN 872:2005 ISO 11923:1997	Periodic	Filtration through glass fibre filter and gravimetry	LoQ: ~ 2 mg/l	In Europe, EN 872 is applied
Toxicity - algae	EN ISO 8692:2012	Periodic	Fresh water algal growth inhibition test with unicellular green algae	NA	—
	EN ISO 10253:2016	Periodic	Marine algal growth inhibition test with *Skeletonema sp.* and *Phaeodactylum tricornutum*	NA	—
	EN ISO 10710:2013	Periodic	Growth inhibition test with the marine and brackish water macroalga *Ceramium tenuicorne*	NA	—
Toxicity - bacteria	EN ISO 11348-1:2008 EN ISO 11348-2:2008 EN ISO 11348-3:2008	Periodic	Inhibitory effect on the light emission of *Vibrio fischeri* (luminescent bacteria test) Part 1: Method using freshly prepared bacteria Part 2: Method using liquid-dried bacteria Part 3: Method using freeze-dried bacteria	NA	—
	EN ISO 10712:1995	Periodic	*Pseudomonas putida* growth inhibition test (Pseudomonas cell multiplication inhibition test)	NA	—
Toxicity - daphnia	EN ISO 6341:2012	Periodic	Acute toxicity (inhibition of the mobility) to *Daphnia magna* Straus	NA	—
Toxicity - duckweed	EN ISO 20079:2006	Periodic	Duckweed (*Lemna minor*) growth inhibition test	NA	—

Parameter/ Substance(s) (1)	**EN or ISO standard** (1)	**Monitoring frequency**	**Monitoring methods**	**Measurement ranges and/or measurement limits** (2)	**Remarks**
Toxicity - fish	EN ISO 7346-1:1997 EN ISO 7346-2:1997 EN ISO 7346-3:1997	Periodic	Acute lethal toxicity of substances to zebrafish (*Danio rerio*) Part 1: Static method Part 2: Semi-static method Part 3: Flow-through method	NA	Standards determine toxicities of individual substances
Toxicity - fish eggs	EN ISO 15088:2008	Periodic	Acute toxicity to zebrafish eggs (*Danio rerio*)	NA	—
Toxicity - genotoxicity	EN ISO 21427-2:2009	Periodic	Genotoxicity by measurement of the induction of micronuclei - Part 2: Mixed population method using the cell line V79	NA	AC:2009 (Technical corrigendum)
	ISO 11350:2012	Periodic	Genotoxicity by salmonella/microsome fluctuation test (Ames fluctuation test)	NA	—
	ISO 13829:2000	Periodic	Genotoxicity by umu-test	NA	—
Turbidity	EN ISO 7027-1:2016	Continuous/periodic	a) Measurement of diffuse radiation (nephelometry), applicable to water of low turbidity (e.g. drinking water) b) Measurement of the attenuation of a radiant flux (turbidimetry), more applicable to highly turbid waters (e.g. waste water)	a) < 0.05 to 400 FNU (formazin nephelometric units) b) 40 to 4 000 FAU (formazin attenuation units)	—

(1) Non-exhaustive list.
(2) As given in the standards. Limits of determination are listed as LoQs.

NB: CFA = continuous flow analysis; FIA = flow injection analysis; LLoA = lower limit of application; LLoQ = lower limit of quantification; LoD = limit of detection; LoQ = limit of quantification; NA = not applicable; NI = no information provided; NS = not specified.

Source: [121, CEN 2016], [122, ISO 2016]

A.3. Examples of mass flow thresholds for the continuous measurement of emissions to air

Table 7.4: Examples of mass flow thresholds for the continuous measurement of emissions to air

Parameter/substance	Mass flow threshold (kg/h)				
	Belgium (Flanders) (1) (2)	**Denmark** (1) (3)	**France** (2) (4)	**Germany** (2) (4)	**Portugal** (2)
Ammonia	—	—	10	—	—
Bromine	—	—	1	—	—
Carbon monoxide	—	—	50	5 (5) 100 (6)	100
Chlorine	—	—	1	0.3	—
Dust	5 (7)	200 (8) (9)	5–50 (10) > 50 (9) (11)	3 (8) (9)	5
Gaseous and vaporous organic compounds, expressed as TVOC	—	25 (8) 2 (12) (13)	15 (7) (8) (14) 10 (7) (14) (15) 2 (7) (12) (13)	2.5 (8) 1 (12)	—
Gaseous chlorides, expressed as HCl	—	—	20	1.5	3
Gaseous fluorides, expressed as HF	—	—	5	0.3	0.5
Hydrogen cyanide	—	—	1	—	—
Hydrogen sulphide	—	—	1	0.3	—
Mercury and its compounds, expressed as Hg	—	2	—	0.0025 (16)	—
Nitrogen oxides, as NO$_2$	30 (7)	200	150	30	30
Sulphur dioxide	50 (7)	200	150	30	50
Sulphuric acid	—	—	—	—	1

(1) The threshold level applies to individual emission sources.
(2) The threshold level refers to the point of discharge to the environment.
(3) The threshold level refers to the mass flow before the abatement systems.
(4) The threshold level applies to all combined emission sources of the installation.
(5) For evaluating the efficiency of combustion.
(6) For all other cases.
(7) Continuous measurements may be replaced by monitoring another representative parameter that correlates with the emissions.
(8) General case.
(9) Lower threshold values apply for dusty emissions of substances with a higher environmental risk.
(10) A continuous estimation is required (e.g. by using an opacimeter).
(11) A continuous measurement based on a gravimetric method is required.
(12) In the case of a list of organic substances with a higher environmental risk.
(13) The threshold value refers to the individual compound.
(14) The threshold value refers to NMVOC.
(15) If specific equipment for abatement is used.
(16) Continuous measurement of mercury is not required when it has been reliably proven that the emission concentrations are less than 20 % of the ELVs.

