

JRC Reference Report on Monitoring of emissions from IED-installations

Monitoring of emissions to air and water

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

> JOINT RESEARCH CENTRE Institute for Prospective Technological Studies Sustainable Production and Consumption Unit European IPPC Bureau

FINAL DRAFT October 2013



Research Centre NORMAGORAFINAPROGRESS

Acknowledgements

This JRC Reference Report on Monitoring (ROM) was produced by the European Integrated Pollution Prevention and Control Bureau (EIPPCB) at the European Commission's Joint Research Centre – Institute for Prospective Technological Studies (IPTS) under the supervision of Serge Roudier (Head of the EIPPCB) and Luis Delgado (Head of the Sustainable Production and Consumption Unit).

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

This report was elaborated by the EIPPCB on the basis of:

- 1. general available information on the monitoring of emissions;
- 2. the experiences derived from the exchange of information taking place under the framework of the implementation of the Industrial Emissions Directive (IED, 2010/75/EU); and
- 3. an exchange of information between an expert group on monitoring (MEG) which was set up for the purpose of elaborating this document.

The following members of the MEG are highlighted as playing an 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, CONCAWE, EURELECTRIC, EUROFER, EUROMETAUX, ECGA/EUROMINES.

Furthermore, the Technical Committee CEN/TC 230 'Water analysis' and CEN/TC 264 'Air quality' of the European Committee for Standardisation actively participated in the working process and provided, among others, the Annexes A.1 EN standards for air measurements and A.2 EN standards for water measurements.

The whole EIPPCB team provided contributions and assisted in peer-reviews.

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PREFACE

The European Commission decided in the period 2011/2012 to develop a JRC Reference Report on Monitoring (ROM) based on the revision of the reference document on the General Principles of Monitoring (MON REF 2003). The ROM aims to cover and update aspects currently covered by the MON REF, as well as to include further relevant topics, e.g. concerning the monitoring of odour emissions. Other aspects included in the MON REF, e.g. compliance assessment, are not covered by the ROM, because of its restricted scope.

The ROM summarises commonly available information collected by the EIPPCB from various sources, such as internet pages, international and national standards, and publications. Some Member States also provided special contributions summarising their measurement practises. All the information gathered was made available to a Monitoring Expert Group (MEG), unless protected by copyright, who carried out an exchange of views. All contributions are gratefully acknowledged.

The ROM is not a legally binding interpretation of the IED - the legally binding text is that of the Directive itself. However, the ROM can act as a reference to enhance the consistent application of the Directive by those involved. Therefore, the document aims to both inform those involved in implementing the Directive about the general aspects of emission monitoring, and also it brings together information on monitoring that may be of use in the production 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 Institute for Prospective Technological Studies at the following address:

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1 INTRODUCTION

The monitoring of emissions represents an important and critical issue for the assessment of the environmental performance of industrial installations and for verification of the emission levels associated with the implementation of best available techniques (BAT-AELs) under the Industrial Emissions Directive (IED, 2010/75/EU). All BAT reference documents (BREFs) and, in particular, BAT conclusions include references to monitoring in association with BAT-AELs. Additionally, the EIPPCB has observed that monitoring is increasingly being discussed during the elaboration process of each of the BREFs.

The way monitoring methods are applied throughout Europe can vary, as can the procedures for handling monitoring results; this can affect the data collection process and comparison of the results.

This JRC Reference Report on Monitoring (ROM) summarises the commonly available information on the monitoring of emissions to air and to water at IED installations and suggests, where possible and appropriate, recommendations or hints for the elaboration of BREFs and their BAT conclusions, also taking into account future data collections.

The information and recommendations provided by this document may help the Technical Working Groups (TWG), set up for each BREF, to define and decide on BAT conclusions concerning monitoring during the BREF elaboration process, on the basis of the requirements set out by the IED and the BREF Guidance for the exchange of information under the IED (Commission Implementing Decision 2012/119/EU). In any case, the BAT conclusions on monitoring in each sectoral BREF have to reflect the results of the information exchange and the specific requirements of each industrial sector. These specifics cannot be anticipated by the ROM, which can only provide general information and recommendations.

The information provided by this document may also help competent authorities define monitoring requirements. However, this is strongly dependent on the compliance assessment regime of every single Member State and on specific local conditions which are outside the scope of this document.

The content of the ROM reflects the experience the EIPPCB has gained during the elaboration of a number of BREFs and their corresponding data collections, and which highlighted the need for a clear, unambiguous and sufficient formulation of monitoring conclusions associated to BAT and/or BAT-AELs.

Therefore, the ROM aims to provide, among other aspects, information on:

- definitions of the common pollutants or parameters being monitored;
- different monitoring regimes (continuous, periodic, operating conditions, etc.);
- approaches used for quality assurance (use of (EN) standards, accreditation, data treatment, measurement uncertainty, etc.);
- timing conditions (time of sampling, sampling duration, frequency, averaging etc.); and
- reporting of monitored data and measuring results.

In addition to the most commonly used monitoring practices, the ROM also provides information on less common, yet nonetheless appropriate, monitoring methods, such as odour measurements and biomonitoring, in view of the anticipated release of related EN standards. In addition to a brief description of the methods, the document tries to clarify which cases these methods may be considered appropriate for, for the monitoring of emissions.

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2 SCOPE

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

- 1. to inform competent authorities and operators of the general aspects of the monitoring of emissions from installations under the scope of the Industrial Emissions Directive (IED) (and, most likely, as relevant to other industrial installations);
- 2. to bring together background information on monitoring that may be of use to the European IPPC Bureau and TWG members 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 Article 14(1)(c) 'emission monitoring requirements' of the IED.

This report addresses general principles and other relevant aspects concerning the monitoring of emissions and associated parameters that are the basis for deciding the approach and frequency of monitoring, as well as for the elaboration and use of monitoring data. Therefore, this document aims to promote the accuracy, reliability, representativity and comparability of monitoring data from industrial installations.

This document covers the following topics:

- general aspects of monitoring such as:
 - different monitoring objectives,
 - different monitoring approaches including the choice of pollutants and parameters to monitor,
 - quality assurance, including personnel and laboratory qualifications and measurement uncertainty,
 - use of CEN (EN), ISO and other standards,
 - costs associated with monitoring;
- monitoring of emissions to in different environmental media such as air (including odours, diffusive and fugitive emissions, biomonitoring) and water (including toxicity tests), etc. using continuous or periodic measurements, covering including:
 - measurement planning,
 - monitoring frequency,
 - measurement, expression, and documentation of auxiliary parameters,
 - data treatment,
 - reporting of measurement results;
- monitoring approaches for other than normal operating conditions;

monitoring of emissions from diffusive and fugitive sources

- monitoring using indirect methods such as surrogate parameters, mass balances and predictive emissions monitoring (PEMs);
- evaluation of monitoring results.

This document focuses on the monitoring of industrial emissions at source; therefore, the following topics are **not covered** by this document:

• Process monitoring

etc

Monitoring 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 should be covered in the sectoral BREFs.

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- Detailed information on monitoring methods For Europe, this belongs to CEN, which is for emission monitoring the only European organisation according to Directive 98/34/EC for the planning, drafting and adoption of European Standards.
- Specific monitoring considerations for industrial sectors Industry-specific aspects will be covered by sectoral BREFs. In this document illustrative examples are given, where useful, to show how the provided information can be used for elaborating BAT conclusions on monitoring.
- *Monitoring of greenhouse gases* This is covered by Commission Regulation (2011) on the monitoring and reporting of greenhouse gas emissions pursuant to Directive 2003/87/EC of the European Parliament and of the Council.
- *Reporting according to EPRTR* This is covered by the Guidance Document for the implementation of the European PRTR (2006). However, the given information on monitoring aspects can also be used in the case of reporting according to EPRTR, to ensure that a harmonised methodology is used, where appropriate.
- Monitoring of the environment quality, such as ambient air or surface water quality
- *Inspection of installations* Issues related to inspections will be not covered by this document.
- Assessing compliance with emission limit values.

The information on monitoring described and the examples given in this document are neither prescriptive nor exhaustive.

3 GENERAL ASPECT OF MONITORING IN DIFFERENT ENVIRONMENTAL MEDIA

3.1 Possible objectives of monitoring

The objectives of monitoring are many and diverse. Monitoring in this report means a systematic surveillance of the variations of a certain chemical or physical characteristic of an emission, discharge, consumption, etc. at the source. 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).

The information can be used for several different purposes. According to the scope of this document (see Chapter 2), one objective of monitoring is to provide information on achieved emission levels associated with the application of BAT and to allow comparison of monitoring these results with defined (established) BAT-associated emission levels (BAT-AELs) for a specific industrial sector.

Another objective can be the monitoring of emissions with the scope of providing suitable data for assisting in the definition of In the elaboration of BAT and associated BAT-AELs, the information provided by the monitoring of emissions is used Tto show the performance of a technique, or a set of techniques, and to make a comparison between techniques. This requires, in general, a great amount of data, gathered over a long time period (e.g. one or more years), to ensure that the data collected is representative of the performance of the techniques under the possible variations of normal operating conditions (NOC).

Monitoring of emissions for assessing the performance of a BAT and associated emission levels (BAT-AELs) can also be based (or include) the control of surrogate parameters (see Sections 4.2.5.1 and 4.3.3.1), with possible when these bring practical and/or cost advantages.

Monitoring data obtained for the purpose of emission monitoring may also serve other purposes, although, in these cases some preliminary treatment of data may be necessary.

In any case, monitoring is a valuable source of information, which can also be used beyond the objectives related to this report, e.g. for assessing whether industrial installations are operating according to BAT, as mentioned above. For example, monitoring can also be applied:

- to assist in finding the optimal balance between process yield, energy efficiency and resource input and associated emission levels optimising the process, for more efficient operation and to minimise emissions;
 - to provide help to analyse the causes of certain types of emission behaviour (e.g. to detect reasons for variations in emissions under normal operating conditions (NOC) or other than normal operating conditions (OTNOC));
- to provide measurements to predict the emission behaviour of a facility or installation, e.g. after operational conversions, operational breakdowns or an increase in capacity;
- to provide feedback on the performance of abatement systems by continuous monitoring systems;
- to determine the relative contribution of different sources to the overall emissions;
- to provide measurements for safety checks;
- to report emissions for specific inventories (e.g. local, national and international, such as E-PRTR);
- to provide data for assessing environmental impacts (e.g. for input to models, pollutant load maps, assessment of complaints);

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- to monitor emissions for the setting or levying of environmental charges and/or taxes or for establishing taxation on behalf of emission trading;
- to monitor emissions for assessing compliance with permit requirements.

Monitoring does not necessarily mean measurement. The terms measuring and monitoring are often interchanged in common usage. In this report 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 current measurements and calculations (see Section 3.2.3.3).

Depending on the objective of monitoring, there is a need to define several parameters to ensure that the selected monitoring regime leads to a sufficient quality of data. The following list gives an overview of possible points to consider, for which more information is given in the related chapters of this report:

- measurements carried out continuously or periodically,
- determination of average or maximum emission levels under normal operating conditions (NOC),
- measurements in cases of other than normal operating conditions (OTNOC),
- control measurements after a certain period to determine the state of the monitoring system,
- measurements for the calibration of continuous emission monitoring systems,
- measurements to test the function of continuous emission monitoring systems.

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 accredited testing laboratories, any other external contractors and other possible users of the monitoring measurement 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/measuring planning and in the reporting of the monitoring results (see Sections 4.2.2 and 4.3.2).

A clearly defined monitoring objective, an appropriate monitoring programme based on standardised methods (e.g. EN standards) and a quality assurance system in accordance with EN ISO/IEC 17025:2005¹ help to ensure reliable, representative and comparable monitoring data.

¹ EN ISO/IEC 17025:2005 General requirements for the competence of testing and calibration laboratories (ISO/IEC 17025:2005)

3.2 General approaches to decide on an appropriate monitoring regime

3.2.1 Overview

In principle there are various approaches that can be taken to monitor a specific parameter, although some of them may not be appropriate for particular applications. In general, these approaches can be classified into three main groups: direct measurements, indirect measurements or other indirect monitoring estimation methods.

When choosing one of these approaches for monitoring there must be a balance between the availability of the method, reliability, representativeness and comparability of results, level of confidence, costs and the environmental benefits.

Selection of the parameter(s) to be monitored depends on the production processes, the raw materials, the chemicals used in the plant and the respective key environmental issues. It is useful if the parameter chosen to be monitored also serves the plant operation control needs. The frequency at which the parameter is monitored varies widely according to the needs and risks to the environment and according to the monitoring approach taken.

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 quantities (e.g. temperature, pressure; see Sections 4.2.2.2.5 and 4.2.2.3.7), air and water flow, raw material input, production capacity. Usually, the number of parameters to be monitored exceeds the ones indicated in a permit or in the BAT conclusions for a given industrial sector. All parameters necessary to describe emissions and the related circumstances such as normal operating conditions (NOC) should be mentioned in the monitoring plan or sampling programme and should be part of the monitoring report.

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

3.2.2 Risk-based approach

It is best practice to assess the overall risk posed by emissions from an installation to the environment and to match the frequency and scope of the monitoring programme or regime to this risk. These aspects of the monitoring programme may be determined by considering and combining several individual risk factors². 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 "continuous and comprehensive" for critical cases. Examples of the risk factors to be considered include:

- the size of the installation, which may determine its environmental impact;
- 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 harm effects resulting from emissions, taking into account the pollutant types and their rates of release, and including the potential failure of abatement equipment;

² IMPEL 2001, European Union Network for the Implementation and Enforcement of Environmental LAW. Best practice in compliance monitoring (modified)

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- the risk of emission limit values and/or ambient quality standards being exceeded;
- 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 level of technical complexity of the installation and the hazardousness of the substances handled toxicological complexity which may increase uncertainties with regard to its operation and environmental impact;
- the degree of public concern, particularly with regard to contentious installations.

An example of how some of these items can be classified into different levels of risk is described below.

In this example, which deals with emissions to water, the main elements influencing the risk of having an actual emission higher than the emission limit value (ELV) are listed in Table 3.1 and classified into different levels of risk, ranging from a low to a high level of risk³. The risk evaluation should take local conditions into consideration, including items that may not be reflected in this table e.g. some of the bullet points mentioned above. The final assessment of likelihood or consequences should be based on the combination of all items, not on a single item, taking legal the requirements into account.

³ MON REF Reference Document on the General Principles of Monitoring, July 2003

Table 3.1:	Example	of	items	influencing	the	likelihood	of	exceeding	the	ELV	and	the
	conseque	ices	of exce	eding the EL	V in	the case of o	emis	ssions to wa	ter			

Items to consider and corresponding risk scoring level	Low Level	Medium Level	High Level				
Items influencing the likelihood of exceeding the ELV							
(a) Number of individual sources contributing to the emission	Single	Several (1 - 5)	Numerous (> 5)				
(b) Stability of operating process conditions	Stable	Stable	Unstable				
(c) Buffer capacity of effluent treatment	Sufficient to cope with upsets	Limited	None				
(d) Treatment capacity of the source for excess emissions	Able to cope with peaks (by dilution, stoichiometric reaction, oversize, spare treatment)	Limited capabilities	No capabilities				
(e) Potential for mechanical failure due to caused by corrosion	No or limited corrosion	Normal corrosion, covered by design	Corrosion conditions still present				
(f) Flexibility in product output	Single dedicated production unit	Limited number of product grades	Many product grades, multipurpose plant				
(g) Inventory of hazardous substance	Not present or production dependent	Significant (compared to ELV)	Large inventory				
 (h) Maximum possible emission load (concentration × flow rate) 	Significantly below the ELV	Around the ELV	Significantly above the ELV				
Items	for assessing the conseque	ences of exceeding the El	LV				
(i) Duration of potential failure	Short (< 1 hour)	Medium (1 hour to 1 day)	Long (> 1 day)				
(j) Acute effect of the substance	No	Potential	Likely				
(k) Location of the Industrial area		Safe distance between industrial and residential area	Residential area nearby				
(1) Dilution ratio in the receiving mediaHigh (e.g. above 1000)		Normal	Low (e.g. less than 10)				

The results of the assessments of these items can then be combined and represented in a simple diagram plotting the likelihood of exceeding the ELV against the consequences of exceeding that ELV, see Figure 3.1. The combinations of these items can be decided on a case-by-case basis and can be done in such a way that more weight may be given to the most relevant items. 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.



Figure 3.1: Monitoring regime according to the risk of exceeding the ELV

The corresponding monitoring regimes for this water related example based on 24-hour flow-proportional composite sampling or spot sampling, as relevant (see Section 4.3.2.5), are:

Occasional - four times per year up to once per month: The main purpose is to check the actual level of emissions with predicted or usual conditions.

Regular (to frequent) - once per month up to once per week and/or spot sampling in special cases: Frequency needs to be high in order to detect unusual conditions or a gradual decrease of performance and to rapidly initiate corrective actions (e.g. diagnostic, repair, maintenance).

- 3. (**Regular to**) **Frequent** once per week up to once per day and/or spot sampling in special cases: Accuracy needs to be high and uncertainties of the monitoring chain minimised in order to ensure no harm of the receiving environment.
- 4. **Intensive** once per day or continuous or high frequency (3 to 24 times per day spot sampling, where appropriate): This is used when, for instance, unstable conditions are

likely to lead to an exceedance of the ELV. The purpose is to determine emissions at any time and/or at the exact period of time and at the level of emission reached.

In case of emissions to air, the approach given in Table 3.1 needs to be adapted by taking into account typical items that qualify the emissions to air, such as the capacity and functioning of the abatement system, the possibility of diffuse emissions, or the risk of accidents causing unexpected air emissions. The corresponding monitoring regimes for air emissions 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, where available.

For details on continuous and periodic measurements in air and associated indicative monitoring see Section 4.2.2

An example of an existing risk-based approach for assigning a monitoring regime to an air emission source can be found in the *Netherlands Emissions Guidelines for Air*⁴. 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 additionally occurs when an emission abatement technique or process-integrated measures 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:

- emission relevant parameters (ERPs), which are measurable quantities in direct or indirect relationship with the emissions to be assessed;
- periodic measurements; and
- continuous measurements.

3.2.3 Different monitoring approaches

3.2.3.1 Overview

As already mentioned, there are several approaches that can be taken to monitor a specific parameter. These include:

- direct measurements;
- indirect methods measurements:
 - indirect monitoring using surrogate parameters,
 - calculation of mass balances,
- other indirect monitoring methods:
 - other calculations,
 - use of emission factors.

⁴ Netherlands Emission Guidelines for Air, Section 3.7, Monitoring of emissions, June 2012

In principle, direct measurements (specific quantitative determination of the emitted compounds at the source) 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 should be considered to find the best monitoring solution. For instance, in those cases in which the use of surrogate parameters provides an equally good assessment of the actual emission as a direct emission 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 other than direct measurements are used, the relationship between the method used and the parameter of interest should be demonstrated, well documented and established on a regular basis.

Also, the IED and national regulations may impose requirements on the monitoring approach that should be used for a particular installation, e.g. the use of relevant EN standards or if not available ISO or national standards. The appropriate monitoring approach or even the relevant standard (EN, ISO, national) that should be used may also be indicated in the Reference Documents on Best Available Techniques (BREFs) and in the BAT conclusions to ensure that an homogenous monitoring regime is applied (see Section 3.3.2). Depending on On the basis of the characteristics of the installation and the local conditions, the monitoring approach might be modified.

When deciding on the monitoring approach associated to a certain BAT, the following considerations are important:

- suitability for the purpose, i.e. is the method suited to the original reason for monitoring, for example, to allow the measurement of the pollutant under the given normal operating conditions (NOC)?
- legal requirements, i.e. is the method in line with EU legislation?

When deciding on the monitoring approach to specify in a permit, in addition, the following considerations are important:

- 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 monitoring adequate for the proposed method, e.g. laboratory accredited according to EN ISO/IEC 17025:2005⁵ with suitable technical equipment and experienced staff?

In cases, some of the mentioned monitoring approaches may not be available for the parameter of interest. The choice depends on several factors, including the likelihood of exceeding the ELV, the consequences of exceeding the ELV (as explained in Section 3.2.1), the required accuracy, costs, simplicity, rapidity, reliability, etc., and the approach taken should also be suited to the form in which the compounds may be emitted and the concentrations expected.

3.2.3.2 Direct measurements

Monitoring techniques for direct measurements (specific quantitative determination of the emitted compounds at the source) vary with the applications, but and can be divided mainly into two types:

⁵ EN ISO/IEC 17025:2005 General requirements for the competence of testing and calibration laboratories (ISO/IEC 17025:2005)

- continuous measurement monitoring;
- periodic measurement monitoring.

3.2.3.2.1 Continuous measurement monitoring

Two types of continuous monitoring measurement techniques are generally considered (for more details see Sections 4.2.2.2 and 4.3.2.4):

- Fixed *in-situ* (or in-line) continuous reading instruments. Here the measuring cell is placed in the duct, pipe or stream itself. These instruments do not need to withdraw any sample to analyse it and are usually approved for specific applications based on optical properties. 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 to each other. Here the measuring analyser is connected via an optical fibre with the receiver. Regular maintenance and calibration of these instruments is essential.
- Fixed on-line (or extractive) continuous reading instruments. This type of instrumentation continuously extracts samples of the emission from the stream along a sampling line, and transports them to an on-line measurement station, where the samples are analysed continuously. The measurement station may be remote from the duct, and therefore care must be taken so that the sample integrity is maintained along the line. This type of equipment often requires pretreatment of the sample.

3.2.3.2.2 Periodic measurement monitoring

The following types of periodic monitoring techniques are generally considered (for more details see Section 4.2.2.3 and 4.3.2.5):

- Portable instruments used for series of measurements. These instruments are carried to and set up at the measurement location. Normally a probe is introduced at an appropriate measurement port 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, 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 to provide a detectable concentration of the emission parameter.
- 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 amount of sample taken has to be sufficient must be enough to provide a detectable concentration of the emission parameter. The sample is then analysed in the laboratory, providing an average over the sampling period, which is representative for the time at which the sample was taken.

Continuous monitoring techniques have an advantage over periodic measurement techniques that they provide a greater number of data points. They therefore provide a larger amount of data that can facilitate statistical analysis and can is statistically more reliable and are able to highlight periods of different operating conditions. Continuous monitoring 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 4.2.2 and 4.3.2, together with recommendations on their uses.

RB/BS/EIPPCB/ROM_Final_Draft

3.2.3.2.3 Campaign monitoring

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

Some situations in which campaign monitoring might be carried out are when:

- 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 determined or assessed by eco-toxicological analytical analyses;
- volatile organic compounds are to be determined for odour;
- uncertainties are to be evaluated e.g. by applying a direct approach based on paired measurements;
- a new process is to be started without previous experience about emission patterns;
- a preliminary study is necessary to design or improve techniques for the prevention or removal 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.

3.2.3.3 Indirect methods

3.2.3.3.1 Indirect monitoring using 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. The use of surrogate parameters either individually or in combination may provide a sufficiently reliable picture of the nature and proportions of the emission.

The surrogate 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 continuous gas concentration data (e.g. total organic carbon (TOC) as a surrogate organic solvents). The surrogate may provide an indication of whether a certain range or value can be satisfied if the surrogate parameter is maintained within a certain range.

Whenever a surrogate parameter is proposed to determine the value of another parameter of interest, the relationship between the surrogate and the parameter of interest must needs to be demonstrated, clearly identified and documented (see campaign monitoring in Section 3.2.3.2.3). In addition, traceability of the parameter's evaluation on the basis of the surrogate is needed.

A surrogate is only likely to be useful for compliance monitoring purposes if:

- it is closely and consistently related to a required direct value (examples are given in Chapter Sections 4.2.4 and 4.3.3);
- it is more economical or easier to monitor than a direct value, or if it can provide more frequent information;
- it is capable of being related to specified limits;
- the process conditions when surrogates 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 must be insignificant for regulatory decisions;
- it is properly described, including regular evaluation and follow-up.

Different categories of surrogate parameters may be distinguished on the basis of the strength of the relationship between the emission and surrogate.

- Quantitative surrogates give a reliable quantitative picture of the emission and can substitute for direct measurements.
- Qualitative surrogates give reliable qualitative information of the composition of the emission.
- Indicative surrogates give information about the operation of an installation or process and therefore give an indicative impression of the emission.
- Indirect monitoring Indicative surrogates using biological test methods/systems is a special group of surrogate parameters. They include toxicity tests to assess the possible hazardous character of waste water (see Section 4.3.4) and a bioindication biomonitoring to determine the contribution that the emission of an industrial installation makes to an environmental impact (see Section 4.2.5.2).

Key advantages and disadvantages of the use of surrogate parameters are discussed in more detail in Sections 4.2.5, 4.3.3 and 4.3.4, together with practical examples of the different kinds of surrogate parameters and examples of the use of surrogates in BAT conclusions.

3.2.3.3.2 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.

Therefore 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.

For example, in combustion processes the emissions of SO_2 are directly related to the amount of sulphur in the fuel, and in some cases it might be simpler and more accurate to monitor the sulphur in the fuel instead of the emission of SO_2 .

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.

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

The following simple equation can be applied when estimating emissions by a mass balance:

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:

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 facility				
Transfers =	include substances discharged to sewer, substances deposited into landfill				
	and substances removed from a facility 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.				

Care must be taken when using mass balances, since although they 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 uncertainties 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 total facility emissions. 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.

Despite their potential uncertainty, mass balances can sometimes be a useful tool to better understand emission and consumption levels.

3.2.3.3.3 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 physical/chemical properties of the substance (e.g. vapour pressure) and on mathematical relationships (e.g. ideal gas law).

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

- if the model is based on valid assumptions, as is demonstrated by previous validations,
- if their inherit uncertainty is as low as possible,
- if suitable sensitivity analyses results are presented alongside it,
- if the scope of the model corresponds to the case studied, and
- if input data are reliable and specific to the conditions of the facility.

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Fuel analysis is an example of an engineering calculation. Depending on the industrial sector, it can be used to predict SO_2 , metals and other emissions based on the application of conservation laws, if the fuel mass flow rate is available. For example, the basic equation used in fuel analysis emission calculations is the following:

Equation 3.1: $E = Q \times c/100 \times (M_W/M_{WE}) \times t \times R$

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 fuel (wt %)

 M_W = molecular weight of the chemical species emitted (kg/kmol)

 M_{WE} = elemental weight of the pollutant in fuel (kg/kmol)

t = operating hours (h/yr)

R = retention factor (kg/h).

3.2.3.3.4 Emission factors

Emission factors are numbers that can be multiplied by an activity rate or by throughput data from a facility (such as the production output, water consumption, number of animals), in order to estimate the emissions from the facility. They are applied under the assumption that all 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.

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 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). In the absence of other information, default emission factors (for example 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 data', which are combined with the emission factor to generate the estimated emission. The generic formula is:

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

Appropriate conversion factors for units may need to be applied. For example, if the emission factor is expressed as 'kg pollutant/m³ of fuel burned', then the activity data required would be expressed in terms of 'm³ fuel burned/h', thereby generating an emission estimate of 'kg pollutant/h'.

In the standard EN $11771:2010^6$, a generic method for the determination and the reporting of time-averaged mass emissions from a specific installation or from a family of installations (or common source type) is specified, using data collected by measurements, and by establishing:

⁶ EN ISO 11771:2010 Air quality - Determination of time-averaged mass emissions and emission factors - General approach (ISO 11771:2010)

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- mass emission rates by the simultaneous measurement of concentration and gas flow, using standardised manual or automatic methods, and also the estimation of the uncertainty of the measurements;
- time-averaged mass emission rates using time series of mass 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.

In the elaboration of the BREFs, the use of emissions factors is rare, with the exception of some BREFs for special industrial sectors such as 'Iron and Steel Production', 'Manufacture of Glass' and 'Intensive Rearing of Poultry and Pigs'. Instead, in general, collected data are generated by other monitoring regimes. Therefore, emission factors may need to be reviewed and approved by competent authorities when used for emissions estimation.

Emission factors are often generated for emission inventory purposes and can be obtained from several sources (e.g. EMEP/EEA⁷, EPA AP 42⁸ or VDI 3790:2010 part 3⁹). They are usually expressed as the weight of a substance emitted divided by the unit weight, volume, distance, or duration of the activity emitting the substance (e.g. kilograms of sulphur dioxide emitted per tonne of fuel burned).

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 similar operation 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.

⁷ EMEP/EEA air pollutant emission inventory guidebook 2009 - Technical guidance to prepare national emission inventories; EEA Technical report No 9/2009

⁸ US EPA AP 42, Fifth Edition, Compilation of Air Pollutant Emission Factors, Volume 1: Stationary Point and Area Sources; 2009

 ⁹ VDI 3790:2010 part 3 Environmental meteorology - Emission of gases, odours and dusts from diffuse sources - Storage, transhipment and transportation of bulk materials

3.3 Quality assurance

3.3.1 Overview

Data quality is the most critical aspect of monitoring. Reliable data are needed for assessing and comparing the performances of emission/consumption control techniques, for decision making concerning allowable levels of emissions/consumptions, 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 Over the last ten years, several changes have occurred in the regulatory framework and in the standardisation of measurement methods that which have a significant effect on the quality assurance of measurements and the quality of data received. In April 2009, the European cooperation for Accreditation (EA)¹⁰ was established according to Regulation No 756/2008¹¹, 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 17025:2005¹² and this requires that each laboratory applies a proven quality management system. This also covers the validation of methods, data treatment, determination of measurement uncertainty and the reporting of results. Applying the same rules given in EN ISO/IEC 17025:2005 guarantees a given level of quality assurance in accredited laboratories, and of the results provided by them.

For measurement uncertainty, EN ISO/IEC 17025:2005 refers to the *Guide to the Expression of Uncertainty in Measurement*¹³. Based on this Guide, a European Standard for measurements in air is available (EN ISO 20988:2007¹⁴).

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

3.3.2 Personnel and laboratory qualification

In EN ISO/IEC 17025:2005, general requirements are specified to evaluate the competence of laboratories carrying out tests (measurements) using standard methods, non-standard methods and laboratory developed methods. Accredited laboratories 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 non-standard methods and laboratory-developed methods, measurement traceability, sampling and reporting.

One key element to ensure the quality of the measurements is to operate with highly qualified personnel. This is reflected by EN ISO/IEC 17025:2005, where a high level of personal and

¹⁰ http://www.european-accreditation.org

¹¹ REGULATION (EC) No 765/2008 OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 9 July 2008 setting out the requirements for accreditation and market surveillance relating to the marketing of products and repealing Regulation (EEC) No 339/93

¹² EN ISO/IEC 17025:2005 General requirements for the competence of testing and calibration laboratories (ISO/IEC 17025:2005)

¹³ JCGM 100:2008 (GUM 1995 with minor corrections) Evaluation of measurement data — Guide to the expression of uncertainty in measurement

¹⁴ EN ISO 20988:2007 Air quality - Guidelines for estimating measurement uncertainty (ISO 20988:2007)

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technical qualifications is required for managerial and technical personnel. It is stated that '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.' In CEN/TS 15675:2007¹⁵, an informative annex with example competence criteria for personnel carrying out emission measurements is included.

To implement this, some Member States have introduced additional guidance or standards to provide more detailed information and criteria for the application of EN ISO/IEC 17025:2005¹⁶, covering also personnel qualification and making use of EN ISO/IEC 17024:2003¹⁷. For the determination of emissions, knowledge of the various technologies, including operational processes causing emissions and abatement techniques is required. Among others, audits and measurement reports are used to prove the knowledge in different technical fields.

Different levels of personnel qualification are identified relating to of the required experience and skills. In Ireland¹⁸, and England and Wales^{19,20} 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 Level 1 and 2, formal exams are set and the responsible personnel can achieve gets a certification accordingly.

In other Member States (e.g. Germany²¹) the laboratory is required to have at least one technical supervisor, at least one deputy of the technical supervisor and competent laboratory personnel, which consists of at least two more persons. The qualification of these persons is assessed during (re-) accreditation and the regular audits by the accreditation body.

Other key elements mentioned in EN ISO/IEC 17025:2005, which are needed to assure the quality of results are interlaboratory comparisons and proficiency testing. General requirements for the development and operation of proficiency testing schemes and for the competence of their providers are given in EN ISO/IEC 17043:2010²².

To follow an accreditation procedure, and to cover and fulfil all these requirements is a real challenging and requires a significant huge effort. The fulfilment of these requirements is assessed through in the course of an extensive accreditation procedure at the beginning and again during a complete reaccreditation every four²³ to five²⁴ years. Between reaccreditations, an auditing scheme is applied with a tight time schedule, including inspection surveillance visits every year or two up to three times at fixed intervals.

¹⁸ Air Emissions Monitoring Guidance Note #2 (AG2), Ireland Environmental Protection Agency 2007
 ¹⁹ MCERTS Manual stack emission monitoring Performance standard for organisations, Environment Agency November 2011 Version 7.2
 ²⁰ MCERTS Description of the formula of the formula

- ²¹ VDI 4220:2011 Quality assurance Requirements on bodies for the determination of air pollutants at stationary sources and in ambient air
- ²² EN ISO/IEC 17043:2010 Conformity assessment General requirements for proficiency testing (ISO/IEC 17043:2010)
- ²³ United Kingdom accreditation Service The Route to Accreditation <u>http://www.ukas.com/library/About-Accreditation/Apply-for-</u>
- Accreditation/The%20Route%20to%20Accreditation.pdf
 Deutsche Akkreditierungsstelle GmbH (DAkkS)
 http://www.dakks.de/en/content/how-does-accreditation-procedure-work

¹⁵ CEN/TS 15675:2007 Air quality - Measurement of stationary source emissions - Application of EN ISO/IEC 17025:2005 to periodic measurements

¹⁶ VLAREL - Order of the Flemish Government of 19 November 2010 establishing the Flemish regulation on recognitions relating to the environment

¹⁷ EN ISO/IEC 17024:2003: Conformity assessment - General requirements for bodies operating certification of persons (ISO/IEC 17024:2003)

MCERTS Personnel Competency Standard for Manual Stack-Emission Monitoring, Environment Agency Version 8 April 2012

This does not necessarily mean that a non-accredited laboratory cannot achieve the same quality of measurements as an accredited one. But if the results are questionable, comparability and reliability of the applied methods will have to be demonstrated by the not-accredited laboratory even if it applies CEN standards. For accredited laboratories this is already done systematically and in a transparent manner during accreditation and can be proven at any time. Therefore, in particular in cases of compliance assessment, the majority of Member States²⁵ only accept the results of measurements carried out by accredited laboratories.

Accredited laboratories can be run by plant operators, authorities or third parties (e.g. consultants, experts) but need to be independent. In general, air quality emission measurements are carried out by third party laboratories, whereas emission measurements in water are carried out to a large extent by plant operators. This is mainly related to several facts detailed below.

For water measurements, the main parameters measured are the key process parameters. 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, sampling is relatively easy, and also the results can be used to show the amount of pollutants released to the receiving environment.

For air measurements, the key process parameters differ from the measurement of releases to the environment (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 and, also complex and expensive sampling equipment is needed, independent from the analysing equipment for on-site measurement. For these reasons, air emission measurements are mainly carried out by (accredited) third parties, in particular periodic measurements and the calibration of continuous measurement equipment.

In the UK, a special Operator Monitoring Assessment (OMA) scheme for emissions to air and/or water from industrial installations regulated under the Environmental Permitting Regulations is in place to strengthen the auditing of operators' self-monitoring arrangements. The OMA scheme is used by the Environment Agency²⁶, 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.

For the EIPPCB and the TWGs, the use of data generated by accredited laboratories has another advantage. During the elaboration of BREFs and in the exchange of information according to Article 13 of the IED²⁷, a lot of data-sets are provided and in assessing them, it is quite obvious that there are sometimes deviations which cannot be explained. Therefore, it is advisable to take into account accreditation as an additional criterion for 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.

²⁵ See references to different member states in Section 3.3.2.

MCERTS Guidance on undertaking an Operator Monitoring Assessment of emissions to air and /or water - Industrial installations regulated under the Environmental Permitting Regulations, Version 3, April 2009
 April 2009

²⁷ DIRECTIVE 2010/75/EU OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 24 November 2010 on industrial emissions (integrated pollution prevention and control)

3.3.3 Use of standardised methods

According to Directive 98/34/EC²⁸, the only European Standardisation Body is CEN (European Committee for Standardisation), with the exception of those for electrotechnology (CENELEC) and telecommunication (ETSI). In the elaboration of European Standards (ENs), the National Standardisation Bodies of 33 National Members including all EU Member States are involved.

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 at least these laboratories are working according to these standards and applying them in a harmonised way.

The currently (2013) available EN standards for the measurements of emissions to air are listed in Annex A.1 and of emissions to water in Annex A.2.

The precedence of the CEN standards is reflected in the text used in the IED in Article 70, Annex V and Annex VI for the monitoring of emissions: *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.* Whenever the objective of the measurement is to provide data for compliance assessment, as is the case in the IED, EN standards shall be used with priority, to guarantee comparable, repeatable and reproducible data all over Europe.

In the formulation used in the IED, the second priority is given to ISO, national or other international standards. The elaboration of ISO standards is not in any case similar to the one for CEN standards, but in many cases, in particular for measurements in water, ISO standards are transferred into CEN standards without any alteration.

For CEN standards, the elaboration process requires a validation during the standardisation process as described in CEN Guide 13 *Environmental test methods*²⁹. In the validation of a method, the suitability of the measuring principle for the intended measurement objective is demonstrated. It 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 test laboratories on industrial plants in different parts of Europe.

For national or other international standards the elaboration process may also be different. Experiences and quality requirements of other Member States may not be included in these standards. Therefore it has to be shown in a transparent manner that the provision of data is of an equivalent scientific quality.

In EN ISO/IEC 17025:2005, laboratory-developed and non-standard methods are also mentioned and it is stated that these methods need to be validated. During validation, the range and accuracy of the values have to be assessed e.g. the uncertainty of the results, detection limit, selectivity of the method, linearity, limit of repeatability and/or reproducibility, robustness against external influences and/or cross-sensitivity against interference from the matrix of the sample/test object. By analysing these data, it should be possible to decide on the scientific quality of the measurement results.

²⁸ DIRECTIVE 98/34/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 22 June 1998 laying down a procedure for the provision of information in the field of technical standards and regulations

²⁹ CEN Guide 13:2008 Validation of environmental test methods

General requirements on how to show in a transparent manner that the provision of data derived by other than EN standards or by laboratory-developed methods is of an equivalent scientific quality are laid down in EN ISO/IEC 17025:2005, EN ISO/IEC 17043:2010³⁰ and in CEN/TS 14793:2005³¹. Further information is available in several standards and technical specifications (EN 15259:2007, CEN/TS 15674:2007, CEN/TS 15675:2007, EN 5677-n, and can be found in more detail in Sections 4.2 'Emissions to air' and 4.3 'Emissions to water'.

The following list summarises the hierarchy that generally applies for the application of standards:

- 1. EN standards;
- 2. ISO standards, other international standards, national standards;
- 3. validated laboratory-developed and non-standard methods.

The national requirements for compliance assessment of several Member States are in line with the described use of standards for emission measurement, also including compiled lists of which standard should be used for the measurement of specific pollutants e.g. Germany^{32,33}, Ireland³⁴, Netherlands³⁵, Poland³⁶ and UK^{37,38,39}.

Even in compliance assessment it can be appropriate to use simplified test methods e.g. in cases when it is proven that the exceedance of an emission limit value is very unlikely. One way to prove this is to carry out a full set of emission measurements with standardised methods under normal operating conditions. If the results show that the values are far from the emission limit value given in the permit, it may be reasonable to use simplified indicative monitoring methods. If operating conditions change, leading to higher emissions levels, standardised methods should again be used for emission measurements until the emissions

It is also advisable to apply standardised measurement methods regularly in time, following a defined calendar, for instance carrying out periodic measurements once every three years and using indicative methods in between. This might be the case for smaller installations which emit only small loads of pollutants.

Sometimes, in addition to the regular application of standardised measurement methods, it might be advisable to also use indicative or simplified test methods. However, the use of indicative or simplified test methods in compliance assessment is, if at all, very limited. They might be appropriate when, e.g. between periodic measurements carried out for compliance assessment, an indication of the emissions is sufficient.

EN ISO/IEC 17043:2010 Conformity assessment - General requirements for proficiency testing (ISO/IEC 17043:2010)

CEN/TS 14793:2005 Stationary source emission - Intralaboratory validation procedure for an alternative method compared to a reference method

³² Air Pollution Prevention - Manual on Emission UBA-Texte 06/08, ISSN 1862-4804, UBA, Germany 2008

³³ German Waste Water Ordinance 2004

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- ³⁴ Air Emissions Monitoring Guidance Note #2 (AG2), Ireland Environmental Protection Agency 2007
- ³⁵ Manual Measurement of Air Emissions- InfoMil Netherlands June 2012
- ³⁶ Comment derived during elaboration of a BREF (Poland)
- ³⁷ MCERTS Technical Guidance Note (Monitoring) M3 How to assess monitoring arrangements for emissions to air in EPR permit applications, Environment Agency, England and Wales, Version 1, 2011
- ³⁸ Scottish Release Inventory (SPRI) Operator Guidance on Release Estimation Techniques (RET), Scotland 2011
- ³⁹ MCERTS Technical Guidance Note (Monitoring) M2 Monitoring of stack emissions to air. Environment Agency, England and Wales, Version 8.1, 2011

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Another important factor that can have an influence on the use of standardised methods is the potential environmental risk associated with the pollutant (measurand) in combination with the location of the installation. If the environmental risk is high because there are sensitive subjects in the surroundings, it might be is advisable to always use standardised methods to give 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. However, in the case of compliance assessment, the use of standardised methods is, in general, 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 to achieve (unless it is stated otherwise by a specific legislation e.g. EU Emissions Trading Scheme).

To summarise the different options presented above, it can be stated that, in general most cases, the use of EN standards is required by the regulatory authority recommended when the results are to be used for compliance assessment, because this guarantees comparable, reliable and reproducible measurement results, 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 is of an equivalent scientific quality. The use of Ssimplified indicative methods is very limited, might be used in special cases as described above.

In general, The following standard text is currently (2013) used in 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.'