Source: [24, Directive 2010/75/EU 2010, Annex VII, Part 6], [57, BE (Flanders) 2014, Section 4.4.4.1], [58, DK 2002, Section 5.3.3.3], [60, FR 2016, Article 59], [61, DE 2002, Section 5.3.3], [137, PT 1993, Anexo VII]

A.4. *Toxic equivalence factors for PCDDs/PCDFs*

Table 7.5: Toxic equivalence factors for PCDDs/PCDFs

Compound	Toxic equivalence factor				
	I-TEF	**WHO-TEF 1998**			**WHO-TEF 2005**
	Not specified	**Humans and mammals**	**Fish**	**Birds**	**Humans and mammals**
Chlorinated dibenzo-*p*-dioxins					
2,3,7,8-Tetrachlorodibenzo-*p*-dioxin (TCDD)	1	1	1	1	1
1,2,3,7,8-Pentachlorodibenzo-*p*-dioxin (PeCDD)	0.5	1	1	1	1
1,2,3,4,7,8-Hexachlorodibenzo-*p*-dioxin (HxCDD)	0.1	0.1	0.5	0.05	0.1
1,2,3,6,7,8-Hexachlorodibenzo-*p*-dioxin (HxCDD)	0.1	0.1	0.01	0.01	0.1
1,2,3,7,8,9-Hexachlorodibenzo-*p*-dioxin (HxCDD)	0.1	0.1	0.01	0.1	0.1
1,2,3,4,6,7,8-Heptachlorodibenzo-*p*-dioxin (HpCDD)	0.01	0.01	0.001	< 0.001	0.01
Octachlorodibenzo-*p*-dioxin (OCDD)	0.001	0.0001	< 0.0001	0.0001	0.0003
Chlorinated dibenzofurans					
2,3,7,8-Tetrachlorodibenzofuran (TCDF)	0.1	0.1	0.05	1	0.1
2,3,4,7,8-Pentachlorodibenzofuran (PeCDF)	0.5	0.5	0.5	1	0.3
1,2,3,7,8-Pentachlorodibenzofuran (PeCDF)	0.05	0.05	0.05	0.1	0.03
1,2,3,4,7,8-Hexachlorodibenzofuran (HxCDF)	0.1	0.1	0.1	0.1	0.1
1,2,3,6,7,8-Hexachlorodibenzofuran (HxCDF)	0.1	0.1	0.1	0.1	0.1
1,2,3,7,8,9-Hexachlorodibenzofuran (HxCDF)	0.1	0.1	0.1	0.1	0.1
2,3,4,6,7,8-Hexachlorodibenzofuran (HxCDF)	0.1	0.1	0.1	0.1	0.1
1,2,3,4,6,7,8-Heptachlorodibenzofuran (HpCDF)	0.01	0.01	0.01	0.01	0.01
1,2,3,4,7,8,9-Heptachlorodibenzofuran (HpCDF)	0.01	0.01	0.01	0.01	0.01
Octachlorodibenzofuran (OCDF)	0.001	0.0001	< 0.0001	0.0001	0.0003
Non-*ortho*-substituted PCBs					
3,3',4,4'-Tetrachlorobiphenyl (PCB 77)	—	0.0001	0.0001	0.05	0.0001
3,4,4',5-Tetrachlorobiphenyl (PCB 81)	—	0.0001	0.0005	0.1	0.0003
3,3',4,4',5-Pentachlorobiphenyl (PCB 126)	—	0.1	0.005	0.1	0.1
3,3',4,4',5,5'-Hexachlorobiphenyl (PCB 169)	—	0.01	0.00005	0.001	0.03
Mono-*ortho*-substituted PCBs					
2,3,3',4,4'-Pentachlorobiphenyl (PCB 105)	—	0.0001	< 0.000005	0.0001	0.00003
2,3,4,4',5-Pentachlorobiphenyl (PCB 114)	—	0.0005	< 0.000005	0.0001	0.00003
2,3',4,4',5-Pentachlorobiphenyl (PCB 118)	—	0.0001	< 0.000005	0.00001	0.00003

Compound	Toxic equivalence factor				
	I-TEF	**WHO-TEF 1998**			**WHO-TEF 2005**
	Not specified	**Humans and mammals**	**Fish**	**Birds**	**Humans and mammals**
2',3,4,4',5-Pentachlorobiphenyl (PCB 123)	—	0.0001	< 0.000005	0.00001	0.00003
2,3,3',4,4',5-Hexachlorobiphenyl (PCB 156)	—	0.0005	< 0.000005	0.0001	0.00003
2,3,3',4,4',5'-Hexachlorobiphenyl (PCB 157)	—	0.0005	< 0.000005	0.0001	0.00003
2,3',4,4',5,5'-Hexachlorobiphenyl (PCB 167)	—	0.00001	< 0.000005	0.00001	0.00003
2,3,3',4,4',5,5'-Heptachlorobiphenyl (PCB 189)	—	0.0001	< 0.000005	0.00001	0.00003

NB: I-TEF = International toxic equivalence factor; WHO-TEF = World Health Organisation toxic equivalence factor.

Source: [24, Directive 2010/75/EU 2010] [50, Van den Berg et al. 2006] [228, Van den Berg et al. 1998]

A.5. Cost examples for monitoring of emissions to air

Table 7.6: Cost examples for monitoring of stack emissions from different industry sectors in the United Kingdom provided by plant operators

Plant	**Continuous measurements**								**Periodic measurements**		
	Parameter/ substance(s)	**Monitoring method**	**Investment costs in GBP (1)**			**Operating costs in GBP (1)**					
			System purchase	**Installation (2)**	**Other items**	**Maintenance, service, and calibration (per year)**	**QAL2**	**AST**	**Parameter/ Substance(s) monitored**	**Frequency of tests**	**Costs per set of tests**
Gas-fired combustion plant	NO$_X$, CO, O$_2$	IR, UV, electrochemical	175 000 (for 5 systems)	21 000 (for 5 systems)	- Spares: 24 000 - Training: 3 500	9 000	22 000 (for 5 systems)	7 000 (for 5 systems)	NO$_X$, CO, O$_2$	Once per year	7 000 (for 5 systems)
Coal-fired combustion plant (4 units)	Dust, NO, SO$_2$, H$_2$O, CO, O$_2$	Light scatter, *in situ* NDIR, zirconia	25 500 (for upgrade of one AMS)	NI (Minimal retrofit to existing system)	- Instrument air compressor plant: 9 000 - Reporting software: 20 000 - Software license: 3 500	7 000	7 500 (for 1 system)	3 000 (for 1 system)	Dust, NO, SO$_2$, H$_2$O, CO, O$_2$	NI	NI
Coal-fired combustion plant without FGD	Dust, NO$_X$, SO$_2$, O$_2$	Extractive IR, opacity	257 000 (for 4 systems)	NI	- Software: 16 000 - Training: 3 000	16 500	24 000 (for 4 systems)	18 000 (for 4 systems)	NI	NI	NI
Combustion plant	HCl, CO, NO$_X$, SO$_2$, O$_2$, H$_2$O, TVOC	FTIR	160 000	32 000	- Data acquisition: 20 000 - Back-up system: 141 000	NI	NI	NI	NI	NI	NI