3.3.4 General aspects of data treatment

3.3.4.1 Overview

When evaluating data to be used for the elaboration of BAT-AELs and also for checking permit conditions, it is important to have information available about the treatment of the submitted measurement results and the operating and reference conditions covered by the reported data (for reporting see Sections 4.2.2.2.7 and 4.3.2.7).

Information on the averaging of measurement results and the measurement uncertainty related to these results is of fundamental importance. Also, some performance characteristics of the analytical method, such as the limit of detection and the limit of quantification, have to be taken into account when assessing data as well as outlier values, their detection and their treatment. In the following sections, the aforementioned items will be discussed with regards to their relevance for the elaboration of BAT-AELs and for checking permit conditions.

3.3.4.2

Averaging measurement results

How to average measurement results or how to aggregate data are questions which occur after every measurement series. The choice strongly depends on the measurement frequency (continuous - periodic) and the compliance assessment regime applied.
For the results of **continuous measurements,** it is obvious that averaging is necessary to summarise the results. Depending on the time period (e.g. day, month, year) and the number of validated values⁴⁰, the result of the measurement can be called a daily, monthly or yearly average. There are rules available on how to validate data (see Section 4.2.2), which data should be accepted and which excluded (e.g. other than normal operating conditions, see Section 3.4), including measurement uncertainty. If the number of valid results is sufficient, the result is considered representative for the operating conditions covered.

For **periodic measurements**, the result of a measurement is, in any case, an average over the sampling period, which can be e.g. 30 minutes for air emission measurements or 24 hours for water emission measurement (some examples for different sampling periods are given in Chapter 4 for different environmental media). Establishing how many samples are necessary to determine a representative daily or monthly or yearly average (e.g. 30 minutes for air or 24 hours for water) is a very complex task and which requires taking into account several criteria.

For calibrating permanently installed systems or for carrying out assessments of process control, it might be useful not to average the real time data provided by portable instrumental analysers.

In most cases, it is not possible to guarantee representativeness solely by the number of samples taken. Other assumptions need to be made, as explained in more detail in Section 4.2.2.3. Therefore, in general, it is assumed that, if the samples are taken under well-defined and controlled normal operating conditions (NOC), the results of the measurements are representative for these conditions.

For the averaging of the results obtained by periodic measurements, there are different approaches in different legislations, as well as in different environmental media. The averaging periods are from ten minutes, thirty minutes, one hour, and twenty-four hours up to yearly averages. To avoid misinterpretation of the monitoring results, clear and unambiguous definitions should be used. An example is given in Table 3.2, based on the averaging periods commonly used in BAT conclusions.

40 DIRECTIVE 2010/75/EU OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 24 November 2010 on industrial emissions (integrated pollution prevention and control)

Air							
а	Daily average	Average over a period of 24 hours measured by continuous measurements (*)					
b	Monthly average	Average calculated from all daily averages obtained by continuous measurements (*)					
с	Average over the sampling duration	Average over at least 30 minutes measured by periodic measurements (**)	C				
d	Daily/Monthly/Yearly average (***) (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					
Wat	er						
e	Daily average	Average over a sampling period of 24 hours taken as a flow- proportional composite sample					
f	Monthly/Yearly average	Average (****) calculated from all daily averages obtained during one month/one year					
g	Average of samples obtained during one month	Average (****) of at least four (i.e. at least one sample every week) 24-hours flow-proportional composite samples taken per month					
h	Average of samples obtained during one year	Average (****) of at least 12 (i.e. at least one sample taken every month) 24-hours flow-proportional composite samples taken per year					
i	Daily/Monthly/Yearly average (^{***}) (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					
(*)	Continuous measurement means,	according to EN 14181:2004, measurements with an automated					
(**) Periodic measurement means, according to EN 15259 2007, determination of a measurement at specified							
time intervals using manual or automated reference methods.							
(***) 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.							
(Weighted average considering the daily flows.							

Table 3.2: Examples for averages for air and water emissions

In practice, there are two common approaches for assessing the results of periodic measurements, based on different averaging rules.

In some Member States (e.g. UK, Germany) each measurement result, after applying the measurement uncertainty, is assessed individually. This procedure is also used e.g. in IED Annex VI for heavy metals and dioxins and furans. The Directive on urban waste water treatment⁴¹ also uses this approach, based on 24-hours composite samples and, in addition, a 'maximum permitted number of samples which fail to conform' is defined.

Other Member States (e.g. Italy, 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 e.g. in IED Annex VII for installations and activities using organic solvents for total organic carbon.

Averaging the results of individual measurements may require some additional provisions, such as how to deal with values below the limit of detection (or quantification; see further down) or how to apply measurement uncertainty. For instance, in the Netherlands, the total measurement

⁴¹ COUNCIL DIRECTIVE 91/271/EEC of 21 May 1991 concerning urban waste water treatment

uncertainty has to be divided by \sqrt{n}^{42} before it is subtracted from the calculated average of 'n' measurements.

3.3.4.3 Uncertainty of measurement

In the last 10 years, there have been several new developments related to the determination and the use of the measurement uncertainty. The most significant is that measurement uncertainty should be treated in a standardised way according to the GUM - *Guide to the expression of uncertainty in measurement*⁴³. The standard 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'. In addition to the GUM, there is a standard available for air measurement (EN ISO 20988:2007⁴⁴), which applies the general recommendations of the GUM to the conditions of air quality measurement.

For each (new) CEN standard dealing with measurement methods, there is the requirement to address the uncertainty of the measurement. 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.

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. This statement. The estimated uncertainty is necessary in the case of checking permit conditions and of great importance in the data collection used for the elaboration of BREFs.

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

- 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.

For continuous measurements according to EN 14181:2004⁴⁵, the uncertainty of the results is determined when calibrating automated air emission measuring systems (AMS) using standard reference methods (SRM). According to the IED (Annex V, Part 3, No 10; Annex VI Part 8 No 1.2), the resulting measurement uncertainty is used to calculate validated averages. The results of continuous measurements should always be reported with the associated calculated

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⁴² Netherlands Emission Guidelines for Air, Section 3.7, Monitoring of emissions, June 2012

⁴³ JCGM 100:2008 Evaluation of measurement data - Guide to the expression of uncertainty in measurement (GUM 1995 with minor corrections) issued by BIPM, IEC, IFCC, ILAC, ISO, IUPAC, IUPAP and OIML.

⁴⁴ EN ISO 20988:2007 Air quality - Guidelines for estimating measurement uncertainty (ISO 20988:2007)

⁴⁵ EN 14181:2004 Stationary source emissions - Quality assurance of automated measuring systems

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measurement uncertainty, to allow a comparison with the requirements given in the IED or in national regulations.

For periodic measurements in air and water, the uncertainty of the results obtained with the measurement method 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 sub steps. This leads directly to the expanded uncertainty, which defines an interval within which the measurement result falls. The expanded uncertainty can be applied on each result or on averaged values, e.g. before comparing them with the emission limit value given in a permit. 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 sub steps of the applied measurement method (see also factors mentioned above). To calculate the measurement uncertainty, an analytical equation ('method model equation') is needed that combines all contributing sub steps. Finally the indirect approach leads to a combined uncertainty, which needs to be multiplied by a coverage factor to obtain an expanded uncertainty. (For further information on direct and indirect approaches see^{46,47, 48, 49,50}).

The importance of the uncertainty of the measurement results is also reflected by the way it is used in special monitoring rules in the IED (e.g. Annex V, Part 3, No 9 and 10; Annex VI Part 6 No 1.3 and Part 8 No 1.2) and by different Member States. The estimated expanded measurement uncertainty has to be taken into account when assessing measurement results. The most common approach is to subtract the measurement uncertainty from the result of a periodic measurement, and then to use this value for further elaboration-assessment.

In the data collection during the elaboration of a BREF, the measurement uncertainty should be provided together with the measurement results of continuous and periodic measurements, to allow a sound assessment of data. By taking into account the uncertainty of a measurement (BREF Guidance⁵¹, Section 3.1), the definition of the lower and the upper range of a BAT-AEL may be influenced. However, BAT-AELs are, in general, expressed without mentioning the measurement uncertainty. The consideration of the measurement uncertainty should be done according to the rules laid down in the IED, in the national regulations and/or in the relevant (EN) standards.

JCGM 100:2008 (GUM 1995 with minor corrections) Evaluation of measurement data — Guide to the expression of uncertainty in measurement

- EN ISO 20988:2007 Air quality Guidelines for estimating measurement uncertainty (ISO 20988:2007)
- VDI 4219:2009 Determination of the uncertainty of emission measurements by use of discontinuous measurement methods
- ⁴⁹ Review on Danish Emission Control of Industrial Wastewater. December 2012. Internal information to the EIPPCB
- ⁵⁰ MCERTS Technical Guidance Note (Monitoring) M2 Monitoring of stack emissions to air. Environment Agency, England and Wales, Version 8.1, 2011
- ⁵¹ COMMISSION IMPLEMENTING DECISION of 10 February 2012 laying down rules concerning guidance on the collection of data and on the drawing up of BAT reference documents and on their quality assurance referred to in Directive 2010/75/EU of the European Parliament and of the Council on industrial emissions (2012/119/EU).

3.3.4.4 Limit of detection/limit of quantification

Each laboratory has to determine its performance characteristics in relation to the different measurement methods applied. According to EN ISO/IEC 17025:2005, this determination has to be done on the basis of validated measurement methods, e.g. as described in EN standards, showing the performance of the laboratory, especially addressing the following characteristics:

- limit of detection (LoD) and limit of quantification (LoQ);
- measurement uncertainty;
- linearity;
- selectivity;
- reference material (e.g. calibration gas).

Other parameters, such as leakage of and absorption in the sampling line should be addressed as well.

The definitions for the limit of detection and the limit of quantification according to Directive $2009/90/EC^{52}$ are:

- **'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 determinant of interest;
- **'limit of quantification**' means a stated multiple of the limit of detection at a concentration of the determinant 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.

Directive 2009/90/EC lays down the technical specifications for the chemical analysis and monitoring of water status pursuant to the Water Framework Directive. The monitoring of industrial waste water is not covered by this Directive. However, the issue is similar and it is therefore desirable to address it in a similar way, whenever possible.

For air emissions measurements, a similar but more general definition is given e.g. in CEN/TS 14793:2005⁵³, and the method, how to assess the LoD, is then specified in each (EN) standard (e.g. EN 1948-3:2006⁵⁴):

- Limit of detection (L_D or LoD): Smallest measurand concentration which can be detected, but not quantified, in the experiment conditions described for the method.
- Limit of quantification (L_Q or LoQ): Smallest measurand concentration which can be quantified, in the experiment conditions described for the method.

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

⁵² COMMISSION DIRECTIVE 2009/90/EC of 31 July 2009 laying down, pursuant to Directive 2000/60/EC of the European Parliament and of the Council, technical specifications for chemical analysis and monitoring of water status

⁵³ CEN/TS 14793:2005 Stationary source emission - Intralaboratory validation procedure for an alternative method compared to a reference method

⁵⁴ EN 1948-3:2006 Stationary source emissions - Determination of the mass concentration of PCDDs/PCDFs and dioxin-like PCBs - Part 3: Identification and quantification of PCDDs/PCDFs

Any measurement method applied should have an appropriate limit of detection and related to this, an appropriate limit of quantification in relation to the emission level, which should be monitored and controlled.

As a general rule, the LoD should be less than 10 % of the emission limit value, otherwise it cannot be guaranteed that the limit of quantification (LoQ) is clearly below a set emission limit value and, consequently, that the result of the measurement can be used for compliance assessment. In Directive $2009/90/\text{EC}^{55}$, it is stated that the LoQ shall be equal to or below a value of 30 % of the relevant environmental quality standards.

The limit of detection and limit of quantification strongly depend on the performance of the laboratory and the possible modifications or adaptations to specific circumstances. Therefore, it is essential that, together with the measurement results, the LoD, and preferably also the LoQ, is reported. This would allow a more proper use of data when assessing the performance of techniques and elaborating BAT conclusions and associated BAT-AELs for a given industrial sector and could ensure a suitable assessment of measurement results for compliance assessment.

Defining the lower end value of the BAT-AEL ranges as at least the typical LoQ guarantees a level which can be quantified by applying the available measurement methods.

If the LoQ is not known or not reported, it can be estimated as a multiple of the LoD. This can be done by using the LoD given in the relevant (EN) standard, multiplied by three to derive an estimated LoQ, but preferably, the laboratory-specific performance characteristics of the method applied should be used.

If the results of measurements need to be averaged, it needs to be defined how values below the LoD or LoQ should be taken into account. 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 and to report any data. If there are indications that the pollutant can 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. Some examples are given in the following paragraphs.

In Directive 2009/90/EC, laying down technical specifications for the chemical analysis and monitoring of the water status, for the calculation of average values for water measurements the following rules based on the LoQ are given:

- 1. 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 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.'

2.

⁵⁵ COMMISSION DIRECTIVE 2009/90/EC of 31 July 2009 laying down, pursuant to Directive 2000/60/EC of the European Parliament and of the Council, technical specifications for chemical analysis and monitoring of water status

In Denmark⁵⁶, the approach of Directive 2009/90/EC is modified for the monitoring of industrial waste water, because Danish experience shows that for pollutants with very low concentrations (organic micro-pollutants) useful information can be lost by applying these rules. The following approach based on the LoD is used in such cases.

- 1. If less than 10 % of all samples have concentrations above the LoD no average will be calculated.
- 2. If more than 10 % but less that 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 calculation of the average.
- 3. 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 calculation of the average.

In Scotland⁵⁷, 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. Where there is reason to believe that a pollutant is present, the measurement results should be taken as $\frac{1}{2}$ LoD. Where 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 equal to $\frac{1}{2}$ LoD.

In Austria, according to the Austrian air emissions measurements directive⁵⁸, validated average values, which are negative (<LoD/LoQ), have to be set as zero.

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, in particular, when reporting emission data that may be used for the elaboration of BREFs and related BAT conclusions.

If appropriate, it is useful to clearly state in the permit the necessary arrangements for dealing with values under the LoD or LoQ, if it is not stated elsewhere in the national regulation. A consistent approach should be applied either for the sector or for the specific country, so that a fair comparison of the data is possible. However, as mentioned above, defining the lower value of the BAT-AEL ranges as at least the LoQ guarantees a level that can be quantified by applying the available measurement methods

3.3.4.5 Outliers

An outlier can be defined as a result deviating significantly from the others in a measurement series (typically a series of monitoring data), and which cannot be directly assigned to the operation of a facility or process under normal or other than normal operating conditions (NOC, OTNOC). Outliers can be identified by expert judgement on the basis of considerations, such as an abnormal emission pattern in the particular facility or by a statistical test. In air and in water measurements the Grubbs' test^{59,60} is used to determine outliers in the comparison of results of

⁵⁶ Review on Danish Emission Control of Industrial Wastewater. December 2012. Internal information to the EIPPCB

⁵⁷ Scottish Release Inventory (SPRI) Operator Guidance on Release Estimation Techniques (RET), Scotland 2011

⁵⁸ Verordnung BgBl. (Bundesgesetzblatt) II; 153. Verordnung: Emissionsmessverordnung-Luft – EMV-L §9, point 2, 09.05.2011

⁵⁹ CEN/TS 14793:2005 Stationary source emission - Intralaboratory validation procedure for an alternative method compared to a reference method

⁶⁰ DIN 38402-71:2002 German standard methods for the examination of water, waste water and sludge; General information (group A) — Part 71: Equivalence of two analytical methods based on the

two different methods if more than six data pairs are available. A standardised approach for the determination of outliers to meet the requirements of EN $14181:2004^{61}$ e.g. is given in the Monitoring Quick Guide 14^{62} .

The only difference between an outlier and an exceptional emission is whether a reason has been identified in the operating conditions of the plant. A close analysis of these operating conditions is always 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 permits, and possibly taking past outliers in previous monitoring periods into account.

This checking should generally be done 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.

Errors in sampling or analysis performance are a common cause of deviating results when an operational cause of an outlier cannot be identified. In this case, the performing laboratory can be notified with reference to a critical revision of their performance and monitoring data.

If no cause can be identified, and a critical examination of the measurements does not lead to a correction of the results, the outlier 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 (NOC, OTNOC) when reported.

The basis for the identification of an outlier, as well as all actual data, should always be reported to the authorities.

comparison of results and their statistical evaluation; Procedure for quantitative characteristics with continuous set of values

⁶¹ EN 14181:2004 Stationary source emissions - Quality assurance of automated measuring systems

⁶² MCERTS RM-QG14 Monitoring Quick Guide 14 Dealing with data points and outliers in monitoring data, Environmental Agency England Wales 2012

3.4 Normal operating conditions – other than normal operating conditions – corresponding measurement conditions

BAT-associated emission levels (BAT-AELs) for a given industrial process should refer to normal operating conditions (NOC). Therefore, a difference should be made between 'normal operating conditions' (NOC) and 'other than normal operating conditions' (OTNOC) in all BREFs and permits, according to the requirements of the industrial sector. This implies that the operating conditions during monitoring have to be known, as far as possible, and whether that finally the emissions could be related to NOC or OTNOC.

The IED requirement that BAT-AELs should refer to NOC does not imply that OTNOC are excluded from any observation. For instance, in IED Annex VI, Part 3, Point 2, it is stated that the emission limit values 'shall under no circumstances' be exceed, which includes all operating conditions. In particular, OTNOC should also be assessed if it is obvious that relevant environmental impacts can be expected, e.g. possible emission of toxic substances or emissions of high concentrations of odorous substances (malodours, nauseating odours) close to residential areas.

Examples for OTNOC are given in the IED Art. 14(1)(f), such as start-up and shutdown operations, leaks, malfunctions, momentary stoppages and definitive cessation of operations. The BREF Guidance⁶³ refers to IED Art. 14(1)(f) and therein it is stated that data used for elaborating BREFs will be qualified as far as possible with details on operating conditions. Consequently, the operating conditions should be clearly stated when submitting data during the elaboration of BREFs.

In order to have the possibility to classify measurement results as caused by NOC or by 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. This implies that different NOC should be identified if they have an influence on the amount of 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, and the averaging of the values can then be done 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 in the measuring planning^{64,65}. If different NOC occur with significant differences in emissions, it is

⁶³ COMMISSION IMPLEMENTING DECISION of 10 February 2012 laying down rules concerning guidance on the collection of data and on the drawing up of BAT reference documents and on their quality assurance referred to in Directive 2010/75/EU of the European Parliament and of the Council on industrial emissions (2012/119/EU).

⁶⁴ EN 15259:2007 Air quality - Measurement of stationary source emissions - Requirements for measurement sections and sites and for the measurement objective, plan and report.

⁶⁵ ISO 5667-1:2006 Water quality - Sampling - Part 1: Guidance on the design of sampling programmes and sampling techniques.

recommended to carry out periodic measurements for each distinguishable NOC, or at least for the one with the highest expected emissions. If measurements are deemed necessary also for OTNOC, this will depend on the specific situation and the expected emissions.

Some examples (A, B, C and D) on, how emissions can vary over time are given in Figure 3.2^{66} , where the horizontal axis (x-axis) gives the time and the vertical axis (y-axis), the amount of emission.



Figure 3.2: Examples of how emissions 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:

- <u>Process A</u> represents a very stable process. It can be assumed that NOC are prevailing. The results of measurements will be similar, independent from the time when the samples were taken. Periodic measurements with a minimum frequency might be sufficient. If in cases of permitting 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 high and low emission levels, which are typical for e.g. cyclic or batch processes. It can be assumed that the whole process represents NOC with two distinct emission levels.
 - The monitoring approach to be 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 emission can be characterised or the difference between the two emission phases can be taken into account when averaging.

⁶⁶ MON REF Reference Document on the General Principles of Monitoring, July 2003

If single samples are taken, it needs to be clarified in advance if the average emission (e.g. for estimating loads) or the emission of each distinct phase should be determined. It might be advisable to choose sampling times which clearly address the two different emission phases or, depending on the case, to measure only under the highest expected emission.

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

• <u>Process C</u> 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 a 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 differentiating 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 shortening the sampling duration. Whether the peaks need to be reflected in BAT conclusions or in permits depends on the relevance of the emission and on the qualification as NOC or OTNOC.

• <u>**Process D</u>** represents a highly variable process which nevertheless represents NOC. It seems to be difficult to distinguish between NOC and OTNOC, although, after looking at the process, OTNOC might be identifiable.</u>

If the whole emission process can be classified as NOC, it is necessary to evaluate the contribution of that process to the total emissions of the installation, and then continuous measurements might be the only possible monitoring solution to cover all the emission variations.

It would be very unlikely to use periodic measurements to describe the emissions of such a process type. Only if the contribution to the total emission of the installation is very low, might it be advisable to developed a measuring plan which guarantees that at least the highest emissions are covered.

A BAT-AEL or an ELV for such a process should reflect the special conditions and be associated with an appropriate monitoring regime.

As shown in Figure 3.2, different operating conditions or different emission profiles will affect the monitoring regime and planning in different ways. This will be covered in more detail in Section 4.2 for air and Section 4.3 for water emissions.

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4 MONITORING OF EMISSIONS IN DIFFERENT ENVIRONMENTAL MEDIA

4.1 Overview

In Europe, the monitoring of emissions in different environmental media (e.g. air, water) is widely covered by e.g. regulations, standards, and guidelines, wherein the whole monitoring data production chain is addressed, such as sampling (including the storage and treatment of samples), the measurement of reference parameters, analysis of the samples, data processing and reporting. The amount of information reflects the need to achieve reliable, representative and comparable results that can be used in permitting to prevent and control industrial emissions and to demonstrate compliance with permit conditions.

Furthermore, during the data collection period for the elaboration or review of a BREF, a large amount of emission data is typically provided and has to be compared and evaluated. This exercise is carried out with the aim of assessing the candidate BAT and BAT-AELs, where applicable; for these reasons, the data provided should be reliable, representative and comparable.

In the following sections, specific information is given on the monitoring of air and water emissions covering the whole data production chain, as far as it is of relevance, to help define monitoring regimes for use in permits and in BAT conclusions for the specific industrial sector. In addition, recommendations or hints are given to aid decisions on different monitoring approaches and to help to express and report monitoring data in a way that can be used properly in the elaboration process of BREFs and their BAT conclusions and, most likely, by permit writers.

Information concerning the different monitoring approaches applied in different Member States has been taken into account as much as possible, whenever available, in the following sections. Furthermore, information about the measurement of specific pollutants covered in the current (2013) EN standards is listed in Annex A.1 and Annex A.2, grouped according to the related Technical Committee (CEN/TC 264 'Air quality', CEN/TC 230 'Water analysis'), sorted by pollutant, and complemented by important additional information, such as the limit of detection.

Some general aspects concerning the monitoring of air and water emissions are already mentioned in Chapter 3, such as the objectives of monitoring, different monitoring approaches including the use of (EN) standards, qualification and accreditation of personnel and laboratory, and general aspects of data treatment.

In Section 4.2, some definitions of air pollutants are given and the direct monitoring approaches, i.e. continuous and periodic measurements of air emissions, are covered in more detail, including possible criteria for the choice of an adequate monitoring regime. Furthermore, a section on the monitoring of odour emissions has been included and also one covering indirect monitoring approaches, such as the control of surrogate parameters, predictive monitoring systems (PEMS), and bioindication with plants.

Paragraph rephrased

In Section 4.2, some definitions of air pollutants are given. The direct monitoring approaches, i.e. continuous and periodic measurements, and indirect monitoring approaches, i.e. the control of surrogate parameters and predictive monitoring systems (PEMS), are also covered in more detail. Furthermore, sections have been included on the monitoring of diffuse emissions, the monitoring of odour emissions and the monitoring of emissions using biological monitoring with plants.

Section 4.3 covers the monitoring of emissions to water, addressing as well and gives some definitions of water pollutants. It also covers direct (continuous and periodic measurements of

water emissions) and indirect (such as the control of surrogate parameters and biomonitoring with toxicity tests) monitoring approaches.

4.2 Monitoring of emissions to air

4.2.1 Definitions of air pollutants

In Table 4.1, the definitions generally used for common air pollutants are given in the way that they currently (2013) appear or can be used in the BREF chapter containing the BAT conclusions. This list is subject to modification, according to the needs of the BREF under elaboration or to the required permit conditions.

Table 4.1:	Definitions of some common	air pollutants currently	(2013) used in BREFs
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Dust	Total suspended particles including fine particulate matter					
NO _X expressed as NO ₂	The sum of the concentrations of nitrogen oxide (NO) and nitrogen dioxide (NO ₂), expressed as NO ₂					
SO _X expressed as SO ₂	The sum of the concentrations of sulphur dioxide (SO_2) and sulphur trioxide (SO_3) , expressed as SO_2					
H_2S	Hydrogen sulphides. Carbonyl sulphide and mercaptan are not included					
Inorganic gaseous Hydrogen chloride expressed as HCl	All inorganic gaseous chlorine chlorides compounds, expressed as HCl					
Inorganic gaseous Hydrogen fluoride expressed as HF	All inorganic gaseous fluorine fluorides compounds, expressed as HF					
Mercury expressed as Hg	The sum of the concentrations of the mercury and mercury compounds, independent of their state (gaseous, dissolved in droplets, solid, adbsorbed on particles), expressed as Hg					
Metals	Metals and metal compounds, independent of their state (gaseous, dissolved in droplets, solid, adsorbed on particles), and sampled according EN 14385:2004 ⁶⁷					
Odour emission expressed as European odour units	Volatile substances measured by olfactometry (EN 13725) and expressed as European Odour Units (ou_E)					
TVOC expressed as C	Total volatile organic carbon; the sum of all gaseous and vaporous organic compounds expressed as C					
voc	Volatile organic compound as defined under Directive 2010/75/EU ⁶⁸ 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					
PCDD/F	Polychlorinated dibenzodioxins/furans					
РСВ	Polychlorinated biphenyls					

In addition to the most common definitions, for the air pollutants: dust, SO_x , TVOC (TOC), PCDD/F, dioxin-like PCBs and odour mentioned in Table 4.1, it is appropriate to consider the following general remarks in the elaboration of BREFs and in permits.

Dust

In order to better qualify the environmental impact of total dust emissions; in addition to concentration measurements of dust, it may be advisable or even necessary to determine the dust particle size distribution, in particular the fractions $PM_{10} \ll 10 \mu m$ and $PM_{2.5} \ll 2.5 \mu m$. This

⁶⁷ EN 14385:2004 Stationary source emissions - Determination of the total emission of As, Cd, Cr, Co, Cu, Mn, Ni, Pb, Sb, TI and V

⁶⁸ Directive 2010/75/EU on industrial emissions (integrated pollution prevention and control (IED)

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type of characterisation may have to be repeated whenever the process generating dust emissions undergoes significant changes (including e.g. fuel, raw material catalysts used).

SO_X

 SO_x is defined as the sum of the concentrations of sulphur dioxide (SO₂), and sulphur trioxide (SO₃) and sulphuric acid aerosols, expressed as SO₂. For most industrial emission sources, SO₂ SO_x -emissions are highly predominated by SO_2 in SO_x (i.e. >90 %). The measurement of SO_x is generally carried out by periodic measurements, since as continuous measurements of SO_x are cannot be very difficult to performed. However, the continuous measurement of SO₂ is common practice in several industrial sectors. For the accounting of SO₃ in a continuous monitoring system, the corresponding concentration, measured periodically e.g. at the time of the calibration of the continuous measuring device, could be is included in the calculation of the SO_x emission. (For calculation of the SO_x emission based on the fuel analysis, see Section 3.2.3.3)

Metals

EN standard EN 14385:2004⁶⁹ specifies the determination of the mass concentration of the following specific elements: antimony (Sb), arsenic (As), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), lead (Pb), manganese (Mn), nickel (Ni), thallium (Tl), and vanadium (V). It includes all metal compounds, independent of whether they are gaseous, dissolved in droplets, solid or adsorbed on particles.

TVOC (TOC)

EN standard EN 12619:2012⁷⁰ gives a definition for total volatile organic carbon (TVOC) as a sum of all gaseous and vaporous organics expressed as total carbon. For measurement, FID analysers are used, which have a sample gas cleaning system that prevents contamination by particles and/or condensation inside the instrument. It is stated in the EN standard that 'hydrocarbons of a higher order, entering the analyser as solids, will be filtered, and consequently not measured. Although the Directives prescribe the measurement of TOC (Total Organic Carbon) the FID analyser actually measures TVOC (Total Volatile Organic Carbons).'

PCDD/F and dioxin-like PCBs

According to the IED and EN 1948-1:2006⁷¹, PCDD/F are expressed in the unit ng I-TEQ/Nm³, where I-TEQ means International Toxicity Equivalent, derived by applying International Toxicity Equivalency Factors (I-TEFs). These factors indicate the toxic potential of a single PCDD or PCDF's congener relative to the toxic effect of 2,3,7,8-TCDD, which is the congener with the highest toxicity. If there is a need to cover also dioxin-like PCBs, it is advisable to use the unit ng WHO-TEQ/Nm³, applying International Toxicity Equivalency Factors from the World Health Organisation (WHO-TEFs 2005⁷²). In addition to I-TEFs, the WHO-TEFs include toxicity equivalency factors for the 12 dioxin-like PCBs⁷³.

Odour emission

The standard EN 13725:2003⁷⁴ describes the periodic measurement of the odour concentration in a sample of air emissions by dynamic olfactometry using selected and trained panel members

- EN 14385:2004 Stationary source emissions Determination of the total emission of As, Cd, Cr, Co, Cu, Mn, Ni, Pb, Sb, TI and V
- ⁷⁰ EN 12619:2012 Stationary source emissions Determination of the mass concentration of total gaseous organic carbon Continuous flame ionisation detector method
- ⁷¹ EN 1948-1:2006 Stationary source emissions Determination of the mass concentration of PCDDs/PCDFs and dioxin-like PCBs - Part 1: Sampling of PCDDs/PCDFs
- ⁷² Van den Berg, M. et al. Toxic Equivalency Factors (TEFs) for PCBs, PCDDs, PCDFs for humans and wildlife. Environ Health Perspect, 106, 1998
- ⁷³ EN 1948-4:2010 Stationary source emissions Determination of the mass concentration of PCDDs/PCDFs and dioxin-like PCBs - Part 4: Sampling and analysis of dioxin-like PCBs
- ⁷⁴ EN 13725:2003 Air quality Determination of odour concentration by dynamic olfactometry

and expressed as European odour unit (ou_E) (see Section 4.2.3). The standard includes the methodology for the determination of emission rates. It is widely applied in Europe (e.g. Belgium⁷⁵, France⁷⁶, Germany⁷⁷, The Netherlands⁷⁸, UK⁷⁹, see Section 4.2.3) and is part of the accreditation of testing laboratories.

4.2.2 Continuous/periodic measurements

4.2.2.1 When to measure continuously or periodically?

In Table 4.2, some important characteristics of continuous and periodic measurements are listed that can which might help to decide on the measurement regime⁸⁰, where:

- continuous measurement is defined as measurements made with an automated measuring system (AMS) permanently installed on site for the continuous monitoring of emissions (according to EN 14181:2004⁸¹); and
- periodic measurement is defined as the determination of a measurand at specified time intervals using manual or automated methods (according to EN 15259:2007⁸²).

- ⁷⁵ BE: VLAREL Order of the Flemish Government of 19 November 2010 establishing the Flemish regulation on recognitions relating to the environment
- ⁷⁶ FR: French odour regulation; INERIS- DRC-13-133185-07843A; KAd- 13/09/13 (special contribution)
- ⁷⁷ DE: Detection and Assessment of Odour in Ambient Air (Guideline on Odour in Ambient Air GOAA) 2008
- ⁷⁸ NL: Netherlands technical agreement NTA 9065:2013 Air quality Odour measurements Odour measurement and calculation
- ⁷⁹ UK: H4 Odour Management 2011, Environmental Agency of England and Wales
- ⁸⁰ MCERTS Technical Guidance Note (Monitoring) M2 Monitoring of stack emissions to air. Environment Agency, England and Wales, Version 8.1, 2011
- ⁸¹ EN 14181: 2004 Stationary source emissions Quality assurance of automated measuring systems
- ⁸² EN 15259:2007 Air quality Measurement of stationary source emissions Requirements for measurement sections and sites and for the measurement objective, plan and report

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Characteristic	Continuous measurements with permanently installed AMS	Periodic measurements
	All or most of the times that	Snapshots of the long-term emissions
Sampling period	substances are emitted are covered	profile
Speed of results generation	Almost always real-time output of results	Real-time results, if instrumental analysers are used; delayed results if a manual method with a laboratory
	P esults continuously gathered and can	
Averaging of results	be averaged over a given period, e.g. typically over 30 minutes, 1 hour, or 24 hours	Result over the sampling period, typically 30 minutes to several hours
Calibration and traceability	AMSs require calibration against a standard reference method (SRM) 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; also instruments calibrated with certified reference gases can be used
Certification of equipment	Certification of equipment available	Certification of transportable equipment available
Accreditation of monitoring	Quality assurance of the calibration and maintenance of AMSs according to EN 14181:2004. Calibration has to be done by a laboratory accredited according to EN ISO/IEC 17025:2005	Accreditation to EN ISO/IEC 17025:2005 and CEN/TS 15675:2005 for organisations carrying out periodic measurements, including personal qualification
Capital costs	Tends to be higher than the costs of periodic monitoring equipment	Tends to be lower than the cost of AMSs
Maintenance cost	Tends to be higher than the costs of periodic monitoring equipment, because it includes e.g. QAL2, QAL3 and AST (see Section 4.2.2.2.2)	Tends to be lower than the cost of AMSs
Operating cost	Tends to be lower than that for the periodic approach, as not usually labour intensive; routine maintenance and calibration is required	Tends to be higher than the AMSs approach as it is labour intensive, depending on the number of measurement series per year; trained team on site for the whole duration of measurement series

 Table 4.2:
 Important characteristics of continuous and periodic measurements

In addition to Table 4.2, when deciding whether to considering the use of continuous measurement against or periodic measurements, the following aspects may be taken into consideration: issues may provide the general background for the decision making process:

- sometimes continuous measurement may be is the most economical option (e.g. if continuous measurement is also needed for process control);
 - if total loads need to be determined, it might be necessary required to measure continuously;
 - the availability and reliability of continuous measurement equipment, depending on the industrial sector or on a specific emission source e.g. under certain flue-gas conditions; such as high humidity content, the presence of aerosols or the settlement of particles at the sampling equipment; continuous measurements might not be feasible;
- the capability to control a highly variable and/or excessive emission;
- availability of a system to promptly act, according to the continuously generated data;
- continuous measurement provides feedback on the operating condition of pollution abatement system;
- to operate within the required level of measurement uncertainty (the accuracy of on line process analysers may be lower than that for periodic laboratory analyses).

In individual cases, the decision to use continuous measurements might also be driven by one or a combination of the following requirements:

- continuous measurement is a legal requirement for the specific industrial sector;
- continuous measurement may be indicated as the associated monitoring in a specific BAT conclusion for the sector;
- environmental quality standards (IED Article 18) may be a criterion for continuous measurement in individual cases;
- continuous measurement is prompted by the extent of the environmental risk associated to the emission (see Section 3.2.1);
- continuous measurement is prompted by local issues, such as the process is the source of higher emission levels or is heavily contributing to a locally reduced ambient air quality;
- the source presents strongly variable emissions with levels close to existing limits (BAT-AELs, ELVs).
- public confidence tends to be higher when using continuous measurement.

The IED specifies that continuous monitoring is required, e.g. for large combustion plants greater than 100 MW thermal input (e.g. for SO_2 , NO_x and dust) and waste incineration plants (e.g. for NO_x , provided that emission limit values are set for CO, total dust, TOC, HCl, HF, SO_2).

In some Member States (e.g. Belgium⁸³, Denmark⁸⁴, France^{85,86}, Germany⁸⁷), a mass flow threshold is used to decide if continuous measurements are required. In general, it is assumed that below that threshold periodic measurements are sufficient, unless the conditions of the individual case require a different approach. Some examples for mass flow thresholds for the most common pollutants are given in Annex A.3 Table 4.3. For the sake of clarity, possible variations for different industrial sectors and for special substances are not mentioned.

Former Table 4.3 Mass flow thresholds for continuous measurement of emissions moved to an annex.

In the elaboration of BAT conclusions on monitoring, the decision between continuous and/or periodic measurements needs to be done in the sectoral BREFs based on the requirements of the individual industrial sector and the information provided. The aforementioned issues and examples might help to come to a well-founded decision.

4.2.2.2 Continuous measurements

4.2.2.2.1 EN standards

The following general EN standards or technical reports (TR) deal with continuous measurements of air emissions (Table 4.3). Some of them are also related to ambient air measurements.

For the general use of EN standards and other standardised methods see Section 3.3.3.



- ⁸⁴ Email communication
- ⁸⁵ France: Arrêté du 2 février 1998 (2/2/98) relatif aux prélèvements et à la consommation d'eau ainsi qu'aux émissions de toute nature des installations classées pour la protection de l'environnement soumises à autorisation
- ⁸⁶ French contribution to the elaboration of ROM, Contribution to the chapter 3 dealing with the general aspects of monitoring, INERIS-DRC-12-126076-13244A, 06/12/12 K.Adam
- ⁸⁷ Germany: First General Administrative Regulation Pertaining the Federal Immission Control Act (Technical Instructions on Air Quality Control – TA Luft) of 24 July 2002



Standard No	Title					
EN 14181:2004	Stationary source emissions - Quality assurance of automated measuring systems					
CEN/TR 15983:2010 Stationary source emissions - Guidance on the applicate EN 14181:2004 (informative)						
EN ISO 14956:2002	Air quality - Evaluation of the suitability of a measurement procedure by comparison with a required measurement uncertainty (ISO 14956:2002)					
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 15267-3 applies EN ISO 14956 for new AMS)					
EN ISO 9169:2006	Air quality - Definition and determination of performance characteristics of an automatic measuring system (ISO 9169:2006)					

 Table 4.3:
 General
 EN
 standards
 or
 technical
 reports
 (TR)
 dealing
 with
 continuous

 measurements of air emissions

In EN 14181:2004, a quality assurance system, based on different Quality Assurance Levels (QAL1, QAL2, QAL3) for automated measuring systems (AMSs) is defined. This standard is applicable to AMSs installed on emission sources for the determination of the flue-gas components and other flue-gas parameters. Also a procedure for annual surveillance tests (AST) is included in EN 14181:2004. In conjunction with this standard, for some pollutants such as dust⁸⁸ and mercury⁸⁹, there are specific EN standards for AMSs available.

In EN 15267 Parts 1, 2 and 3, the Quality Assurance Levels QAL1 and the procedures on how to achieve the required certificatione are defined, and these have to be applied before the AMS gets installed at the emission source.

The technical report CEN/TR 15983:2010 provides supporting guidance for the application of EN 14181:2004 and is based on growing experience with EN 14181:2004 throughout the Member States and the CEN member countries. For functional tests such as zero and span checks, CEN/TR 15983:2010 refers to EN ISO 9169:2006.

There are other EN standards (see Annex A.1) dealing with specific parameters measured by an AMS and their quality assurance such as dust^{90,91}, and velocity and volume flow rate⁹².

Currently (2013), a working group of the Technical Committee CEN/TC 264 is working on a new EN standard on 'Requirements for treatment of AMS output, data processing, data reduction and data substitution for monitoring of environmental data'.

- EN 13284-2:2004 Stationary source emissions Determination of low range mass concentration of dust Part 2: Automated measuring systems
- ³⁹ EN 14884:2005 Air quality Stationary source emissions Determination of total mercury: automated measuring systems
- ⁹⁰ EN ISO 13284-2:2004 Stationary source emissions Determination of low range mass concentration of dust - Part 2: Automated measuring systems
- ⁹¹ EN 15859:2010 Air Quality Certification of automated dust arrestment plant monitors for use on stationary sources Performance criteria and test procedures
- ⁹² EN ISO 16911-2:2013 Stationary source emissions Manual and automatic determination of velocity and volume flow rate in ducts Part 2: Automated measuring systems (ISO 16911-2:2013)

The quality assurance systems given by EN 15267 and EN 14181:2004 are described in more detail in the following sections.

4.2.2.2.2 Quality assurance system

QAL1 is a procedure defined in EN 15267, and referred to in EN 14181:2004, to demonstrate that the AMS is suitable for the intended purpose before installation on site, i.e. by its meeting required performance standards and the maximum expanded uncertainty according to the requirements given in the IED, Annex V and VI. This suitability test has to be done by the manufacturer and leads to a certification of the measuring device and is carried out before an AMS gets installed (for certified measuring systems, see Table 4.4).

QAL2 as defined in 14181:2004 involves testing laboratories that are should be accredited (see Section 3.3.1) or approved directly by the relevant competent authority. It describes the procedures for validation and calibration using Standard Reference Methods (SRMs), after the AMS has been installed. The SRMs are defined in specific EN standards.

The procedure needs to be repeated periodically every three, or at least every five years or more frequently if required by legislation or by the competent authority, or after major changes of the AMS or of process/operating conditions. In general, it consists of at least 15 parallel measurements between AMS and SRM. If normal operating conditions (NOC) consist of distinct operating modes (e.g. use of different fuels, manufacture of different products), the need for additional calibrations has to be checked are necessary.

QAL3, as defined in 14181:2004, involves the operators of the installation. QAL3 describes a frequent quality assurance procedure to maintain and demonstrate the required quality of the AMS during its normal operation, by checking the zero and span readings. The implementation and performance of the QAL3 procedure is the responsibility of the plant operator. It does not require an accredited or approved laboratory to carry out the procedures.

AST (annual surveillance test) involves testing laboratories that are should be accredited (see Section 3.3.1) 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 (QAL2). In general, an AST consists of at least five parallel measurements between AMS and SRM.

4.2.2.2.3 Certified measuring systems according to EN 15267:2009

The QAL1 suitability test is a very complex and costly procedure, divided into a laboratory and a field testing phase⁹³. Manufacturers of measuring instruments normally commission third parties to carry out the suitability tests and to obtain get the certification.