Plant	Continuous measurements								Periodic measurements		
			Investment costs in GBP (1)			Operating costs in GBP (1)					
	Parameter/ substance(s)	Monitoring method	System purchase	Installation (2)	Other items	Maintenance, service, and calibration (per year)	QAL2	AST	Parameter/ Substance(s) monitored	Frequency of tests	Costs per set of tests
Cement plant 1	H_2O, O_2, TVOC, NO, NO_2, N_2O, NH_3, HCl, CO, SO_2, CO_2	FTIR, FID, zirconia	70 000 (for 1 system)	6 500	14 000	10 000	- Gases: 5 000 - Dust: 4 000	- Gases: 3 200 - Dust: 1 600	SO_2, NO_X, TVOC, CO_2, CO, HCl, HF, NH_3, N_2O, metals, PCBs, PAHs, O_2, H_2O, flow, C_6H_6, C_8H_8, CH_3Cl, C_4H_6, CH_4, C_2H_6, C_2H_4, C_3H_8, NMVOC, PCDDs/PCDFs	Twice per year	4 500 (per test) 200 (dust test)
Cement plant 2	Dust, NO_X, SO_X, CO, TVOC, HCl, O_2	FTIR	136 000	20 000	NI	20 000	6 500	1 700	HF, metals, PCDDs/PCDFs, PCBs, PAHs, NH_3,CH_4	Twice per year	26 500
Lime plant	Dust (multiple stacks)	Triboelectric	40 000	15 000	NI	10 000	NI	900	Dust, SO_X, NO_X, CO	Once every 3 months	6 500
Waste incineration plant with power generation	HCl, CO, NO_X, SO_2, O_2, H_2O, TVOC, dust	FTIR, FID, zirconia, triboelectric	115 000	5 000 (estimated)	4 500	10 000	18 000 (initial QAL2)	NI	HCl, CO, NO_X, SO_2, O_2, H_2O, TVOC, dust, HF, metals, PCDDs/PCDFs	Once per year	27 000
Foundry	Dust (silica)	Triboelectric	4 000 (for 1 stack)	4 500	None	2 000	NA	NA	Dust (silica)	Once per year	2 000
Metal finishing	Dust	Triboelectric	10 000 (for 2 stacks)	3 000	None	4 500	NA	NA	Dust (Zn, Cu, Ni)	Once per year	2 000
Batteries (finishing)	Dust	Triboelectric	7 200 (for 1 stack)	2 500	None	6 000	NA	NA	Dust	Once per year	2 000

Plant	Continuous measurements								Periodic measurements		
			Investment costs in GBP (1)			Operating costs in GBP (1)					
	Parameter/ substance(s)	Monitoring method	System purchase	Installation (2)	Other items	Maintenance, service, and calibration (per year)	QAL2	AST	Parameter/ Substance(s) monitored	Frequency of tests	Costs per set of tests
Aluminium recycling/ remelting	Dust	Triboelectric	5 000 (for 1 stack)	1 000	None	2 000	NA	NA	TVOC, metals (Pb, Cd), HCl	Once per year	1 000
Metal refining and chemical	Dust, TVOC, NO_X, Cl_2	Dust monitoring *in situ*, extractive FID, chemiluminescence, and chlorine monitoring	- Dust: 15 000 - FID: 20 000 - Cl_2: 24 000 - NO_X: 18 000–26 000	- Dust: 1 500 - FID: 1 500 - Cl_2: 6 000 - NO_X: 10 000	- NO_X initial spares: 20 000 - Training: 900/d	- Dust: 4 500 - FID: 1 800 - Cl_2: 11 000 - NO_X: 22 000	NA	NA	NI	NI	NI
Rubber production	Dust	Triboelectric	8 500 (for 2 stacks)	4 000	4 000	3 000	NA	NA	Dust (kaolin)	Once per year	3 000
Pigment production	Filter leak	Triboelectric	15 000 (for 10 silos)	6 000	None	3 500	NA	NA	None	NA	NA
Chemical production	NO_X, CO	Extractive IR	NI	NI	NI	2 500 (yearly) 1 500 (weekly calibration)	8 400	6 500	NO_X, CO	NI	NI
Sugar beet drying (animal feed)	Dust	Triboelectric	12 000 (for 3 stacks)	4 300	4 300	4 500	NA	NA	Dust	Once per year	4 500

(1) Original costs reported in GBP. EUR 1 is equal to GBP = 0.8124 (average currency conversion rate for 2012).
(2) Costs for construction works (e.g. for the installation of a platform) are not included [245, Cefic and CONCAWE 2013].

NB: AMS = automated measuring system; FGD = flue-gas desulphurisation; FID = flame ionisation detection; FTIR = Fourier transform infrared spectrometry; IR = infrared spectrometry; NA = not applicable; NDIR = non-dispersive infrared spectrometry; NI = no information provided; QAL = quality assurance level; UV = ultraviolet spectrometry.

Source: [68, UK STA 2012]

Table 7.7: Cost examples for continuous measurements of stack emissions in the United Kingdom provided by instrument manufacturers and suppliers

Typical application	Parameter/ substance(s)	Monitoring method	Approvals and certification range	Typical lifetime of instrument	Period between calibrations	Investment costs in GBP (1)		Maintenance costs in GBP (1)	
						System purchase excluding works	Any significant option	Annual service contracts	Periodic manual sampling costs
Multi-component gas monitoring									
Coal-fired combustion plant	SO_2, NO, NO_2, O_2	Extractive UV and IR	MCERTS	10–15 yr	12 months	25 000–40 000	Analyser house or shelter: 6 000–40 000	4 000	3 000
		In situ IR	MCERTS	NI	NI	20 000	- Acid gas protection: 5 000 - Compressor air: 4 500	NI	
		Extractive IR and paramagnetism	MCERTS	NI	1 week	40 000–50 000 including analyser housing	Automated QAL3: 7 500	NI	
Coal-fired combustion plant with SCR	SO_2, NO, NO_2, O_2, NH_3, CO, CO_2	Extractive UV and IR	MCERTS	10–15 yr	12 months	30 000–50 000	Analyser house or shelter: 6 000–40 000	4 000	4 000
		FTIR and zirconia	MCERTS	NI	NI	82 000	Automated QAL3: 7 500	NI	
		Extractive IR, paramagnetism, and across-stack TDL for NH_3	MCERTS	10 yr (min. for lasers)	6–12 months for laser	50 000 and 28 000 for laser and purge panel	Laser purge panel: 2 500	NI	
Cement production	CO, NO_X, SO_2. O_2	Extractive UV and IR	MCERTS	10–15 yr	12 months	30 000–50 000	- Analyser house or shelter: 6 000–40 000 - Water-cooled probe: 10 000	NI	4 500
		Extractive IR and paramagnetism	MCERTS	NI	NI	40 000–50 000	Automated QAL3: 7 500	NI	