These suitability tests include a certification range, which is the range over which the AMS has been certified. The certification range is related to the ELV given in relevant EU Directives of the processes under which the AMS will be used. In EN 15267-3:2007⁹⁴, it is stated that the



 ⁹³ Air Pollution Prevention - Manual on Emission UBA-Texte 06/08, ISSN 1862-4804, UBA, Germany 2008
 ⁹⁴ ENV15267 2 2007 Air of the Cartification of the text of tex of text of text of text o

⁹⁴ 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 15267-3 applies EN ISO 14956 for new AMS)

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certification range 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 and other types of processes⁹⁵.

Currently (2013) in Europe, the suitability tests are carried out or coordinated by the following organisations:

- Environment Agency of England and Wales and their Monitoring Certification Scheme (MCERTS);
- TÜV Rheinland and German Federal Environment Agency (UBA) (including publication of the test results in the Joint Ministerial Gazette).

The current (2013) list of certified measuring systems is available on the following internet pages:

- <u>http://www.siraenvironmental.com/UserDocs/mcerts/MCERTSCertifiedProductsCEMS.p</u> <u>df</u>
- <u>http://www.qal1.de/info/_qal1_uebersicht.pdf</u> (in German and English).

For the measurement of air emissions, certified AMSs are available for the pollutants and reference parameters listed in Table 4.4.

In the continuous measurement of emissions, the measured 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 (http://www.qal1.de/info/_qal1_uebersicht.pdf;

<u>http://www.siraenvironmental.com/UserDocs/mcerts/MCERTSEnvironmentalDataManagement</u> <u>Software.pdf</u>), which are not included in Table 4.4.

⁹⁵ MCERTS Technical Guidance Note (Monitoring) M20 Quality assurance of continuous emission monitoring systems - application of EN 14181 and BS EN 13284-2; Version 2.4 April 2012

 Table 4.4:
 List of pollutants and other reference parameters for which certified AMSs are available according to EN 15267:2009 (status January 2013 of the web pages mentioned above)

Pollutants					
Dust (Particulates)					
Carbon monoxide - CO					
Nitrogen monoxide - NO					
Nitrogen dioxide - NO ₂					
Nitrogen oxide – NO _X					
Dinitrogen monoxide- N ₂ O					
Sulphur dioxide - SO ₂					
Chlorine compounds - HCl (inorganic					
gaseous)					
Fluorine compounds - HF (inorganic					
gaseous)					
Ammonia - NH ₃					
Mercury - Hg $(^1)$					
Methane - CH ₄					
Total volatile organic carbon - TVOC					
(¹) Since 2011 and 2012, a new generation of					
certified AMSs for mercury are available,					
which show a significantly better					
used ^{96,97}					
useu.					

Reference Other]
parameters	
Oxygen - O ₂	
Humidity - H ₂ O	
Carbon dioxide - CO ₂]
Volume flow rate]
ROCR	

For the certification of continuous dust monitors, there is another EN standard available, EN 15859:2010⁹⁸, which provides the performance criteria and test procedures for dust arrestment plant monitors used to ensure that dust arrestment plants, which are used on stationary sources, are working satisfactorily.

Two types of dust arrestment plant monitors are covered by this standard:

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

Continuous dust measurements certified to the requirements of EN 15859:2010 may be used in cases, where only qualitative monitoring of the arrestment plants is needed, as an alternative to the more cost intensive quantitative AMSs, even if the measurements made by these dust monitors do not necessarily fulfil all the requirements of EN 14181:2004.

⁹⁶ Schröder, Klaus-Dieter 2012: First experiences in functional testing and calibration of mercury monitors of the new generation. VDI-Tagung Anlagenbezogenes Monitoring. VDI-Bericht 2178, 39-51.

 ⁹⁷ Boness, Michael 2011: New measuring technique for total mercury CEMs, CEM 2011 10th International Conference and Exhibition on Emissions Monitoring, Prague, Czech Republic

⁹⁸ EN 15859:2010 Air Quality - Certification of automated dust arrestment plant monitors for use on stationary sources - Performance criteria and test procedures

4.2.2.2.4 Measurement point, sampling and analysis

It is essential to define a representative measurement location point for continuous measurements. The technical report CEN TR 15983:2010 EN ISO 16911-2:201399 and EN 15259:2007¹⁰⁰ give guidance, for instance, on how the location of the sampling location point of an AMS should be defined to give reliable results. It is critical that the AMS is located in the correct a position, such that it allows measuringes a representative sample of the emissions. Furthermore, the sampling ports for periodic measurements, in the case of calibration and AST, also need to be located in a position that provides a representative sample, and which allows a reliable comparison of sampled emissions with the emissions measured by the AMS. Therefore, EN 14181:2004 requires operators to ensure that the AMS is are installed in the correct a suitable location, and that there is sufficient access to assess, control and maintain it. EN 15259:2007 provides guidance on the location of both the AMS and sampling ports, as well appropriate provisions for measurements including a homogeneity test as (see Section 4.2.2.3.4).

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 4.4 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 detection unit, which is physically separated from the sampling point. 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 emission measuring device must be made from 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 must be heated to above the dew point temperature of the measured component.

In the case of a **non-extractive AMS**, the detection unit is installed across the stack in the gas stream or in a part of it (*in situ* measurement). Therefore, no extractive sampling is necessary; however, components in the gas stream can hamper a correct measurement, e.g. cross-interference with other gas components. High humidity in the gas stream can hamper non-extractive AMS dust measurements and may require the use of an extractive AMS. Because the measurements are carried out on a wet condition and at the operating temperature in the stack, this needs to be considered in the data processing.

4.2.2.2.5 Reference conditions - Standard conditions

The measured concentrations of pollutants are affected by the temperature, pressure, moisture and oxygen concentration in the flue-gas. Therefore, and according to EN 14181:2004, concentrations of air pollutants are converted expressed to standard conditions (temperature 273.15 K, pressure 101.3 kPa), after the deduction of water content (dry gas), with (or without) a correction of oxygen content.

As a consequence, a formulation often used in BAT conclusions for the applicable reference conditions is: 'Concentrations are expressed as mass of emitted substance per volume of flue-

⁹⁹ EN ISO 16911-2:2013 Stationary source emissions - Manual and automatic determination of velocity and volume flow rate in ducts - Part 2: Automated measuring systems (ISO 16911-2:2013)

¹⁰⁰ EN 15259:2007 Air quality - Measurement of stationary source emissions - Requirements for measurement sections and sites and for the measurement objective, plan and report.

gas under standard conditions (273.15 K, 101.3 kPa), after the deduction of water content (dry gas), with (or without) correction of oxygen content.'

When calculating mass emissions, for example in kg/h, different temperature, pressure, oxygen and moisture levels do not affect the <u>calculated</u> result, because they are considered in the measured mass concentration (mg/Nm³ dry), as well as in the measured volume flow rate (Nm³/h), assuming that both are calculated for the same standard conditions. Therefore, for the calculation of mass emissions, no conversion correction to standard conditions is needed^{101,102}.

There are several documents^{103,104,105} that provide information about all the calculations necessary to convert the measured mass concentration and the measured flue-gas volume to standard conditions.

4.2.2.2.6 Data treatment

An AMS provides collect short-term data. The response time¹⁰⁶ is about 5 up to a maximum value of 200 60 seconds. And, depending on the specific requirements set by the permit, an averaging period is applied. The averaging time can usually vary from 10 to 60 minutes. Most commonly, half-hourly or hourly averages are calculated. In the same way, data from peripheral measurements (e.g. oxygen, moisture) are averaged and the half-hourly or hourly averages of the pollutants are converted corrected to the time corresponding standard conditions.

On the standardised half-hourly or hourly results, the measurement uncertainty is subtracted to be applied to obtain validated averages¹⁰⁷. Negative validated averages are accounted for as equivalent to zero. Based on the validated averages, daily or, if required, other averages, such as monthly or yearly, are calculated, and can be used for further assessment. Mass emissions are calculated on the basis of the measured values, without subtraction of the measurement uncertainty.

4.2.2.2.7 Reporting of measurement results

The reporting of measurement results covers, among others, the following items:

- reporting of calibration (QAL2 report) and the annual surveillance functional test (AST report) of the AMS;
- reporting of measurement results, including reference conditions (temperature, oxygen, water vapour, pressure) and operating/process conditions.

The **calibration report (QAL2 report)** shows that the requirements of EN 14181:2004 are fulfilled. A calibration report should be prepared for Normal Operating Conditions (NOC) after

- ¹⁰¹ MCERTS Technical Guidance Note (Monitoring) M2 Monitoring of stack emissions to air. Environment Agency, England and Wales, Version 8.1, 2011
- ¹⁰² EN 15259:2007 Air quality Measurement of stationary source emissions Requirements for measurement sections and sites and for the measurement objective, plan and report.
- ¹⁰³ MCERTS Technical Guidance Note (Monitoring) M2 Monitoring of stack emissions to air. Environment Agency, England and Wales, Version 8.1, 2011
- ¹⁰⁴ InfoMil (NL): Manual Measurement of Air Emissions 2012
- ¹⁰⁵ EN 15259:2007 Air quality Measurement of stationary source emissions Requirements for measurement sections and sites and for the measurement objective, plan and report.
- ¹⁰⁶ 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 15267-3 applies EN ISO 14956 for new AMS)
- ¹⁰⁷ IED Annex V Part 3 Point 10; IED Annex VI Part 8 Point 1.2

installing an AMS on site and then every three to five years afterwards, depending on the calibration cycle. This might include different calibrations for distinct operating modes under NOC.

According to EN 14181:2004, a report of the results of the annual surveillance test (**AST report**) should be prepared once every year during operation of the AMS.

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 the full characterisation of the daily/monthly/yearly emissions, it is advisable that the reports should contain at least the following data:

- data related to the daily operating conditions and hours indicating NOC and Other Than Normal Operating Conditions (OTNOC);
- half-hourly averages, standardised half-hourly averages, and validated half-hourly averages of the specific day (or for any other required averaging period);
- frequency distribution of the 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.

4.2.2.2.8 Elaboration of BREFs

During the data collection for the elaboration or the review of BREFs, it is normally not necessary to provide complete daily, monthly or yearly **reports of continuous measurements**. However, it is advisable to report at least, the (validated) averages (daily, monthly, yearly), the measurement uncertainty, minimum and maximum values, and the 95-percentile, if available, together with unambiguous information on the operating conditions, to allow a correlation between the provided data and NOC or OTNOC.

If there is a need to calculate mass emissions, the measured values without subtraction of the measurement uncertainty are necessary.

BAT-AELs (or ELVs) do not directly indicate the **measurement uncertainty**. The measurement uncertainty is applied before comparing the measurement results with a BAT-AEL or a limit value. In addition, the measurement uncertainty will vary from data-set to data-set, depending on the applied AMS on site. Therefore, for the elaboration or the review of BREFs, it is advisable to provide the measurement data together with the dedicated measurement uncertainty. This allows the calculation of daily or monthly or yearly averages for the elaboration of BAT-AELs, without considering the measurement uncertainty (see Section 4.2.2.2.6 on data treatment above).

Furthermore, if sufficient data are available, it might be possible to mention a specific measurement uncertainty in connection to the BAT-AEL range associated with a BAT conclusion. the associated BAT conclusion in connection to the lower and upper values of the BAT-AEL range.

For further information on data gathering and reference information accompanying emission data, see the 'BREF guidance'¹⁰⁸.

4.2.2.3 Periodic measurements

4.2.2.3.1 EN standards

The following general EN standards or technical specifications (TS) deal with periodic measurements of air emissions (Table 4.5). Some of these are also related to ambient air measurements.

Furthermore, there are several individual standards dealing with the periodic measurement of specific pollutants in air (e.g. PCDD/F and dioxin-like PCB¹⁰⁹, 'Metals'¹¹⁰), defining standard reference methods (SRMs) for the calibration of an AMS (e.g. HCl¹¹¹, CO¹¹²), including the measurement of associated parameters, such as oxygen¹¹³ and water vapour¹¹⁴. A list of the current (2013) EN standards for air emission measurements, sorted by pollutant, is included in Annex A.1.

For the general use of EN standards and other standardised methods see Section 3.3.3.

Table 4.5:	General	EN	standards	or	technical	specifications	(TS)	dealing	with	periodic
	measure	ment	s of air emis	sion	S					

Standard No	Title					
	Air quality - Measurement of stationary source emissions -					
EN 15259:2007	Requirements for measurement sections and sites and for the					
	measurement objective, plan and report					
	Stationary source emissions - Intralaboratory validation procedure					
CEN/TS 14793:2005	for an alternative method compared to a reference method (see also					
	Section 3.3.3)					
	Air quality - Measurement of stationary source emissions -					
CEN/TS 15674:2007	Guidelines for the elaboration of standardised methods (contains a					
	summarising list of definitions)					
	Air quality - Measurement of stationary source emissions -					
CEN/TS 15675:2007	Application of EN ISO/IEC 17025:2005 to periodic measurements					
	(see also Section 3.3.1)					

EN 15259:2007 applies to periodic measurements of flue-gases using manual or automated reference methods (RMs) and aims for reliable and comparable results, representative of the

¹⁰⁸ COMMISSION IMPLEMENTING DECISION of 10 February 2012 laying down rules concerning guidance on the collection of data and on the drawing up of BAT reference documents and on their quality assurance referred to in Directive 2010/75/EU of the European Parliament and of the Council on industrial emissions (2012/119/EU).

¹⁰⁹ EN 1948 Part 1-4 Stationary source emissions - Determination of the mass concentration of PCDDs/PCDFs and dioxin-like PCBs

¹¹⁰ EN 14385:2004 Stationary source emissions - Determination of the total emission of As, Cd, Cr, Co, Cu, Mn, Ni, Pb, Sb, TI and V

¹¹¹ EN 1911:2010 Stationary source emissions - Determination of mass concentration of gaseous chlorides expressed as HCl - Standard reference method

¹¹² EN 15058:2006 Stationary source emissions - Determination of the mass concentration of carbon monoxide (CO) - Reference method: Non-dispersive infrared spectrometry

¹¹³ EN 14789:2005 Stationary source emissions - Determination of volume concentration of oxygen (O₂) - Reference method - Paramagnetism

¹¹⁴ EN 14790:2005 Stationary source emissions - Determination of the water vapour in ducts

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emissions from the source or installation. This EN standard harmonises definitions such as 'reference quantity', 'measurement section' and 'measurement or sampling plane', and specifies requirements for emission measurements of air pollutants in flue-gas ducts at industrial installations. It covers in particular:

- measurement sites, including working platforms, measurement ports, energy supply;
- measurement sections, including sampling plane;
- measurement objective (see also Section 3.1);
- measurement plan;
- measurement report; and
- reference quantities, which are needed for conversion of the measurement result to standard conditions.

Furthermore, EN 15259:2007 specifies:

- generic principles which can be applied to perform periodic emission measurements at different installation types and to meet different measurement objectives; and
- procedures for taking representative samples in flue-gas ducts.

4.2.2.3.2 General remarks

Periodic measurements are defined as the determination of a measurand at specified time intervals. For these measurements, the flue-gas sample is extracted from the channelled emission and the pollutant is analysed instantly with portable measuring systems or afterwards in the laboratory. To ensure that reliable and comparable results are obtained which are representative of the emissions, it is common practice to describe and to define the measurement site and section, the measurement objective, the determination of the operating conditions of the plant, the measurement plan, the sampling strategy, as specified in the measurement plan, and to provide a measurement report.

The personnel responsible in the testing laboratories need to have a sound knowledge and experience in carrying out emission measurements. This also includes a good understanding of the process to be monitored, which is essential for the development of a qualified measurement plan and for obtaining reliable and comparable results. The testing laboratories should meet the requirements of EN ISO/IEC 17025:2005 and CEN/TS 15675:2007. This will be checked during accreditation and related audits , and therefore, testing laboratories should be accredited (see Section 3.3.1).

4.2.2.3.3 Measurement sites and sections

According to EN 15259:2007, measurement sites and sections should be designed to enable representative sampling of the flue-gas and to measure the distribution of measurands and reference quantities. 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.

Furthermore, homogeneous and stable flow conditions are required in the measurement plane without turbulences and backflows, so that the flue-gas velocity and the mass concentration of the measured component can be determined representatively. According to EN 15259:2007, the requirement for homogeneous flow conditions is generally fulfilled if the measurement plane is:

• as far downstream and upstream from any disturbance, that could produce a change in direction of flow (e.g. disturbances can be caused by bends, fans or partially closed dampers);

- in a section of a 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 diameters: quotient of four times the area and the perimeter of the measurement plane); and
- in a section of a duct with a constant shape and cross-sectional area.

Further requirements for the measurement plane are also described in EN 13284-1:2001¹¹⁵.

In some Member States, in addition to EN 15259:2007, clear rules are set on how measurement sites, including measurement sections (sampling plane, inlets, outlets etc), should look. But in practice, in particular in the case of older installations, measurement sites and sections are, at times, not fit for the purpose and do not allow carrying out a correct sampling procedure.

4.2.2.3.4 Measurement objective and measurement plan

The measurement objective specifies the work to be carried out, the installation operating conditions (Normal Operating Conditions (NOC) and/or Other Than Normal Operating Conditions (OTNOC), if known in advance) under which measurements are to be taken, any installation or process-related information to be collected, working procedures to be used, and any associated requirements. In the measurement plan, these considerations should be taken into account and outlined in detail. The feasibility of the measurement objective should also be assessed during the elaboration of the measuring plan considering NOC and possible OTNOC, if appropriate.

To reflect the measurement objective, the measuring plan has to define, among others:

- how to monitor the operating conditions during measurements;
- where and when the samples should be taken;
- how many samples should be taken; and
- which measurement methods should be applied.

Operating conditions

The measurement plan should ensure that, depending on the measurement objective, the operating conditions, NOC or OTNOC normal operating conditions (NOC) or other than normal operating conditions (OTNOC), are clearly defined and that measures are taken that these conditions are present during the measurements. It is good practice to measure to carry out measurements representative for at-the highest emission state of the operating conditions under investigation (normally NOC), which is characterised by the highest emission mass flow. This usually corresponds to the maximum (permitted) installation output.

It has to be considered that the maximum emission mass flow is not necessarily equivalent to the maximum emission concentration of a pollutant. Furthermore, the individual emission behaviour of pollutants can proceed in opposite directions (e.g. CO and NO in combustion processes). Therefore, in the measurement objective, taking permit conditions into account, it should be defined, as to whether the results refer to concentrations or to mass flows or to both.

To identify the conditions associated with the highest emission state, it is advisable to make use of the following:

• specialist discussions with the installation operator and, if necessary, with the inspection authorities;

¹¹⁵ EN 13284-1:2001 Stationary source emissions - Determination of low range mass concentration of dust - Part 1: Manual gravimetric method

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- site visitsing the to installation and the measurement sites;
- knowledge of the installation type and the associated emission behaviour based on measurements which have already been made at the installation in question or at comparable plants;
- literature knowledge (e.g. emission factors).

It is the responsibility of the testing laboratory to define in the measurement plan all the circumstances relevant to the measurement objective, including related parameters mentioned in Section 4.2.2.3.7. If necessary, all deviations from the requirements set by EN or any other standard should already be mentioned in the measurement plan, if known in advance. A site visit is important to develop a measurement plan and to discover necessary adaptations or modifications, in particular, if the situation on site is unknown or current changes need to be determined, and furthermore to take into account safety aspects.

Sampling strategy

The sampling strategy is one major part of the measurement plan and ensures that a representative sample is taken. This requires determining the homogeneity of the flue-gas. In EN 15259:2007, there are defined procedures to follow in order to take into account the degree of homogeneity of the measurand distribution in the flue-gas and any anticipated variability over time. The procedures allow identifying the number of sampling positions and placement of the sampling points, and the sampling duration at each point.

Homogeneity test

EN 15259:2007 requires a homogeneity test to verify the profile of concentrations across the measurement plane of the conveyed flue-gas. This test is carried out usually only once, by determining the measurand in a given grid of measurement points (grid measurement sampling) and simultaneously at one point. The EN standard distinguishes three sampling methods in the case of air emissions:

- a measurement at any measuring point, if the distribution of the measurand is homogenous;
- a measurement at a representative measuring point, if it can be shown that the local mass flow density of the substance to be determined is equal to the mass flow density averaged over the measurement plane;
- a grid measurement, if the distribution of the measurand is not homogenous.

It is often wrongly assumed that the distribution of the measurand in the flue-gas is homogeneous, but in practice, influencing factors such as the design of the conducted source, temperature differences, relatively high flue-gas velocity and short retention times may cause the flue-gas to mix poorly.

Sampling

Furthermore, some pollutants, for example metals and dioxins, are present in both the particulate and vapour phases. Other pollutants, for example hydrogen chloride, may be present in an aerosol phase and gaseous vapour phase. Aerosols are normally treated as particulates. In all such cases, **grid measurement sampling** is required and the sampling train should be equipped with a combined system for the simultaneous collection of both particulate and gaseous compounds.

In summary, EN 15259:2007 requires grid measurements for:

- sampling particulates;
- sampling multiphase pollutants;
- wet chemistry sampling when droplets are present;
- velocity measurements for determining mass emission;

- sampling gases that are not distributed homogeneously, due to effects, such as stratification;
- determining a representative sample location for AMSs.

In addition, dust and particulate matter require **isokinetical sampling** according to EN 13284-1:2001¹¹⁶. If the sampling velocity is too low, a percentage of small particles will not be sampled, whereas more of the larger particles will enter the sampling probe (nozzle). This could lead to an overestimation of the dust concentration. If the sampling velocity 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^{117,118}.

Generally, the sampling should be carried out without changes in the **composition of the fluegas** (e.g. separation of water, particulate filtration) 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).

All parameters which are necessary to convert the extracted gas volume to standard conditions (see below) also need to be measured as well. Also, changes of the sample composition during transportation and storage need to be avoided.

Number of individual measurements

The number of 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, it is recommended to increase the number of samples, should be increased (e.g. up to six) to meet the measurement objective. In special cases, up to 8-10 measurements may be necessary.

Depending on the permit conditions and the related averaging (see Section 3.3.4.2), 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.

In the case of compliance monitoring for regulatory purposes, the minimum number of individual measurements in one measurement series should be specified, at the latest in the permit.

Timing and duration of sampling

The timing and duration of the emission measurement should be specified in the measurement plan in accordance with the measurement objective. The most common sampling duration is 30 minutes, but 60 minutes is applied as well, but this also depends on the pollutant (e.g. the measurement of dioxins requires a measurement duration of at least 6 hours) and the emission profile of the process.

¹¹⁶ EN 13284-1:2001: Stationary source emissions - Determination of low range mass concentration of dust - Part 1: Manual gravimetric method

¹¹⁷ InfoMil (NL): Manual Measurement of Air Emissions 2012

¹¹⁸ MCERTS Technical Guidance Note (Monitoring) M2 - Monitoring of stack emissions to air. Environment Agency, England and Wales, Version 8.1, 2011

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When choosing the sampling duration, it has to be taken into account that a sufficient mass of pollutant needs to be sampled to achieve an adequate limit of detection/quantification (see Section 3.3.4.4). For this reason, some EN standards specify that the sampling duration is dependent on the expected concentration of the pollutant in the flue-gas, the limit of detection, and on the range of the analytical procedure used by the laboratory. 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:

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

Continuous processes are characterised by approximately constant material characteristics of the fuels used and raw materials, and operating conditions, and therefore, the emission profile is relatively constant over longer time periods. For this reason, the emission measurement can be made at any point in time. A 30-minute sampling duration and three consecutive measurements in one measurement series can be considered as sufficient for a representative sampling. Examples for typical continuous processes are combustion plants, drying plants, coating plants, rotary kiln plants and crushing and classification plants.

Continuous processes with a variable emission profile can be characterised by substantially constant material feed, but time-dependent process steps that can affect the emission profile. The timing of the emission measurements should give adequate consideration to these conditions and take the changes in emission profile over time sufficiently into account. This may lead again to at least a 30-minute sampling duration, and but to several measurement series for the different emission patterns, each series consisting of at least three consecutive measurements. Examples for 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.

Discontinuous processes are predominantly characterised by the fact that the emission profile 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 sampling in order to enable evaluation of the operating state. Examples for 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.

4.2.2.3.5 Measurement frequency

In general, the measuring plan as described before, refers to one or a set of measurement series, consisting each of at least three consecutive measurements at a certain date and time. In addition, it is also advisable to define the time intervals in which periodic measurements should be performed (measurement frequency). In practice, the following frequencies related to measurement series of at least three consecutive measurements are applied, taking into account also costs aspects and potential impacts risks for the environment (see Section 3.2.1).

• 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 done yearly. Furthermore, it may be advisable to carry out indirect monitoring between measurements to ensure that no severe changes in air emissions occur between direct measurements (see also Section 4.2.5).

- Once every three years: This may be the appropriate frequency, if it can be shown over several years (e.g. 5 years) that the emission level of the NOC is clearly below the BAT-AEL or ELV (e.g. <50% of the required value). 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 carry out indirect monitoring between measurements to ensure that no severe changes in air emissions occur between direct measurements (see also Section 4.2.5).
- **Higher frequencies** (e.g. weekly, monthly, every two months, quarterly): This might be required in cases where higher emissions are expected e.g. due to OTNOC or in cases of during commissioning or decommissioning. In these cases, the higher monitoring frequency should be maintained until as long as an acceptable emission level under NOC is reached.

4.2.2.3.6 Analysis of the collected samples

For periodic measurements, the flue-gas sample is extracted from the emission source and the pollutant is either analysed on-line by mobile monitoring devices or fixed in an absorption fluid, on a filter or adsorbent. Afterwards, this fluid 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 currently (2013) available EN standards for the analysis of specific pollutants are listed in Annex A.1 together with additional information.

4.2.2.3.7 Reference conditions - standard conditions

The standard conditions for air emissions are defined at as a temperature of 273.15 K and a normal pressure of 101.3 kPa, after deduction of the water content (dry gas) and with (or without) a correction of the oxygen content. Therefore in general, the parameters: flue-gas temperature, flue-gas pressure, humidity water vapour and oxygen content need to be measured to convert the measurement results to standard conditions. In addition, to describe the sampling conditions, ambient pressure and ambient temperature are measured as well.

Order of paragraphs changed according to 4.2.2.2.5

In BAT conclusions, the applicable standard conditions are specified for temperature, pressure, moisture and, if necessary, for different oxygen contents. A formulation often used is: 'Concentrations are expressed as mass of emitted substance per volume of flue-gas under standard conditions (273.15 K, 101.3 kPa), after deduction of the water content (dry gas), with (or without) a correction of the oxygen content.' Moreover the required oxygen reference values conditions are defined for every process, where relevant.

When calculating mass emissions, for example in kg/h, different temperature, pressure, oxygen and moisture levels do not affect the <u>calculated</u> result, as because they are already considered in the measured mass concentration (mg/Nm³ dry), as well as in the measured volume flow rate (Nm³/h), assuming that both are calculated for the same standard conditions. Therefore, for the calculation of mass emissions, no conversion correction to standard conditions is needed^{119,120}.

¹¹⁹ EN 15259:2007 Air quality - Measurement of stationary source emissions - Requirements for measurement sections and sites and for the measurement objective, plan and report.

¹²⁰ MCERTS Technical Guidance Note (Monitoring) M2 - Monitoring of stack emissions to air. Environment Agency, England and Wales, Version 8.1, 2011

Several documents^{121,122,123} provide information about all the calculations necessary to convert the measured mass concentration and the measured flue-gas volume to standard conditions.

4.2.2.3.8 Data treatment

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 3.3.3).

In any case, in the measurement report (see below), all individual measurement results and references to the methods and standards applied should be listed, and any calculations should be described in detail and in a traceable way.

Furthermore, the measurement uncertainty should be stated. For periodic measurements, it is not possible to assess the measurement uncertainty for every individual measurement or every measurement series. As described in Section 3.3.3, special experimental designs, such as independent pair measurements, are necessary to assess the measurement uncertainty. Therefore, in measurement reports, a measurement uncertainty for the method is included mentioned, calculated on an experimental design that is which should be applicable under the current circumstances, taking into account the specific requirements of the related EN standard.

4.2.2.3.9 Reporting of measurement results

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 process operating conditions. In several Member States, for regulatory purposes, standard report formats are specified, which have to be used for reporting the measurement results. 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 reported¹²⁴.

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 track the way and treatment of every sample, from the measurement point to the analysis of the sample, including the data treatment, and the documentation of the result.

According to EN 15259:2007, an emission measurement report shall include at least the following items:

- a. general information, such as operator's name, the address of the installation, name and address of the testing laboratory;
- b. definition of the project by specification of the measurement objective(s);
- c. description of the installation and materials handled;
- d. identification of measurement section and measurement site;
 - identification of the measurement methods and apparatus according to individual standards for the measured pollutants and reference parameters;

e.

¹²¹ MCERTS Technical Guidance Note (Monitoring) M2 - Monitoring of stack emissions to air. Environment Agency, England and Wales, Version 8.1, 2011

¹²² InfoMil (NL): Manual Measurement of Air Emissions 2012

¹²³ EN 15259:2007 Air quality - Measurement of stationary source emissions - Requirements for measurement sections and sites and for the measurement objective, plan and report.

¹²⁴ CEN/TS 15674:2007 Air quality - Measurement of stationary source emissions - Guidelines for the elaboration of standardised methods

- f. operating conditions of the production process during measurement, including flue-gas cleaning units;
- g. identifications of deviations from the measurement plan;
- h. reference on how to access and use the original data for verification purposes;
- i. measurement results and other relevant data necessary for the interpretation of results, including sampling date (hour, day, month and year) and measurement uncertainties;
- j. calculation procedures, such as the conversion of data to specific standard conditions;
- k. 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.

4.2.2.3.10 Elaboration of BREFs

In general, for the elaboration or the review of BREFs, complete measurement **reports for periodic measurements** are not submitted. However, in order to allow a correlation between the data and NOC or OTNOC it is advisable to report at least, 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.

If averaged values are reported, in addition, the number of individual measurements and the minimum and the maximum values are relevant for assessment of the data.

The provided data are the basis for the elaboration of BAT conclusions and, where appropriate and reasonable, for BAT-AELs. Associated with to BAT-AELs, the monitoring regime needs to be defined. Based on the aforementioned information and on the data provided during the current (2013) BREF elaboration processes, the following general conditions for periodic measurements are widely-used in BAT conclusions:

- reference conditions (temperature 273.15 K, pressure 101.3 kPa, dry gas, defined oxygen content);
- at least 30-minutes sampling duration, if appropriate;
- 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 NOC, if appropriate.

Depending on the industrial sector and the pollutant, the reference conditions for periodic measurements might be adapted, such as expression of the odour measurements on wet gas, or at least six hour a deviant sampling duration for PCCD/F. Also, more than three consecutive measurements and a lower or higher measurement frequency might be appropriate, in some cases.

Furthermore, if sufficient data are available, it might be possible to mention a specific **measurement uncertainty** in connection to the BAT-AEL range associated with a BAT conclusion.

In addition, a reference to the measurement uncertainty might be introduced in the BAT conclusion as a rationale for the lower and/or upper end of specific BAT-AELs, if sufficient data is available.

For further information on data gathering and reference information accompanying emission data, see the 'BREF guidance'¹²⁵.

4.2.3 Indirect monitoring of emissions using surrogate parameters

Former Section 4.2.5 'Indirect monitoring of emissions - Surrogate parameters and biological monitoring using plants' split in two parts, the current section and Section 'Indirect monitoring of emissions using biological monitoring with plants'

4.2.3.1 General remarks

As already pointed out in Section 3.2.3.3.1, surrogate parameters are measurable or calculable parameters that can which may be used instead of the direct measurements of specific pollutant values for some practical purposes and/or for economical reasons. The use of surrogate parameters, either individually or in combination, may provide a sufficiently reliable picture of the nature and proportions of the emission.

Key advantages of the use of surrogate parameters may include:

- easily and reliably measured or calculated;
- cost savings, thus greater cost effectiveness;
- more continuous information may be possible than with direct periodic measurements;
- more release points may be monitored for the same or lower costs and resource;
- sometimes they are more accurate than direct emission measurements;
- can give an early warning of possible upset conditions or abnormal emissions, e.g. combustion temperature changes to alert of a potential increase in dioxin emissions;
- less disruption to the process operation than direct emission measurements;
- information from several direct measurements may be combined, thereby giving a more complete and useful picture of a process performance, e.g. a measurement of temperature may be useful for energy efficiency, pollutant emissions, process control and control of raw material;
- recovery of corrupted emission monitoring data.

Key disadvantages of the use of surrogate parameters may include:

- more resources may be are needed for calibration with direct emission measurements;
- may only provide a relative measurement rather than an absolute value;
- may only be valid for a restricted range of process conditions;
- may not lead to as much public confidence as direct emission measurements;
- less accurate sometimes than direct emission measurements;
- sometimes they may not be used for legal purposes.

Some national regulations include provisions for the use of surrogate parameters. For example, when polluting substances in flue-gas are in a constant relationship to each other, then continuous measurement of the leading component can be used as a surrogate for the rest of the pollutant substances.

¹²⁵ COMMISSION IMPLEMENTING DECISION of 10 February 2012 laying down rules concerning guidance on the collection of data and on the drawing up of BAT reference documents and on their quality assurance referred to in Directive 2010/75/EU of the European Parliament and of the Council on industrial emissions (2012/119/EU).
Similarly, continuous emission measurements of a specific compound may be waived if the attainment of emission standards can be sufficiently proven by applying other tests as surrogates, e.g. the continuous measurement of the efficiency of the emission control system, composition of fuels or raw materials, or process conditions.

There are conditions and practices applied at the installation level that support a good use of surrogate parameters instead of direct emission measurements; these include:

- a well operated maintenance system;
- an environmental management system;
- a good history of measurements;
- limited production or emission load.

4.2.3.2 Examples of the different categories of surrogate parameters

As described in Section 3.2.3.3.1, the following three categories of surrogates may be distinguished on the basis of the strength of the relationship between the emission and surrogate:

- quantitative surrogate parameters;
- qualitative surrogate parameters;
- indicative surrogate parameters.

Examples of these are provided below. Combinations of the surrogates mentioned may result in a stronger relationship and therefore, in a stronger surrogate.

Quantitative surrogates provide a reliable quantitative picture of the emission and can substitute for direct emission measurements. Examples of their use may include:

- the assessment of total VOCs instead of the individual components, when the composition of the gas flow is constant;
- calculation of the flue-gas concentration from the composition and throughput of fuel, raw materials, and additives and from the flow rates;
- continuous dust measurements, as a good indication of the maximum potential metal emissions;
- the assessment of dust instead of PM₁₀ and PM_{2.5}, when the PM-composition of the fluegas is constant.

Qualitative surrogates provide reliable qualitative information on the composition of the emission. Examples may include:

the temperature of the combustion chamber of a thermal incinerator and the residence time (or flow rate);

- the temperature of the catalyst in a catalytic incinerator;
- the measurement of CO or total VOCs of the flue-gas from an incinerator;
- the temperature of the gas from a cooling unit.

Indicative surrogates provide information about the operation of an installation or process and therefore give an indicative impression of the emission. Examples may include:

- temperature of the gas flow from a condenser;
- pressure drop, flow rate, pH and humidity of a biofilter;
- pressure drop and visual inspection of a fabric filter to control the cleaning mechanism.

4.2.3.3 Examples of plants using surrogates as monitors

In Table 4.6, some examples of plants that use different surrogates, and an indication of the surrogate type are given.

Plant	Surrogate parameter	Type of surrogate
Furnaces	Calculation of SO_2 emissions: mass balance based on raw material, fuel quality and final product	Quantitative
Thermal Incinerators	Temperature of the combustion chamber	Qualitative
	Residence time (or flow rate)	Indicative
Catalytic incinentana	Residence time (or flow rate)	Indicative
Catarytic incluerators	Temperature of the catalyst	Indicative
	Flow rate	Indicative
Electrostatic Precipitators	Voltage	Indicative
	Quantity of removed dust	Indicative
	Air flow	Indicative
Wet Dust Separators	Pressure in the pipe system for washing liquid	Indicative
	Functioning of the pump/flow washing liquid	Indicative
	Temperature of the treated gas	Indicative
	Pressure drop over the scrubber	Indicative
Fabric Filters	Pressure drop over the filter to control the cleaning mechanism	Indicative

 Table 4.6:
 Examples of plants that use different surrogates including the type of surrogate

4.2.3.4 Predictive Emissions Monitoring Systems (PEMS)

Predictive Emissions Monitoring Systems (PEMS) are systems used to determine the emissions concentration of a pollutant based on its 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.

Systems for predicting emissions (e.g. for NO_X^{126}) are currently (2013) under investigation, combining 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 done and validated under a broad range of conditions, but the advantage is that calculated values can be determined based on the continuous process control parameters and systems operating in the control room. In any case, PEMS need to be proven, as to whether they are applicable for a certain process. At present, there are activities in the Technical Committee CEN/TC 264 'Air quality' to standardise PEMS¹²⁷.

In some industrial sectors it might be useful to apply PEMS. In the definitions of the BAT conclusions of the 'Mineral Oil and Gas Refineries' (REF 2013) BREF, PEMS are already mentioned as an indirect monitoring method.

¹²⁶ Netherlands technical agreement NTA 7379 (en) Guidelines for Predictive emission monitoring systems (PEMS) - Execution and quality assurance

¹²⁷ CEN/TC 264/WG 37 Predictive Emission Monitoring systems - Applicability execution and quality assurance

4.2.3.5 Elaboration of BREFs

The use of monitoring of surrogate parameters in BAT conclusions BREFs is limited due to the fact that the comparison with BAT-AELs requires, generally, a quantification of the emission to air. But there are several examples where surrogate parameters are used, in particular, if a qualitative or an indicative assessment is of interest.

In the 'Manufacture of Glass' (GLS 2012) BREF in BAT conclusion No 7, it is mentioned that surrogate parameters can be used to ensure that the treatment system is working properly between periodic measurements of dust, NO_X and SO_2 emissions. Furthermore, the continuous monitoring of surrogate parameters can be performed to ensure that the waste gas treatment system is working properly and that the emission levels are maintained between periodic measurements. As examples for surrogate parameters, reagent feed, temperature, water feed, voltage, dust removal, and fan speed are listed.

In the 'Iron and Steel Production' (IS 2012) BREF in BAT conclusion No 46, for the reduction of diffuse emissions from coke oven plants, the control of the visible emissions from all doors is used as a surrogate parameter.

In the 'Tanning of Hides and Skins' (TAN 2013) BREF in BAT conclusion No 3, for the regular control of dust emissions, the indicative monitoring of the pressure drop across the bag filters is used as a indicative surrogate parameter. Also, in the Draft 3 of the 'Non-ferrous Metals Industry' (NFM 2013) BREF for dust emissions from especially defined sources, it is stated monitoring could be based on the measurement of surrogate parameters such as the pressure drop.

In the 'Mineral Oil and Gas Refineries' (REF 2013) BREF, indirect monitoring methods are mentioned in BAT conclusion No 4 on the monitoring of air emissions. In a footnote, it is described that for combustion units the 'continuous measurement of SO_2 emissions may be replaced by calculations based on measurements of the sulphur content of the fuel or the feed, where it can be demonstrated that this alternative leads to an equivalent level of accuracy'. Furthermore, for the sulphur recovery units (SRU), the surrogate parameter 'continuous material balance' may be applied to replace SO_2 emissions measurements, if appropriate measurements of the SRU efficiency can be provided.

4.2.4 Monitoring of diffuse diffusive and fugitive emissions

4.2.4.1 Overview

The quantification of the total emissions of an installation often requires an assessment of **diffuse and fugitive emissions** including fugitive emissions (see definitions Section 4.2.4.3). It is recognised that these emissions can potentially account for a considerable amount of total emissions and can cause relevant impacts on the environment. Sometimes diffuse and fugitive emissions may also have economic significance for an installation. For these reasons, IED permits and BAT conclusions include, where appropriate and reasonable, provisions to properly monitor and reduce these emissions.

The quantification of diffuse and fugitive emissions, including fugitive 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 results might be low. Furthermore, and, due to the extended number of potential sources, the assessment of the total amount of diffuse and fugitive emissions may be more costly than point source emission measurements. However, there are ongoing activities, in particular by the Technical Committee CEN/TC 264, to define standardised methods for the measurement of diffuse and fugitive emissions.

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4.2.4.2 Definitions

Section moved

Commonly used definitions of diffuse and fugitive emissions are¹²⁸:

• **Diffuse emissions:** Emissions of pollutants into the environment arising from a direct (non-channelled) contact of volatile or dusty substances with the environment under normal operating conditions.

Diffuse emission sources can be point, linear, surface or volume sources. Multiple emissions inside a building are normally considered as diffuse emissions. Other examples of diffuse emissions include venting from storage facilities during loading and unloading, the storage of solid matter in the open air, separation pools in oil refineries, vents, doors in coke plants, mercury emission from electrolysis cells, etc.

• **Fugitive emissions:** Emissions of pollutants into the environment resulting from a gradual loss of tightness of a piece of equipment designed to contain an enclosed fluid (gaseous or liquid). Fugitive emissions are a subset of diffuse emissions.

4.2.4.3 EN standards

The following general EN standards or drafts deal with diffuse and fugitive emissions (Table 4.7).

For the general use of EN standards and other standardised methods see Section 3.3.3.

Standard No	Title	
	Fugitive and diffuse emissions of common concern to industry	
EN 15445:2008	sectors - Qualification of fugitive dust sources by Reverse	
	Dispersion Modelling	
	Fugitive and diffuse emissions of common concern to industry	
EN 15446:2008	sectors - Measurement of fugitive emission of vapours generating	
	from equipment and piping leaks	
	Air quality - Atmospheric measurements near ground with active	
FprEN 16253:2013	Differential Optical Absorption Spectroscopy (DOAS) - Ambient air	
	and diffuse emission measurements	

 Table 4.7:
 General EN standards or EN drafts (FprEN) dealing with the measurements of diffuse and fugitive air emissions

EN 15445:2008 deals with dust emissions and is based on reverse dispersion modelling, and therefore, takes into account field data such as number, height and width of diffuse dust sources, the results of ambient air dust measurements, sampling distances between emission source and sampling location, and meteorological information. The standard method is a tool to identify relevant diffuse dust emission sources and to implement reduction and control measures. In the standard, it is stated that it should not be used for compliance assessment or for the comparison of different installations belonging to the same industrial sector.