Typical application	Parameter/ substance(s)	Monitoring method	Approvals and certification range	Typical lifetime of instrument	Period between calibrations	Investment costs in GBP (1)		Maintenance costs in GBP (1)	
						System purchase excluding works	Any significant option	Annual service contracts	Periodic manual sampling costs
Waste (co-)incineration	CO, NO_X, SO_2 O_2, HCl, TVOC	Extractive FTIR and FID	MCERTS	10–15 yr	12 months	80 000–110 000	Analyser house or shelter: 30 000–40 000 - Automated QAL3: 7 500	7 000	12 000–20 000
		Extractive IR, paramagnetism, and across-stack TDL for HCl	MCERTS	10 yr (min. for lasers)	6–12 months for laser	50 000 and 28 000 for laser and purge panel	Laser purge panel: 2 500	NI	
	CO, NO_X, SO_2 O_2, HCl	Extractive FTIR and zirconia	MCERTS	10–15 yr	12 months	82 000	Automated QAL3: 7 500	7 000	7 000
		Extractive IR and paramagnetism	MCERTS	10 yr (min. for lasers)	6–12 months for laser	56 000	Automated QAL3: 7 500	NI	
Gas turbine	NO, NO_2, CO, O_2	Extractive UV and IR	MCERTS	10–15 yr	12 months	25 000–40 000	Analyser house or shelter: 6 000–30 000	NI	4 000
	NO, NO_2,CO_2, CO, O_2	Extractive NDIR, chemiluminescence, and paramagnetism	MCERTS	NI	NI	43 000	Automated QAL3: 7 500	NI	
ATEX area applications	SO_2, NO, NO_2, O_2, NH_3, CO, CO_2	Extractive UV and IR	MCERTS	10–15 yr	12 months	40 000–60 000	Analyser house or shelter: 30 000–80 000	4 000	NI
Single component gas monitoring									
Aluminium, chemical production, incineration	HCl or HF	Across-stack TDL	MCERTS	NI	NI	18 000–28 000	NI	NI	3 000–5 000
Combustion	O_2	*In situ* zirconia, across-stack TDL	MCERTS/TÜV	3–10 yr	3–6 months	5 000–12 000	NI	NI	1 000
Crematoria	O_2, CO	Electrochemical	MCERTS/TÜV	2–6 yr	3–6 months	5 000–8 000	NI	NI	1 000–2 000
Chemical production, solvent use, incineration	TVOC	FID	MCERTS/TÜV	NI	NI	24 000	NI	NI	1 000–3 000

Typical application	Parameter/ substance(s)	Monitoring method	Approvals and certification range	Typical lifetime of instrument	Period between calibrations	Investment costs in GBP (1)		Maintenance costs in GBP (1)	
						System purchase excluding works	Any significant option	Annual service contracts	Periodic manual sampling costs
Main stack	Mercury (Hg)	Semi-continuous	NI	5–10 yr	3–6 months	38 000– 57 000	NI	1 000	3 000– 15 000
Incineration	Long-term dioxin	Semi-continuous	NI	7–10 yr	NI	100 000	NI	NI	3 000– 15 000
Ammonia slip for SCR	NH_3	TDL	None	10–15 yr	6 months	25 000	Purge: 2 000	2 000	3 000
Single component dust monitoring									
Incineration plant/ cement kiln	Dust	*In situ* scatter	MCERTS/TÜV 0–15 0– 100 mg/m^3	10 yr	12 months	8 500 including blower	Extended probe length: 1 000	2 000	1 500
Combustion plant and large stack with electrostatic precipitator	Dust	Across-stack transmission	MCERTS/TÜV 0–150 mg/m^3	10 yr	12 months	7 500 and 1 000 blower	NI	2 000	1 500
Combustion plant with dry FGD	Dust	*In situ* backscatter	0–50 mg/m^3	10 yr	12 months	6 000 and 1 000 blower	NI	2 000	1 500
Stack with wet collector (e.g. wet FGD, lime kiln)	Dust	Extractive system with heating chamber and scatter probe	TÜV 0–15 mg/m^3	10 yr	12 months	32 000 (complete system including blower)	Corrosion resistance against SO_2: 10 000	7 000	1 500
Large stack	Dust	*In situ* laser/scatter	MCERTS	5–15 yr	3–6 months	8 000–12 000	Dual range: 5 000–8 000	NI	2 000
Stack with bag filter (e.g. steel, non-ferrous, chemical industries)	Dust	*In situ* triboelectric	MCERTS/TÜV 0–15 mg/m^3	10 yr	12 months	6 000	Additional sensors for multiple stack applications: 4 000	1 400	1 500
Dust monitoring in explosive zone	Dust	*In situ* scatter	MCERTS/TÜV ATEX categories 1, 2, 3	10 yr	12 months	9 500	NI	1 400	2 000
Single component filter leak monitoring									

Typical application	Parameter/ substance(s)	Monitoring method	Approvals and certification range	Typical lifetime of instrument	Period between calibrations	Investment costs in GBP (1)		Maintenance costs in GBP (1)	
						System purchase excluding works	Any significant option	Annual service contracts	Periodic manual sampling costs
Leak of bag filter in all industries	Filter leak	*In situ* triboelectric	TÜV EN 15859	10 yr	12 months	3 000	Extended operating range for ceramic filters (250–800 °C): 1 000	700	Not required
Leak of compartment in multi-chamber bag filter	Chamber leak	*In situ* triboelectric	NI	10 yr	12 months	1 500	NI	600	Not required
Single component flow rate monitoring									
Coal-fired combustion plant and large stacks	Flow	Across-stack ultrasound	MCERTS	NI	NI	15 000	NI	NI	1 000–3 000
		Averaging Pitot tube	MCERTS	NI	NI	10 000–15 000	NI	NI	1 000–3 000
Point measurement for smaller stacks	Flow	Ultrasound	MCERTS/TÜV	NI	NI	5 000–12 000	NI	NI	1 000–3 000
		Thermal mass	MCERTS/TÜV	NI	NI	5 000	NI	NI	1 000–3 000
		Pitot tube	MCERTS/TÜV	NI	NI	3 000	Purging if high dust: 2 000	NI	1 000–3 000
		Vane anemometer	MCERTS/TÜV	NI	NI	4 000	NI	NI	1 000–3 000
Data acquisition									
DAHS for AMS	DAHS	Data recording	MCERTS	NI	NI	10 000–20 000	Annual licence, number of substances to be recorded: 3 500	NI	NA
DAHS for dust	Dust	Recording from multiple dust monitors	MCERTS/TÜV	3–10 yr	3–6 months	1 000–5 000	NI	NI	NA

(1) Original costs reported in GBP. EUR 1 is equal to GBP = 0.8124 (average currency conversion rate for 2012).

NB: AMS = automated measuring system; DAHS = data acquisition and handling system; FGD = flue-gas desulphurisation; FID = flame ionisation detection; FTIR = Fourier transform infrared spectrometry; MCERTS = Monitoring Certification Scheme; IR = infrared spectrometry; SCR = selective catalytic reduction; NA = not applicable; NI = no information provided; QAL = quality assurance level; TDL = tunable diode laser absorption spectrometry; TÜV = Technischer Überwachungsverein (Technical inspection body); UV = ultraviolet spectrometry.

Source: [68, UK STA 2012]

Table 7.8: Cost examples for periodic measurements of stack emissions in the United Kingdom provided by testing laboratories

Parameter/ substance(s)	EN standard	Costs (1) (2)		
		Single test	Triplicate tests	QAL2
Dust	EN 13284-1	GBP 600–3 000 (EUR 700–3 700)	GBP 1 000–4 000 (EUR 1 200–4 900)	GBP 5 000–15 000 (EUR 6 200–18 500)
Combustion gases (i.e. O_2, H_2O, SO_2, NO_X, CO)	EN 14789 EN 14790 EN 14791 EN 14792 EN 15058	Add up to GBP 3 000 (EUR 3 700)	Add up to GBP 1 000–4 000 (EUR 1 200–4 900)	Add up to GBP 5 000 (EUR 6 200)
TVOC	EN 12619	Add up to GBP 2 000 (EUR 2 500)	Add up to GBP 1 000–4 000 (EUR 1 200–4 900)	Add up to GBP 5 000 (EUR 6 200)
Gaseous chlorides, expressed as HCl	EN 1911	Add up to GBP 2 000 (EUR 2 500)	Add up to GBP 1 000–4 000 (EUR 1 200–4 900)	Add up to GBP 5 000 (EUR 6 200)
PCDDs/PCDFs	EN 1948	Add up to GBP 3 000 (EUR 3 700)	Add up to GBP 3 000–6 000 (EUR 3 700–7 400)	NI
Metals	EN 14385	Add up to GBP 3 000 (EUR 3 700)	Add up to GBP 3 000–5 000 (EUR 3 700–6 200)	NI

(1) Original costs in GBP. EUR 1 is equal to GBP = 0.8124 (average currency conversion rate for 2012).

(2) The costs are based on a test site regulated under the IED that is within 160 km of the monitoring organisation's main office/laboratory. The costs of dust monitoring include all the travel and equipment set-up costs. The costs for monitoring of each subsequent parameter/substance are in addition to the costs for dust monitoring.

NB: NI = no information provided.

Source: [68, UK STA 2012]

A.6. Examples of the calculation of flow-weighted average concentrations and the specific load in waste water

Table 7.9: Calculation of monthly averages for a parameter measured daily - flow-weighted average concentration and specific load for COD for a month with relatively stable flow rates

Date	Flow rate (daily)	Production (daily)	COD concentration (daily average)	COD specific load (daily average)
	q_i	p_i	c_i	$\frac{c_i q_i}{p_i}$
	[m^3]	[t]	[mg/l]	[kg/t]
01/03/2011	7 950	1 530	269	1.40
02/03/2011	8 503	1 432	265	1.57
03/03/2011	7 364	1 516	261	1.27
04/03/2011	7 986	1 388	256	1.47
05/03/2011	7 315	1 503	245	1.19
06/03/2011	7 797	1 517	252	1.30
07/03/2011	7 678	1 588	247	1.19
08/03/2011	7 035	1 508	232	1.08
09/03/2011	7 827	1 474	244	1.30
10/03/2011	7 917	1 515	240	1.25
11/03/2011	7 028	1 477	237	1.13
12/03/2011	7 149	1 492	237	1.14
13/03/2011	7 476	1 511	239	1.18
14/03/2011	7 664	1 080	229	1.63
15/03/2011	7 133	1 540	242	1.12
16/03/2011	7 764	1 575	227	1.12
17/03/2011	7 622	1 579	231	1.12
18/03/2011	7 663	1 499	251	1.28
19/03/2011	7 574	1 587	254	1.21
20/03/2011	7 579	1 540	237	1.17
21/03/2011	8 228	1 546	254	1.35
22/03/2011	7 095	1 527	248	1.15
23/03/2011	8 026	1 301	241	1.49
24/03/2011	7 442	1 541	241	1.16
25/03/2011	7 830	1 544	233	1.18
26/03/2011	7 098	1 582	235	1.05
27/03/2011	8 156	1 573	230	1.19
28/03/2011	7 375	1 586	246	1.14
29/03/2011	7 744	1 579	250	1.23
30/03/2011	7 559	1 501	241	1.21
31/03/2011	8 141	1 520	245	1.31

Monthly average (weighted)	$c_w = \frac{\sum_{i=1}^{n} c_i q_i}{\sum_{i=1}^{n} q_i}$	**244**	**Monthly average (not weighted)** $l_{specific} = \frac{\sum_{i=1}^{n} \frac{c_i q_i}{p_i}}{n}$	**1.24**
Monthly average (not weighted)	$\overline{c_i} = \frac{\sum_{i=1}^{n} c_i}{n}$	**244**		

Table 7.10: Calculation of monthly averages for a parameter measured daily - flow-weighted average concentration and specific load for COD for a month with more variable flow rates

Date	Flow rate (daily)	Production (daily)	COD concentration (daily average)	COD specific load (daily average)
	q_i	p_i	c_i	$\frac{c_i q_i}{p_i}$
	[m^3]	[t]	[mg/l]	[kg/t]
01/05/2011	7 656	1 527	223	1.12
02/05/2011	7 358	1 575	235	1.10
03/05/2011	7 554	1 453	237	1.23
04/05/2011	7 303	1 425	226	1.16
05/05/2011	7 474	1 534	220	1.07
06/05/2011	8 038	1 345	219	1.31
07/05/2011	7 275	1 585	233	1.07
08/05/2011	8 028	1 224	244	1.60
09/05/2011	8 012	1 291	235	1.46
10/05/2011	6 453	1 465	235	1.03
11/05/2011	8 566	1 434	232	1.39
12/05/2011	8 085	1 478	276	1.51
13/05/2011	7 141	1 532	232	1.08
14/05/2011	7 294	1 532	236	1.12
15/05/2011	8 596	785	247	2.71
16/05/2011	7 104	577	194	2.39
17/05/2011	4 208	554	146	1.11
18/05/2011	2 899	975	117	0.35
19/05/2011	7 606	1 408	174	0.94
20/05/2011	6 904	1 071	184	1.19
21/05/2011	6 172	1 454	189	0.80
22/05/2011	7 242	1 422	194	0.99
23/05/2011	6 585	1 504	201	0.88
24/05/2011	7 083	1 536	217	1.00
25/05/2011	7 068	1 294	230	1.26
26/05/2011	7 307	1 554	229	1.08
27/05/2011	6 577	1 504	224	0.98
28/05/2011	7 171	1 460	241	1.18
29/05/2011	6 717	1 530	239	1.05
30/05/2011	7 449	1 541	240	1.16
31/05/2011	7 069	1 325	251	1.34