EN 15446:2008 applies to the measurement of fugitive emissions of volatile organic compounds (VOCs) from process equipment, where VOCs are defined as all products of at least 20 % by weight, with a vapour pressure higher than 0.3 kPa at 20 °C. The method uses portable instruments to detect VOC leaks from individual sources (also called the 'sniffing method') and to measure concentrations. In addition, it gives a procedure to estimate the mass emission rate

¹²⁸ MON REF Reference Document on the General Principles of Monitoring, July 2003

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.

A new standard is currently (2013) under development: **FprEN 16253:2013**. It describes the operation of active Differential Optical Absorption Spectroscopy (DOAS) measuring systems based on a continuous radiation source for measurements in ambient air or in diffuse emissions. It also contains calibration procedures, applications in determining gaseous constituents (e.g., NO₂, SO₂, O₃, Hg, benzene, toluene, xylene and other VOCs), and specifications of performance characteristics and measurement uncertainties. A procedure to estimate the mass emission rates is not given.

In the draft standard, it is mentioned that DOAS might be used as an alternative measuring technique, on which emission estimates can be based in those cases where 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.

Independent from the EN standards aforementioned, the standard EN 15259:2007¹²⁹ can be applied as well if direct emission measurements are carried out at diffuse sources, in particular, the planning and reporting aspects of this standard.

4.2.4.4 Quantification of diffuse and fugitive emissions

As mentioned before for the determination of diffuse diffusive dust emissions with reverse dispersion modelling (RDM), the standard method EN 15445:2008, and for the estimation measurement of fugitive emissions of volatile organic compounds EN 15446:2008, can be used. Furthermore, the draft standard FprEN 16253:2013 provides a methodology based on a DOAS system, which allows the measurement of several gaseous pollutants.

In Germany, a guideline is available (VDI 4285 Part 1 to 3^{130}), which specifies the general principles for the determination of diffuse emissions in Part 1, and which specifies methods for determining diffuse emissions from industrial halls and buildings of livestock farming in Part 2 and allows for the determination of emission rates by indirect and direct methods. In the case of the direct methods, the emission measurement is carried out directly at the source and is always based on the measurement of the volume flow and the concentration. In Part 3 the guideline describes procedures for the determination and quantification of diffuse emitted particulate matter such as PM_{10} and $PM_{2.5}$ from industrial plants including agricultural sources.

There are several other techniques available for detecting and/or quantifying diffuse, which include and fugitive emissions. Some examples are listed and briefly described below:

- estimation of emissions by analogy with channelled emissions;
 - calculation of emissions from storage tanks, loading and unloading, and from water utilities, using emission factors and/or correlations;
- optical gas imaging techniques (OGI);
- mass balances (e.g. solvents, SO_X);
- long path optical monitors (others than those covered by FprEN 16253:2013);
- use of tracer gases;

¹²⁹ EN 15259:2007 Air quality - Measurement of stationary source emissions - Requirements for measurement sections and sites and for the measurement objective, plan and report.

¹³⁰ VDI 4285 Determination of diffusive emissions by measurements; Part 1:2005 Basic concepts; Part 2:2011 Industrial halls and livestock farming; Part 3:2013 Quantification of diffusive emissions of particulate matter from industrial plants including agricultural sources

- monitoring methods using reverse dispersion modelling (others than those covered by EN 15445:2008);
- assessment of wet and dry depositions downwind of the plant;
- leak detection and repair programme (LDAR) as a combination of different methods.

Estimation of emissions by analogy with channelled emissions

This method consists of defining a 'reference surface' through which a flux of matter is measured. For a channelled emission, this reference surface is the cross-section of the pipe; for diffuse and fugitive emissions, however, the reference surface is sometimes complex to define. For instance, such a surface could be a compost pile, a theoretical surface more or less perpendicular to the plume of pollutants downwind of the source, the surface of a liquid, etc. To create a reference surface, wind tunnels or hoods may be are used.

Calculation of emissions from storage tanks, loading and unloading, and from water utilities, using emission factors and/or correlations

Emissions from storage tanks, loading/unloading operations, waste water treatment, and cooling water systems are usually calculated based on general emission factors and/or correlations. Calculation methodologies are published by API (American Petrol Institute), US EPA (United States Environmental Protection Agency) and CEFIC/ECVM (European Chemical Industry Council/European Council of Vinyl Manufacturers). These emissions can also be estimated measured by using the measurement results of DOAS and other long path optical monitors.

Optical gas imaging (OGI) techniques

Optical imaging uses small lightweight hand-held 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 component concerned. This technique is primarily used to easily and rapidly locate significant VOC leaks e.g. on process components, storage tanks fittings, pipeline flanges or vents. OGI is a qualitative monitoring method and but it may be possible to use also to estimate mass emission rates cannot be quantified. OGI techniques are mentioned e.g. in the Mineral Oil and Gas Refineries (REF 2012) BREF.

Mass balances

These procedures normally consider for inputs: accumulations, outputs, and the generation or destruction of the substance of interest, and account for the difference by classifying it as a release to the environment. If materials are transformed in the process, for instance by incineration, it is in principle possible to achieve a balance, not in terms of actual mass of product, but in terms of an element (for example, carbon in combustion processes).

The result of a mass balance is usually a small difference between a large input and a large output, also taking into account the uncertainties involved. Therefore, mass balances are only applicable in practice when accurate input, output and related uncertainties can be determined.

Long path optical monitors

This approach detects and quantifies downwind concentrations by using electromagnetic radiation, which is absorbed and/or diffused by the different pollutants. A simple way to use electromagnetic radiation is through light properties (i.e. ultraviolet, visible or infrared). The travel path of a light beam of a certain wavelength can be modified by contact with emitted substances, e.g. particulates, gaseous molecules. Based on the measurement results, it might be possible to calculate an emission estimate.

In addition to the DOAS system mentioned before, other examples of existing operational techniques are:

• **DIAL** (Differential Infrared Absorption LIDAR): A pulse of lights (e.g. about one per microsecond) with a very well-defined wavelength is diffused and absorbed by molecules and by dust particles. The time analysis of the "echo" observed with an optical device makes it possible to measure the pollutant concentration and location in the ambient

atmosphere. With the additional use of diffusion modelling techniques, a rough indication of the area of emission can be estimated.

• **SOF** (Solar Occultation Flux): A broadband IR or UV/Visible sunlight spectrum is recorded and a spectrometric Fourier Transform analysis is carried out along a given geographical itinerary, crossing the wind direction and cutting through emission plumes, is carried out.

Use of tracer gases

This method consists of releasing a tracer gas in different identified points or areas of the installation site and at various heights above the surface of the factory site. Then the pollutant (e.g. VOCs) and tracer gas (e.g. SF_{6}) concentrations are measured downwind of the factory by portable samplers or portable gas chromatographs. 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.

The use of SF_6 as a tracer gas may be limited because it is a powerful greenhouse gas.

Monitoring methods using reverse dispersion modelling (RDM)

Following the method described in EN 15445:2008 for dust, it is possible with RDM to estimate 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.

Assessment of wet and dry depositions downwind of the plant

A qualitative monitoring of diffuse and fugitive emissions may be performed by analyses of wet and dry depositions downwind of the plant, which then allows an estimation of the evolution of diffuse and fugitive emissions over time (monthly or yearly basis). An alternative measuring method may be used near the emission sources (e.g. biomonitoring; see Section 4.2.5.2). This method is used for stable compounds likely to accumulate (e.g. heavy metals and dioxins), provided that the source of emission can be distinguished unambiguously from the background ambient concentration.

Leak detection and repair programme (LDAR)

LDAR is not a monitoring method. It is a management programme <u>A leak detection and repair</u> programme (LDAR) can be applied to determine and reduce fugitive VOC emissions, . A LDAR programme includinges identification of the leaking components, and repair of these leaks in order to minimise losses. For leak detection, the method described in EN 15446:2008 usinges hand-held analysers (also called the 'sniffing method') and an optical gas imaging (OGI) method. In practice, OGI is used to complement the EN 15446:2008 method, but it can also replace it. Especially for tank roofs, which are difficult to monitor with hand-held analysers, OGI can give useful information on emissions. Depending on the individual case, LDAR programmes may be complemented by one or another of the aforementioned monitoring methods. LDAR are mentioned e.g. in the 'Common Waste Water and Waste Gas Treatment/Management Systems in the Chemical Sector' (CWW 2011) and in the 'Mineral Oil and Gas Refineries' (REF 2012) BREF.

4.2.4.5 Elaboration of BREFs

Diffuse Diffusive and/or fugitive emissions can, in some industrial sectors, account for a relevant part of the total installation emissions, and, as a consequence, in specific BREFs such as 'Iron and Steel Production' (IS 2012), 'Mineral Oil and Gas Refineries' (REF 2013) and 'Non-Ferrous Metals Industries' (NFM 2013), BAT conclusions address diffuse and fugitive emissions.

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One example can be found in BAT conclusion No 16 of the IS BREF, where, in general, the order of magnitude of diffuse emissions from relevant sources has to be determined by direct measurement methods (preferred method), by indirect measurement methods where the emission determination takes place at a certain distance from the source, or by the calculation with emission factors.

In the REF BREF, for the detection of diffuse VOC emissions, the following methods are listed in a BAT conclusion:

- methods using hand-held analysers (also called 'sniffing methods'), according to EN 15446:2006 associated with correlation curves;
- optical gas imaging techniques;
- calculations of chronic emissions based on emissions factors periodically (e.g. once every 2 years) validated by measurements.

As complementary monitoring methods, periodic campaign measurements with optical absorption based techniques, such as differential absorption light detection and ranging (DIAL) or solar occultation flux (SOF) are mentioned.

4.2.5 Odour measurements

Section moved

4.2.5.1 Overview

Odour emissions occur in several industrial sectors, such as the intensive rearing of animals, the food industry, waste water treatment, iron and steel industry, chemical industry, and waste treatment, and 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 H_2S or NH_3 , or organic substances, such as hydrocarbons, sulphur compounds (e.g. mercaptans) or amines.

After the odorous emission is released, depending on the location of the installation, odours 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.

Order of paragraphs changed.

In general, the odour of an emission is composed of several (hundred) 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 of the amount of total odour emission. As a consequence, odour measurements are mainly performed with human sensors. Nevertheless, there are some methods which aim for estimating odours by other methods rather than human assessors (e.g. electronic sensors / 'electronic noses').

There are several methods available for monitoring odours quantitatively or qualitatively, by direct or indirect methods. In the following sections, parameters to describe odours, such as odour concentration, intensity and hedonic tone, and some common methods applied in Europe for the monitoring of odour emissions are presented in more detail.

Further monitoring methods such as odour surveys and electronic noses are summarised in Annex A.4 'Monitoring of odours using survey and electronic noses'.

4.2.5.2 Definitions of odour parameters Section moved

There are several parameters which can be used to describe odours. The following definitions are given in EN 13725:2003¹³¹ and by the Technical Committee CEN/TC 264/WG 27.

Odour detection: To become aware of the sensation resulting from adequate stimulation of the olfactory system.

Detection threshold: The odorant concentration which has a probability of 0.5 of being detected by human assessors under the conditions of the test.

At the detection threshold, the odour can be perceived by humans but not recognised. The detection threshold is characteristic for each chemical substance.

Odour concentration: Number of European odour units in a cubic metre (ou_E/m^3) of neutral (odourless) gas at standard conditions. The A standardised method to measure the odour concentration is given in EN 13725:2003. The odour concentration, in ou_E/m^3 , can be used in the same manner as mass concentrations in kg/m³.

Odour intensity^{132,133}: Strength of odour sensation caused by the olfactory stimulus. The odour intensity can be described by the following category ordinal scale:

- 0 No odour
- 1 Very faint odour
- 2 Faint odour
- 3 Distinct odour
- 4 Strong odour
- 5 Very strong odour
- 6 Extremely strong odour.

When using odour concentrations one should be aware that according to Steven's Law, the relationship between the odour intensity and the odour concentration is not linear, and can follow a different relationship for different (mixtures of) odorants.

Hedonic odour tone¹³⁴: Effect of an odorant, which is recorded in a classificatory assessment of the stimulus between the extremes of 'extremely pleasant' and 'extremely unpleasant'. To assess the hedonic tone the following category ordinal scale is used:



¹³¹ EN 13725:2003 Air quality - Determination of odour concentration by dynamic olfactometry

¹³² VDI 3882 Part 1:1992 Olfactometry – Determination of Odour Intensity

¹³³ H4 Odour Management 2011, Environmental Agency of England and Wales

¹³⁴ VDI 3882 Part 2:1994 Olfactometry; Determination of hedonic odour tone

The hedonic tone, in some cases, changes with increasing odour concentrations but, in general, the hedonic tone is odour composition specific and independent of the concentration.

The measurement of **odour intensity** and the **hedonic tone** of emissions can be done by dynamic olfactometry but the possible variability in human sensors for these parameters is significantly higher than for odour concentration measurements. Therefore, more panel members are necessary to produce reliable results; for measurements of odour intensity, at least 8 panel members¹³⁵ and for measurements of the hedonic tone, at least 15 panel members¹³⁶ are required. This makes these measurements more laborious, more time-consuming, and two to four times more costly than odour concentrations measurements according to EN 13725:2003.

In addition, the range of odour concentrations presented to the panel members need to be higher, to cover different levels of the related category scales than for odour concentration measurement only. This can cause serious contamination problems in the dilution system of the olfactometer.

The additional efforts and the problem of contamination are the reasons why, in practice, odour intensity and the hedonic tone of odour emissions are not, or are only seldom, measured.

In some Member States^{137,138,139} there are methods available and implemented in regulation which makes use of the assessment of odour intensity and hedonic tone in the vicinity of industrial installations.

Odour recognition (in ambient air): An odour sensation in ambient air that allows positive identification of the odour type.

Odour type (in ambient air): Odour that can be recognised and assigned to a certain installation or source.

In the case of the monitoring of odours in ambient air caused by an installation, this encompasses that the recognised odour can be addressed and allocated to defined odour types.

Odour exposure (in ambient air): Contact of a human with a defined odour type, quantified as the amount of odour available for inhalation at any particular moment.

As odours have no effect below the detection threshold limit of the human olfactory system, exposure to recognisable odours may be characterised as the frequency of occurrence of concentrations above a certain odour concentration (the recognition threshold limit).

Odour frequency (in ambient air): The number of hours with recognisable odours during a longer time period (e.g. half a year or one year). It can be determined by the grid method¹⁴⁰ in defined assessment squares in a certain area.

Plume extent (in ambient air): The shape of the plume downwind of the installation or source. It can be determined by the plume method¹⁴¹ by delineating a smooth interpolation polyline

- VDI 3882 Part 1:1992 Olfactometry Determination of Odour Intensity
- ¹³⁶ VDI 3882 Part 2:1994 Olfactometry; Determination of hedonic odour tone
- ³⁷ NF X43-103:1996: Qualité de l'air Mesurage olfactométriques Mesurage de l'odeur d'un effluent gazeux - Méthodes supraliminaires (Air quality - Olfactometric measurements - Measurement of gaseous odour release - Suprathreshold methods).
- ¹³⁸ VDI 3940-3:2010 Measurement of odour impact by field inspection Determination of odour intensity and hedonic odour tone
- ³⁹ VDI 3940-4:2010 Determination of the hedonic odour tone Polarity profiles
- ¹⁴⁰ prEN: Air Quality Determination of odour in ambient air by using field inspection Part 1: Grid method (draft will be available in 2013)

through the plume borders (transition points); the source location and the location determined by the estimation of the maximum plume reach.

4.2.5.3 EN standards

The following European standard is currently (2013) available for the determination of odour emissions:

EN 13725:2003 Air quality - Determination of odour concentration by dynamic olfactometry

EN 13725:2003 describes the periodic measurement of the odour concentration in a sample of air emissions by dynamic olfactometry using selected and trained members composing a panel. The standard includes the methodology for the determination of emissions rates. It is widely applied in Europe and is part of the accreditation of testing laboratories (see Section 3.3.1).

Currently, two new EN standards are under development by the Technical Committee CEN/TC 264/WG 27 'Air quality - Determination of odour exposure in ambient air by using field inspection'. These are the determination of odour in ambient air by using selected and trained panels in the field: the 'grid method' (part 1) and the 'plume method' (part 2)¹⁴².

The relationships between the different odour measurement methods - olfactometry, grid method and plume method - are shown in Figure 4.1^{143} .

The figure shows that for an inspection at source, the preferred method of emissions measurements is olfactometry according to EN 13725:2003. For detection of the odour exposure in the field, the grid method is chosen, whereas for the measurement of the plume extent, and to carry out reverse dispersion modelling of the emission rate, the plume method is applied.

All three methods - olfactometry, grid method and plume method - are described in more detail in the following sections.

141 prEN: Air Quality — Determination of odour in ambient air by using field inspection Part 2: Plume method (draft will be available in 2013)

¹⁴² prEN: Air Quality — Determination of odour in ambient air by using field inspection Part 1: Grid method; Part 2: Plume method (draft will be available in 2013)

¹⁴³ see reference No 141 (prEN: Part 1: Grid method; Part 2: Plume method)



Figure 4.1: Overview of existing odour exposure assessment methods including grid method (Part 1), plume method (Part 2) and dynamic olfactometry according to EN 13725:2003 as given in the prEN from the Technical Committee CEN/TC 264/WG 27.

4.2.5.4 Measurement of odorous emissions by dynamic olfactometry

Generally, measurement of the odour concentration is a special part of periodic emission measurements, therefore, the EN standards for periodic measurements, in particular EN 15259:2007¹⁴⁴ (Requirements for measurement sections and sites and for the measurement objective, plan and report) should be applied (Section 4.2.2.3). However, there are some adaptations or modifications required, which will be mentioned in the following sections, where necessary.

4.2.5.4.1

Measurement of odour concentration

In EN 13725:2003, a method for the objective determination of the odour concentration of gaseous samples using dynamic olfactometry and for the calculation of the emission rate for odours is specified. An olfactometer is used to dilute the sample with neutral gas in a defined ratio and present the diluted gas stream to a panel consisting of at least four selected and trained panel members.

¹⁴⁴ EN 15259:2007 Air quality - Measurement of stationary source emissions - Requirements for measurement sections and sites and for the measurement objective, plan and report.

The odour concentration is measured by determining the dilution factor required to reach the detection threshold of the panel members for the emission sample under investigation. The odour concentration at the detection threshold is by definition one **European odour unit per cubic metre** (ou_E/m^3) and the odour concentration of the examined emission sample is expressed as a multiple of one European odour unit at standard conditions for olfactometry. The multiple is equal to the dilution factor needed to reach the detection threshold limit.

In contrast to the **standard conditions** for 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 olfactometric measurements as well as to volume flow rates of emissions. The conditions were chosen by convention, to reflect typical conditions for smell perception.

To ensure objective, reliable, representative and comparable results, EN 13725:2003 defines the **testing procedure and quality requirements** for the following parts of the method:

- Performance quality requirements for the olfactometer and the pre-dilution system in terms of accuracy and instability.
- Performance quality requirements within one laboratory on reference material (odorant: n-butanol) in terms of accuracy and precision.
- Performance quality requirements within one laboratory for non-reference materials (odorants) in terms of precision.
- Assessment of precision between laboratories (reproducibility) by interlaboratory comparison.
- Performance quality requirements for human assessors to become a panel member.
- Minimum requirements for a set of panel member responses, including a retrospective screening of all responses after each measurement.

A testing laboratory has to comply with these requirements if it wants to get accredited for odour concentration measurements, i.e. the dilution steps of the olfactometer need to be calibrated; the human assessors need to be selected according to strict protocol to become a panel member; and finally, the overall sensory quality requirements in terms of accuracy and precision (repeatability) need to be reached.

Dynamic olfactometry as described in EN 13725:2003 leads to reliable measurement results. Therefore, the method is widely applied in Europe for the measurement of emissions of odorous gases^{145,146,147,148,149}.

4.2.5.4.2 Sampling, storage and transport

In general, the sampling is similar to that of other periodic air pollutants measurements (see Section 4.2.2.3), and comprises e.g. a recommended sampling duration of 30 minutes and at least three consecutive measurements; but it needs to be ensured that the odour does not change in quality and quantity.

145 UK: Stack Emissions Monitoring - Method Implementation Document for EN 13725; MCERTS 2013

¹⁴⁶ H4 Odour Management 2011, Environmental Agency of England and Wales

¹⁴⁷ Netherlands technical agreement NTA 9065:2013 Air quality - Odour measurements - Odour measurement and calculation

¹⁴⁸ DE: Detection and Assessment of Odour in Ambient Air (Guideline on Odour in Ambient Air – GOAA) 2008

¹⁴⁹ VDI 3884 Part 1 draft:2012 Olfactometry - Determination of odour concentration by dynamic olfactometry -Supplementary instructions for application of DIN EN 13725

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Therefore, in general, everything which can cause a change in odour concentration or composition, such as condensation while sampling, using oxygen for pre-dilution instead of nitrogen, should be avoided. All materials which could come into contact with the sample should be odourless.

Normally, the bags for sampling have a size from 10 litres up to 50 litres. It is recommended to use transparent bag materials to allow the possibility to check whether e.g. condensation occurs. For the bag material, polyethyleneterephthalate (e.g. NalophanTM) is widely used.