Monthly average (weighted)	$c_w = \frac{\sum_{i=1}^{n} c_i q_i}{\sum_{i=1}^{n} q_i}$	**223**	**Monthly average (not weighted)** $l_{specific} = \frac{\sum_{i=1}^{n} \frac{c_i q_i}{p_i}}{n}$	**1.21**
Monthly average (not weighted)	$\overline{c_i} = \frac{\sum_{i=1}^{n} c_i}{n}$	**219**		

Table 7.11: Calculation of averages of samples obtained during one year for a parameter measured periodically - flow-weighted average concentration and specific load for AOX for relatively stable flow rates

Date	Flow rate (daily)	Production (daily)	AOX concentration (daily average)	AOX specific load (daily average)
	q_i	p_i	c_i	$\frac{c_i q_i}{p_i}$
	[m^3]	[t]	[mg/l]	[kg/t]
04/01/2011	7 857	1 413	0.13	0.00072
11/01/2011	8 405	1 552	0.28	0.00152
19/01/2011	7 445	1 378	0.24	0.00130
27/01/2011	7 642	1 526	0.15	0.00075
02/02/2011	8 351	1 411	0.13	0.00077
10/02/2011	8 218	1 576	0.20	0.00104
14/02/2011	6 764	934	0.12	0.00087
20/02/2011	6 517	1 393	0.14	0.00066
08/03/2011	7 035	1 508	0.22	0.00103
16/03/2011	7 764	1 575	0.35	0.00173
24/03/2011	7 442	1 541	0.32	0.00155
31/03/2011	8 141	1 520	0.36	0.00193
03/04/2011	7 461	1 510	0.24	0.00119
12/04/2011	7 455	1 424	0.18	0.00094
19/04/2011	8 331	1 388	0.22	0.00132
27/04/2011	8 038	1 327	0.28	0.00170
05/05/2011	7 474	1 534	0.06	0.00029
24/05/2011	7 083	1 536	0.68	0.00314
08/06/2011	7 493	1 366	0.24	0.00132
16/06/2011	7 790	1 524	0.22	0.00112
24/06/2011	7 868	1 476	0.30	0.00160
27/06/2011	7 873	1 554	0.18	0.00091
04/07/2011	8 258	1 581	0.21	0.00110
12/07/2011	7 704	1 446	0.28	0.00149
20/07/2011	7 871	1 534	0.34	0.00175
23/08/2011	7 573	1 577	0.25	0.00120
30/08/2011	8 512	1 498	0.23	0.00131
06/09/2011	7 527	1 397	0.32	0.00172
19/09/2011	7 881	933	0.29	0.00245
04/10/2011	8 485	1 561	0.25	0.00136
11/10/2011	7 462	1 452	0.22	0.00113
18/10/2011	7 971	1 554	0.19	0.00097
25/10/2011	7 371	1 298	0.26	0.00148
02/11/2011	6 873	1 565	0.24	0.00105
07/11/2011	7 858	1 537	0.25	0.00128
16/11/2011	8 591	1 070	0.23	0.00185
01/12/2011	8 318	1 550	0.34	0.00182
07/12/2011	8 418	1 385	0.17	0.00103
12/12/2011	7 899	1 508	0.25	0.00131
21/12/2011	7 472	1 243	0.24	0.00144

<table>
<tr><td>Average of samples obtained during one year (weighted)</td><td>$c_w = \frac{\sum_{i=1}^{n} c_i q_i}{\sum_{i=1}^{n} q_i}$</td><td>0.24</td><td rowspan="2">Average of samples obtained during one year (not weighted)
$l_{specific} = \frac{\sum_{i=1}^{n} \frac{c_i q_i}{p_i}}{n}$</td><td rowspan="2">0.00133</td></tr>
<tr><td>Average of samples obtained during one year (not weighted)</td><td>$\overline{c_i} = \frac{\sum_{i=1}^{n} c_i}{n}$</td><td>0.25</td></tr>
</table>

GLOSSARY

This glossary is meant to facilitate the understanding of the information contained in this document. The definitions of terms in this glossary are not legal definitions (even if some of them may coincide with definitions given in European legislation), they are meant to help the reader understand some key terms in the context of their use in the specific sector covered by this document.

This glossary is divided up into the following sections:

I. ISO country codes
II. Monetary units
III. Unit prefixes
IV. Units
V. Chemical elements
VI. Chemical formulae commonly used in this document
VII. Acronyms and technical definitions

I. Country codes

Code	Country
***Member States* (*)**	
BE	Belgium
DK	Denmark
DE	Germany
IE	Ireland
FI	Finland
FR	France
NL	Netherlands
AT	Austria
PL	Poland
PT	Portugal
UK	United Kingdom
Non-member countries	
US	United States
(*) The protocol order of the Member States is based on the alphabetical order of their geographical names in the original language(s).	

II. Monetary units

Code ([1])	Country/territory	Currency
Member State currencies		
EUR	Euro area ([2])	euro (pl. euros)
GBP	United Kingdom	pound sterling (inv.)
([1]) ISO 4217 codes. ([2]) Includes Austria, Belgium, Cyprus, Estonia, Finland, France, Germany, Greece, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, the Netherlands, Portugal, Slovakia, Slovenia and Spain.		

III. Unit prefixes

Symbol	Prefix	Term	Number
G	giga	10^9	1 000 000 000
M	mega	10^6	1 000 000
k	kilo	10^3	1 000
h	hecto	10^2	100
da	deca	10^1	10
-------	-------	1 unit	1
d	deci	10^{-1}	0.1
c	centi	10^{-2}	0.01
m	milli	10^{-3}	0.001
µ	micro	10^{-6}	0.000 001
n	nano	10^{-9}	0.000 000 001
p	pico	10^{-12}	0.000 000 000 001

IV. Units

Term	Meaning
°C	degree Celsius, centigrade
d	day
g	gram
h	hour
I-TEQ	international toxic equivalent
K	Kelvin
kg	kilogram
kPa	kilopascal (1 kPa = 10 mbar)
l	litre (1 l = 0.001 m^3)
m	metre
m^3	cubic metre
mg	milligram (1 mg = 10^{-3} g)
mol	mole (1 mol = 6.022 × 10^{23} elementary entities of a substance)
min	minute
ou_E	European odour unit (as defined by EN 13725:2003)
Pa	pascal (pressure; 1 Pa = 1 N/m^2)
s	second
t	metric tonne (1 t = 1 000 kg)
vol-%	percentage by volume
WHO-TEQ	World Health Organisation toxic equivalent
wt-%	percentage by weight
yr	year

V. Chemical elements

Symbol	Name	Symbol	Name
Ac	Actinium	Mn	Manganese
Ag	Silver	Mo	Molybdenum
Al	Aluminium	N	Nitrogen
Am	Americium	Na	Sodium
Ar	Argon	Nb	Niobium
As	Arsenic	Nd	Neodymium
At	Astatine	Ne	Neon
Au	Gold	Ni	Nickel
B	Boron	No	Nobelium
Ba	Barium	Np	Neptunium
Be	Beryllium	O	Oxygen
Bi	Bismuth	Os	Osmium
Bk	Berkelium	P	Phosphorus
Br	Bromine	Pa	Protactinium
C	Carbon	Pb	Lead
Ca	Calcium	Pd	Palladium
Cd	Cadmium	Pm	Promethium
Ce	Cerium	Po	Polonium
Cf	Californium	Pr	Praseodymium
Cl	Chlorine	Pt	Platinum
Cm	Curium	Pu	Plutonium
Co	Cobalt	Ra	Radium
Cr	Chromium	Rb	Rubidium
Cs	Caesium	Re	Rhenium
Cu	Copper	Rf	Rutherfordium
Dy	Dysprosium	Rh	Rhodium
Er	Erbium	Rn	Radon
Es	Einsteinium	Ru	Ruthenium
Eu	Europium	S	Sulphur
F	Fluorine	Sb	Antimony
Fe	Iron	Sc	Scandium
Fm	Fermium	Se	Selenium
Fr	Francium	Si	Silicon
Ga	Gallium	Sm	Samarium
Gd	Gadolinium	Sn	Tin
Ge	Germanium	Sr	Strontium
H	Hydrogen	Ta	Tantalum
He	Helium	Tb	Terbium
Hf	Hafnium	Tc	Technetium
Hg	Mercury	Te	Tellurium
Ho	Holmium	Th	Thorium
I	Iodine	Ti	Titanium
In	Indium	Tl	Thallium
Ir	Iridium	Tm	Thulium
K	Potassium	U	Uranium
Kr	Krypton	V	Vanadium
La	Lanthanum	W	Tungsten
Li	Lithium	Xe	Xenon
Lr	Lawrencium	Y	Yttrium
Lu	Lutetium	Yb	Ytterbium
Md	Mendelevium	Zn	Zinc
Mg	Magnesium	Zr	Zirconium

VI. Chemical formulae commonly used in this document

Chemical formula	Name
Ba^{2+}	Barium ion
Br^-	Bromide ion
Ca^{2+}	Calcium ion
CH_2O	Formaldehyde
CH_4	Methane
C_3H_8	Propane
$C_{10}H_{22}$	*n*-Decane
$C_{40}H_{82}$	*n*-Tetracontane
CN^-	Cyanide ion
CO	Carbon monoxide
CO_2	Carbon dioxide
Cl^-	Chloride ion
Cl_2	Chlorine
F^-	Fluoride ion
Fe^{2+}	Ferrous ion
HCN	Hydrogen cyanide
HCl	Hydrogen chloride
HF	Hydrogen fluoride
$HgCl_2$	Mercury dichloride / mercury(II) chloride / mercuric chloride
Hg_2Cl_2	Dimercury dichloride / mercurous chloride
HNO_3	Nitric acid
H_2O_2	Hydrogen peroxide
HPO_4^{2-}	Hydrogen phosphate ion
$HP_2O_7^{3-}$	Hydrogen diphosphate ion
$H_2PO_4^-$	Dihydrogen phosphate ion
$H_2P_2O_7^{2-}$	Dihydrogen diphosphate ion
H_2S	Hydrogen sulphide
H_2SO_4	Sulphuric acid
K^+	Potassium ion
$K_2Cr_2O_7$	Potassium dichromate
$KMnO_4$	Potassium permanganate
Li^+	Lithium ion
Mg^{2+}	Magnesium ion
Mn^{2+}	Manganese(II) ion
Na^+	Sodium ion
NH_3	Ammonia
NH_4^+	Ammonium ion
N_2O	Dinitrogen monoxide (Nitrous oxide)
NO	Nitrogen oxide
NO_2	Nitrogen dioxide
NO_2^-	Nitrite ion
NO_3^-	Nitrate ion
NO_X	Nitrogen oxides (mixture of NO and NO_2)
O_2	Oxygen
PO_4^{3-}	Phosphate ion
SO_2	Sulphur dioxide

Chemical formula	**Name**
SO_3	Sulphur trioxide
SO_4^{2-}	Sulphate ion
SO_X	Sulphur oxides (mixture of SO_2 and SO_3)
Sr^{2+}	Strontium ion

VII. Acronyms

Acronym	Description
AAS	Atomic absorption spectrometry
AFNOR	Association Française de Normalisation (French association for standardisation)
AM	Alternative method
AMS	Automated measuring system(s)
AOX	Adsorbable organically bound halogens
APHA	American Public Health Administration
API	American Petroleum Institute
ASI	Austrian Standards Institute
AST	Annual surveillance test
ATEX	Directive 94/9/EC on equipment and protective systems intended for use in potentially explosive atmospheres (ATEX)
BAT	Best available technique
BAT-AEL	Emission level associated with the BAT
BAT-AEPL	BAT-associated environmental performance level. BAT-AEPLs include BAT-AELs
BOD_n	Biochemical oxygen demand after *n* days
BREF	BAT reference document
CAK BREF	BREF for the Production of Chlor-alkali
Cefic	European Chemical Industry Council (from its French name Conseil Européen des Fédérations de l'Industrie Chimique)
CEMBUREAU	European Cement Association
CEN	European Committee for Standardization
CENELEC	European Committee for Electrotechnical Standardisation
CEN/TC	European Committee for Standardization/Technical Committee
CEN/TR	CEN technical report
CEN/TS	CEN technical specification
Cerame-Unie	European Ceramic Industry Association
CEWEP	Confederation of European Waste-to-Energy Plants
CFA	Continuous flow analysis
CLM BREF	BREF for the Production of Cement, Lime and Magnesium Oxide
COD	Chemical oxygen demand
CONCAWE	European Oil Company Organisation for Environment, Health and Safety
CWW BREF	BREF for Common Waste Water and Waste Gas Treatment/Management Systems in the Chemical Sector
DAHS	Data acquisition and handling system(s)
DEFRA	Department for Environment, Food and Rural Affairs
DIAL	Differential absorption LIDAR
DIN	Deutsches Institut für Normung (German Institute for Standardisation)
DOAS	Differential optical absorption spectroscopy
DOC	Dissolved organic carbon
EA	European co-operation for accreditation
ECGA	European Carbon and Graphite Association
ECVM	European Council of Vinyl Manufacturers
EC_x	Effective concentration
EEA	European Environment Agency
EEB	European Environmental Bureau
EIPPCB	European Integrated Pollution Prevention and Control Bureau
ELV	Emission limit value
EMEP	European Monitoring Evaluation Programme

Acronym	Description
EN	European standard
EPA	Environment Protection Agency
EPF	European Panel Federation
E-PRTR	European Pollutant Release and Transfer Register
EROM	European reference odour mass
ESWET	European Suppliers of Waste-to-Energy Technology
ETSI	European Telecommunications Standards Institute
EuLA	European Lime Association
Eurelectric	Union of the Electricity Industry
EUROFER	European Steel Association
Eurometaux	European Non-ferrous Metals Association
Euromines	European Association of Mining Industries, Metal Ores and Industrial Minerals
FGD	Flue-gas desulphurisation
FIA	Flow injection analysis
FID	Flame ionisation detector/detection
FTIR	Fourier transform infrared (spectrometry)
GC-MS	Gas chromatography mass spectrometry
GFC	Gas filter correlation
GLS BREF	BREF for the Manufacture of Glass
GPS	Global positioning system
GUM	Guide to the expression of uncertainty in measurement
HOI	Hydrocarbon oil index
HpCDD	Heptachlorodibenzo-*p*-dioxin
HpCDF	Heptachlorodibenzofuran
HPLC	High-performance liquid chromatography
HxCDD	Hexachlorodibenzo-*p*-dioxin
HxCDF	Hexachlorodibenzofuran
IC	Inorganic carbon
ICP-OES	Inductively coupled plasma optical emission spectrometry
ICP-MS	Inductively coupled plasma mass spectrometry
ICS BREF	BREF for Industrial Cooling Systems
IEC	International Electrotechnical Commission
IED	Industrial Emissions Directive
INERIS	Institut National de l'Environnement Industriel et des Risques (French National Competence Centre for Industrial Safety and Environmental Protection)
IPCC	Intergovernmental Panel on Climate Change
IPPC	Integrated pollution prevention and control
IR	Infrared (spectrometry)
IRPP BREF	BREF for the Intensive Rearing of Poultry or Pigs
IS BREF	BREF for Iron and Steel Production
ISO	International Organization for Standardization
ISO/DIS	Draft international standard
I-TEF	International toxic equivalence factor
IUPAC	International Union of Pure and Applied Chemistry
LCP BREF	BREF for Large Combustion Plants
LC_X	Lethal concentration
LDAR	Leak detection and repair (programme)
LID	Lowest ineffective dilution
LIDAR	Light detection and ranging or light identification, detection and ranging
LLoA	Lower limit of application
LLoQ	Lower limit of quantification

Acronym	Description
LoD	Limit of detection
LoQ	Limit of quantification
LUA NRW	Landesumweltamt Nordrhein-Westfalen (Environment Agency of the State of North Rhine-Westphalia)
MCERTS	Monitoring Certification Scheme (of the Environment Agency of England)
MEG	Monitoring expert group
NDIR	Non-dispersive infrared (spectrometry)
NDUV	Non-dispersive UV (spectrometry)
NEN	Nederlands Normalisatie-instituut (Dutch standardisation institute)
NFM BREF	BREF for the Non-Ferrous Metals Industries
NH_4-N	Ammonium nitrogen (includes NH_3 and NH_4^+)
N_{inorg}	Total inorganic nitrogen
NIST	National Institute of Standards and Technology
NMVOC	Non-methane volatile organic carbon
NO_2-N	Nitrite nitrogen
NO_3-N	Nitrate nitrogen
NOC	Normal operating conditions
NOEC	No observed effect concentration
NPOC	Non-purgeable organic carbon
NTA	Netherlands technical agreement
OCDD	Octachlorodibenzo-*p*-dioxin
OCDF	Octachlorodibenzofuran
OFC BREF	BREF for the Manufacture of Organic Fine Chemicals
OGI	Optical gas imaging (techniques)
OMA	Operator monitoring assessment
OTNOC	Other than normal operating conditions
PAH	Polycyclic aromatic hydrocarbon
P-AMS	Portable AMS
PBDE	Polybrominated diphenyl ether
PBT	Persistency, bioaccumulation, toxicity
PCB	Polychlorinated biphenyl
PCDD	Polychlorinated dibenzo-*p*-dioxin
PCDF	Polychlorinated dibenzofuran
PeCDD	Pentachlorodibenzo-*p*-dioxin
PeCDF	Pentachlorodibenzofuran
PEMS	Predictive emission monitoring systems
PID	Photo ionisation detector
$PM_{2.5}$	Particulate matter which passes through a size-selective inlet with a 50 % efficiency cut-off at 2.5 µm aerodynamic diameter
PM_{10}	Particulate matter which passes through a size-selective inlet with a 50 % efficiency cut-off at 10 µm aerodynamic diameter
PP BREF	BREF for the Production of Pulp, Paper and Board
prEN	Draft European standard
QAL	Quality assurance level
REF BREF	BREF for the Refining of Mineral Oil and Gas
RDM	Reverse dispersion modelling
ROM	JRC Reference Report on Monitoring
SCR	Selective catalytic reduction
SNCR	Selective non-catalytic reduction
SOF	Solar occultation flux
SPE-AOX	Dissolved adsorbable organically bound halogens after solid phase extraction
SRM	Standard reference method

Acronym	Description
SRU	Sulphur recovery unit
TC	Total carbon
TCDD	Tetrachlorodibenzo-*p*-dioxin
TCDF	Tetrachlorodibenzofuran
TDL	Tunable diode laser absorption (spectrometry)
TKN	Total Kjeldahl nitrogen
TN	Total nitrogen
TOC	Total organic carbon
TP	Total phosphorus
TSS	Total suspended solids
TU	Toxicity unit
TÜV	Technischer Überwachungsverein (German technical inspection body)
TVOC	Total volatile organic carbon
TWG	Technical working group
DE UBA	Umweltbundesamt (German Federal Environment Agency)
US EPA	United States Environmental Protection Agency
UV	Ultraviolet (spectrometry)
VDI	Verein Deutscher Ingenieure (German association of engineers)
VOC	Volatile organic compound
WBP BREF	BREF for the Production of Wood-based Panels
WEA	Whole effluent assessment
WHO	World Health Organisation
WHO-TEF	World Health Organisation toxic equivalence factor
WT BREF	BREF for Waste Treatment

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