The sample bags are conditioned before sampling. Therefore, they are filled with sample gas in advance and then emptied again.

The most common sampling system follows the 'lung principle', where the sample bag is placed in a rigid container. Afterwards, the air is removed from the container using a vacuum pump; the under-pressure in the container 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.

In EN 13725:2003, it is stated that the samples should be analysed as soon as possible after collection. A maximum storage time of 30 hours is indicated. In practice, it is advisable to carry out the olfactometric measurement as soon as possible to minimise the likelihood that any changes during sample storage will occur. Some national guidelines¹⁵⁰ reduce the storage time to six hours and for longer storage times proof should be provided that the odour concentration in the samples has not changed.

In UK¹⁵¹ and in Germany¹⁵², there are documents available which describe, in particular, the sampling for olfactometric measurement of odours according EN 13725:2003.

4.2.5.4.3 Reporting of measurement results and data treatment

Reporting includes the topics given in EN 15259:2007 for periodic measurements (see Section 4.2.2.3). For odour emission, some specific calculations need to be done in addition.

To derive the odour concentration expressed as European odour units per cubic metre (ou_E/m^3) for each emission sample, calculations have to be done based on the dilution factors determined for each panel member. These calculations should be included in the report, as well as any applied pre-dilution. Furthermore, it needs to be shown that each panel member used for the current measurements fulfils the requirements of the EN standard.

As already stated, odour concentration and emission rates are generally expressed for standard conditions of 293.15 K and wet gas.

4.2.5.5

Field measurement of odour exposure using human sensors

Currently (2013) the Technical Committee CEN/TC 264/WG 27 ('Air quality - Determination of odour exposure in ambient air by using field inspection') is working on a standard for the determination of odour in ambient air. It The working group is planninged to investigate and describe two methods; the grid method (part 1) which is mainly based on VDI 3940 Part

¹⁵⁰ VDI 3880:2011 Olfactometry - Static sampling

¹⁵¹ MCERTS 2013 Stack Emissions Monitoring Method Implementation Document (MID) for EN 13725; Air Quality – Determination of odour concentration by dynamic olfactometry; Measurement of odour in stack gas emissions

¹⁵² VDI 3880:2011 Olfactometry; Static sampling (available in English)

 $1:2006^{153}$ and the plume method (part 2) which is mainly based on the plume method used in Flanders¹⁵⁴ and on VDI 3940 Part $2:2006^{155}$.

The results of these methods are typically used to determine the exposure of residents to recognisable odours, or to estimate the total emission rate using reverse dispersion modelling. In particular, the plume method can be useful for estimating emission rates for diffuse odour sources where sampling at source is impracticable.

4.2.5.5.1 Grid method

The grid method is a statistical survey method which should be applied over a sufficiently long period of time (e.g. half a year or one year), to provide a representative map of the exposure of the population to recognisable odours. The results of grid measurements show the frequency distribution of recognisable odours in ambient air in an assessment area under meteorological conditions that are assumed to be representative for the local meteorology.

The parameter measured by human panel members is the 'odour hour frequency'. 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, independently if the odour emissions are channelled or diffuse.

The odour types to be perceived need to be defined in advance in a detailed measurement plan to allow an identification of the originating source. In the measurement plan, also the measurement locations in the assessment area, the measurement times (date, time of the day) and the panel member who will carry out the measurement, need to be defined. The panel member records his perceptions according to a defined procedure on a data record form, assigning the perceived odours to the predefined odour types.

Panel members are selected according to the procedure given in EN 13725:2003. The panel consists of at least eight selected and trained members.

Among others, the grid method can be advantageous in cases where a significant odour problem seems to be present and odour complaints are occurring. Because of the recorded odour types, in most of the cases, it is possible to identify the sources and to quantify their contribution to the measured odour exposure. Furthermore, an estimation of the emission may be feasible via reverse dispersion modelling, even if the sources are diffuse diffusive; but in such cases the plume method is preferred.

4.2.5.5.2 Plume method

The plume method is used to determine the extent of the area in which the plume originating from a specific odour source or an odour emitting installation can be perceived and recognised under specific meteorological conditions. The odour plume extent is described by points where a transition from absence to presence of the recognisable odour under investigation occurs. 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

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¹⁵³ VDI 3940 Part 1:2006 Measurement of odour impact by field inspection - Measurement of the impact frequency of recognizable odours - Grid measurement

¹⁵⁴ I. Bilsen, R. De Fré, S. Bosmans 2008 CODE VAN GOEDE PRAKTIJK - BEPALEN VAN DE GEURVERSPREIDING DOOR MIDDEL VAN SNUFFELPLOEGMETINGEN; VITO, LNE Flanders, Belgium

¹⁵⁵ VDI 3940 Part 2:2006 Measurement of odour impact by field inspection - Measurement of the impact frequency of recognizable odours - Plume measurement

extent measurement is particularly useful as a starting point for estimating emission rates for diffuse odour sources where sampling at source is impracticable.

Panel members used are selected according the procedure given in EN 13725:2003. They have to determine the presence or absence of the specific odour types under study at different points downwind of a source under well-defined meteorological conditions. The meteorological conditions during the field observations are measured and recorded.

Among others, the plume method can be advantageous in cases where diffuse odour emissions of a source need to be determined. The data from plume measurements, with simultaneous consideration of the measured meteorological data, can be used to make an estimation of the emission rate via reverse dispersion modelling.

Former Section 4.2.3.6 'Other odour monitoring methods' moved to Annex / 'Monitoring of odours using survey and electronic noses'.

4.2.5.6 Elaboration of BREFs

Odours are relevant pollutants in several industrial sectors and, therefore, are addressed in some BREFs, e.g. 'Common Waste Water and Waste Gas Treatment/Management Systems in the Chemical Sector' (CWW 2011), 'Pulp and Paper Industry' (PP 2013), 'Tanning of Hides and Skin's (TAN 2013), 'Slaughterhouses and Animal By-products Industries' (SA 2005), 'Food, Drink and Milk Industries' (FDM 2006), 'Intensive Rearing of Poultry and Pigs' (IRPP 2013).

It can be assumed that in most cases, the main driving force for dealing with odour emission is odour complaints in the surroundings of the installation. This very much depends on the local meteorological conditions, the type of source, the odour type, the hedonic tone, the amount of odour emissions (odour emission rate) and maybe other parameters relevant for the individual case under investigation.

Because the local conditions have a major influence on the relevance of odours as pollutants, BREFs give focus more on BAT conclusions containing management and/or other techniques to avoid, to reduce and/or to control the amount of odours created and emitted. This can include special abatement techniques, such as biofilters or afterburners. Often, odour reduction is achieved as a side effect by reducing compounds that are also known as being odorous, such as VOCs or H₂S, or by reducing compounds that can be used as surrogates for odours even if they do not smell at all, such as methane.

If it is necessary to monitor odour emission e.g. in relation to a permit in association to BAT, dynamic olfactometry according to EN 13725:2003 can be applied as a periodic emission measurement, which is, so far, the only standardised method in Europe.

It might be possible to define BAT-AELs expressed in European odour units (ou_E/m^3) , but it can be assumed, because of the influencing factors (see above), that this will be an exception in BAT conclusions.

4.2.6 Indirect monitoring of emissions using biological monitoring with plants

Former Section 4.2.5 'Indirect monitoring of emissions - Surrogate parameters and biological monitoring using plants' split in two parts, in the current section and Section 'Indirect monitoring of emissions using surrogate parameters '

4.2.6.1 General remarks

Biological monitoring, or **biomonitoring**, is the use of biological systems to monitor environmental changes over space and time (for biomonitoring in water see Section 4.3.4). Biomonitoring can complement direct emission measurements and/or dispersion modelling, by demonstrating possible biological effect, in particular, if there are diffuse emissions which do not allow direct emission measurements.

Two biological systems can be distinguished: bioaccumulators and bioindicators.

- A **bioaccumulator** is an organism which accumulates substances present in the environment (air, water or soil) at the surface and/or internally.
- A **bioindicator** is an organism which can indicate environmental conditions and their modification, by either showing specific (molecular, biochemical, cellular, physiological, anatomical or morphological) symptoms or by its presence/absence in the ecosystem.

Furthermore, a differentiation can be made between **active biomonitoring**, which refers to a planned field exposure of standardised biological systems, and **passive biomonitoring**, which refers to *in-situ* sampling and/or observation of selected biological systems already present in the environment.

Currently (2013), there are two CEN technical working groups dealing with biomonitoring using plants in ambient air:

- CEN/TC 264/WG 30 Biomonitoring methods with flowering plants;
- CEN/TC 264/WG 31 Biomonitoring methods with mosses and lichens.

4.2.6.2 EN standards

At the time of writing (2013), the CEN documents elaborated by CEN/TC 264/WG 31 listed in Table 4.8 are under approval.

	Standard No	Title
-	prEN 16413:2012	Air quality - Biomonitoring with lichens - Assessing epiphytic lichen diversity
	prEN 16414:2012	Air quality - Biomonitoring with mosses - Accumulation of atmospheric contaminants in mosses collected in situ: from the collection to the preparation of samples

 Table 4.8:
 Current (2013) EN drafts (prEN) dealing with the biological monitoring using plants

prEN 16413:20121 provides a method for assessing epiphytic lichen diversity. It aims 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 air emissions released by a specific source or installation; however, it could provide indication of the general ambient air quality.

prEN 16414:2012 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 sampling until the preparation for the final analysis are covered. It addresses 'all operators wishing to conduct air quality biomonitoring studies'. The *in situ* mosses are used as collectors for different substances and it is described that it is possible to identify and localise emission sources, as well as background pollution levels.

Another biomonitoring method under preparation by the Technical Committee **CEN/TC 264/WG 30**, concerns the exposure of standardised grass cultures of "Italian Ryegrass" (Lolium multiflorum) in a specific area where the bioaccumulation for substances such as sulphur, chloride, fluoride and especially metals, as well as low volatile organic and halo-organic compounds (e.g. polycyclic aromatic hydrocarbons (PAH), polychlorinated biphenyls (PCB), polybrominated diphenyl ethers (PBDE), polychlorinated dibenzo dioxins (PCDD) and polychlorinated dibenzo furanes (PCDF), is investigated.

Using standardised grass cultures allows the identification and localisation of one or more isolated pollution sources and the tracking of their 'plume' on a local or regional scale. It is also possible to monitor sites in the long term by the repeated application of a clearly defined procedure over several years.

4.2.6.3 Other biological monitoring methods

Other biological monitoring methods using different plants for active biomonitoring (e.g. tobacco, gladiolus, spruce, curly kale) or passive biomonitoring (*in-situ* sampling of leaves such as grazing land grass, maize plants, garden vegetables and needles) are applied in some Member States. The objective of these biological monitoring techniques is the determination and evaluation of the effects of air pollutants on plants. With some biomonitoring methods, it is possible to determine ambient air quality in relation to specific industrial sources^{156,157} but, as for all the biomonitoring methods mentioned, investigations at source (e.g. emissions measurements) and/or dispersion modelling are still necessary.

4.2.6.4 Elaboration of BREFs

With biomonitoring methods, it is not possible to directly quantify emissions. These methods may give some hints e.g. on diffuse emissions which cannot be measured directly. But in the elaboration of BREFs, data directly related to emissions caused by specific sources and controlled by defined techniques are necessary to identify BAT and, if appropriate, BAT-AELs. In general, this kind of data cannot be provided on the basis of biomonitoring measurements only. A typical field of application for biomonitoring is the control of the potential effects in the surroundings of installations where BAT is applied.

¹⁵⁶ VDI 3957 Part 10:2004 Biological measuring techniques for the determination and evaluation of effects of air pollutants on plants (bioindication) - Source-related measurements of ambient air quality using bioindicators

¹⁵⁷ VDI 3957 Part 15:2010 Biological measuring techniques for the determination and evaluation of effects of air pollutants on plants (bioindication) - Investigation strategy following hazardous incidents (passive biomonitoring)

4.2.7 Monitoring costs aspects of emissions to air connected with monitoring

In December 2012, the UK Source Testing Association, whose members comprise Test Laboratories, Process Operators, Instrument Manufacturers and Regulators, conducted a survey to gather information about the costs of stack emissions monitoring of IED installations in the UK. The information is split into the following three tables, which are listed in Annex A.5:

Table 6.4: Installed AMS systems and compliance measurement costs for different sectors regulated under the IED.

Table 6.5: Range of costs for supply of AMSs for sites regulated under the IED.

Table 6.6: Periodic stack emission measurement costs for sites regulated under the IED.

The costs were provided by process operators, AMS manufacturers, AMS installers and stack emissions monitoring companies.

The costs in Table 6.4 are examples provided by industrial operators. The costs provided are for both periodic and continuous measurements with AMSs (where applicable). For periodic measurements, the costs are for the entire measurement campaign, so include for example measurement planning, time spent on site safety inductions and report writing. For AMSs, the costs are broken down into purchase costs, installation costs and other significant costs, such as spares, training, servicing and software. These costs provide a good overview of the costs of stack emission measurements for different industrial sectors (e.g. coal fired power, stations, waste incinerators, cement plants).

The costs in Table 6.5 were provided by a wide range of AMS manufacturers and AMS installers, operating in Europe and internationally. This means that although the costs are from examples in the UK, they will be similar throughout Europe. These costs are useful for providing detailed information on the costs of buying, installing and running different AMSs.

The costs in Table 6.6 were provided by UK stack emissions monitoring companies, who carry out periodic monitoring using reference methods. The table includes the costs of single tests, triplicate tests and completion of a QAL2.

Determining costs per stack or per monitoring activity can be quite difficult because every site is different. Some examples are given in the following paragraphs:

- 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 most other plants, due to the number and complexity of the analysers. There may also be special functions of the process, such as selective catalytic reduction (SCR), which require the measurement of ammonia. This may mean that a multigas analyser is required, which can be more expensive than other options.
- Stack emissions monitoring companies and operators will often combine the calibration of AMSs (QAL2/AST) with routine periodic measurement for compliance with their permit. Also, AMS suppliers may offer discounts for installing more than one system.
- For periodic measurements, there may also be other monitoring activities, besides checking compliance with emission levels or calibration of AMSs. For example, operators of coal fired power stations with flue-gas desulphurisation abatement are required to measure removal efficiency (i.e. to calculate removal efficiency a measurement at both the inlet and outlet is required, which means that two sampling teams may be needed).
- The sampling location also affects the costs of periodic measurements and installation of AMSs. Some examples are:

- Monitoring arrangements at an indoor location with a lift are usually less expensive, than at an outdoor location that does not have a lift and has access via vertical ladders.
- Often, for extractive AMSs, an air conditioned room is required to house the analysers.
- The distance from the analyser location to the sample location also affects the cost. The greater the distance, the greater cost for materials and installation because of the length of lines, especially when they need to be heated.
- The proximity of sampling locations also affects the costs. For example, a coal-fired power station with four stacks in a windshield would be less expensive to measure emissions from, than if the four stacks were in different locations on the plant (i.e. co-location of monitoring locations means that the relative cost of mobilisation and/or installation of the equipment are reduced).

The costs for measuring of odours as described in Section 4.2.5.4 are heavily affected by the use of human sensors and their salaries. For the measurement of the odour emission concentration by dynamic olfactometry, at least four panel members are needed. Experience from Germany shows that depending on the sampling of the odour emission, and the performance and the ability of the panel members to maintain concentration during the day, an expected cost range for a measurement day with approximately 10 to 20 samples will be 2 500 up to 5 000 euros. The costs for applying the grid method, as described in Section 4.2.5.5.1, depends to a large extent on the size of the assessment area, and the number of measurement locations. Experience in Germanys shows that the costs for grid measurements start at approximately 10 000 to 15 000 euros for a half year measuring period.

Furthermore, monitoring costs, in general, are mentioned several times throughout Chapter 3 and Section 4.2, in particular, when different monitoring approaches are mentioned (e.g. Sections 4.2.2.1).

4.3 Monitoring of emissions to water

4.3.1 Definitions of water pollutants

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 can be characterised as quantitative surrogate parameters (see also Section 3.2.3.3.1) representing either a group of substances containing the same chemical element, such as Total Organic Carbon (TOC) or Total Nitrogen (TN), or showing similar characteristics, e.g. the oxidisability by dichromate in the case of the Chemical Oxygen Demand (COD).

Unless stated otherwise, whenever the term 'parameter' is used in this document in relation to waste water, it covers both single substances and sum parameters.

In Table 4.9, some definitions, generally used for waste water parameters are given in the way that they currently (2013) appear or can be used in BAT conclusions of the BREFs. This list is subject to modification, according to the needs of the BREF under elaboration or to the required permit conditions. In particular, there may be a need to cover single substances relevant for the specific industrial sector, e.g. specific metals.

Pollutant/sum parameter	Definition
Adsorbable organically bound halogens (AOX)	The sum of adsorbable organically bound halogens (chlorine, bromine and iodine) expressed as Cl, and measured according to EN ISO 9562:2004 ¹⁵⁸
Free chlorine (Cl ₂)	The sum of dissolved elementary chlorine, hypochlorite, hypochlorous acid, dissolved elementary bromine, hypobromite, and hypobromic acid, measured together and expressed as Cl_2
Mercury (Hg)	The sum of all inorganic and organic mercury species, expressed as Hg
Total hydrocarbon oil index content (HOI)	The sum of compounds extractable with a hydrocarbon solvent, and measured according to EN 9377 Part 2:2000 ¹⁵⁹ , such as long-chain or branched aliphatic, alicyclic, aromatic or alkylsubstituted aromatic hydrocarbons
Phenol Index	The sum of concentrations of phenolic compounds, expressed as phenol concentration and measured according to EN ISO 14402:1999 ¹⁶⁰
Total nitrogen (TN)	The sum of the concentrations of free ammonia and ammonium (NH_4^+-N) , nitrites (NO_2^N) , nitrates (NO_3^N) and organic nitrogen compounds, expressed as N
Total inorganic nitrogen (N _{inorg})	The sum of the concentrations of free ammonia and ammonium (NH_4^+-N) , nitrites (NO_2^N) and nitrates (NO_3^N) , expressed as N
Total Kjeldahl nitrogen (TKN)	The sum of the concentrations of free ammonia and ammonium (NH_4^+-N) , and organic nitrogen compounds, expressed as N
Total organic carbon (TOC)	The sum of all organically bound carbon, dissolved or bound to particles, including elemental carbon, expressed as C

Table 4.9:	Definitions of some waste water	parameters currently	(2013) used in BREFs
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¹⁵⁸ EN ISO 9562:2004 Water quality - Determination of adsorbable organically bound halogens (AOX) (ISO 9562:2004)

¹⁵⁹ EN 9377 Part 2:2000 Water quality - Determination of hydrocarbon oil index - Part 2: Method using solvent extraction and gas chromatography (ISO 9377-2:2000)

¹⁶⁰ EN ISO 14402:1999 Water quality - Determination of phenol index by flow analysis (FIA and CFA) (ISO 14402:1999)

Pollutant/sum parameter	Definition
Chemical oxygen demand (COD)	The mass concentration of oxygen needed for the total oxidation of the organic matter to carbon dioxide, indicating the amount of chemically oxidisable organic matter, expressed as COD
Biochemical oxygen demand (BOD _n)	The mass concentration of dissolved oxygen consumed under specified conditions by biological oxidation of organic and/or inorganic matter in five (BOD ₅) or in seven (BOD ₇) days
Total suspended solids (TSS)	The mass of suspended solids removed by filtration and weighed
Total phosphorus (Total P)	The sum of all organic and inorganic phosphorus compounds, dissolved or bound to particles, expressed as P

In addition to the most common definitions, for AOX, TOC/COD, BOD_n and TN mentioned in Table 4.9, the following general remarks should be considered in the elaboration of BREFs and, if appropriate, in permits.

Adsorbable organically bound halogens (AOX)

Instead of, or together with, AOX, also EOX (extractable organically bound halogens) are determined in some Member States. In EN ISO 9562:2004¹⁶¹, a method for the measurement of AOX is specified, which allows a European wide harmonised measurement, whereas for EOX, no EN standard is available. In practice, AOX values are generally higher than EOX values, because the EOX only covers non-polar substances. However, both methods have limitations, which may have an influence on their applicability (e.g. when a high level of chloride is present).

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

In some Member States, there is a trend to replace COD by TOC for economic and environmental reasons. The use of chromate and mercury, necessary for the COD determination, can be avoided by determining TOC, which can be measured continuously by on-line analysers. Both methods have limitations, which may have an influence on their applicability (e.g. content of suspended solids, content of chloride).

It has to be mentioned that the COD values are higher than TOC values. In general, COD/TOC factors are between 2.0 and 4.0; however, theoretically, the COD/TOC ratio can vary from 0.67 (oxalic acid) to 5.3 (methane). The correlation between the two parameters is usually plant-or site-specific.

Biochemical oxygen demand (BOD_n)

The parameter BOD_n has since long been used and is still used to monitor effluents from biological waste water treatment plants. However, at present (2013) in the elaboration of BREFs, there is a tendency to not define BAT-AELs for use the BOD_n in but rather to use it as a parameter to describe the efficiency of the biological treatment of a waste water treatment plant. The parameter TOC may be used instead because it is faster to determine than BOD_n , although TOC actually represents the amount of carbon in the sample and not the actual oxygen demand.

and furthermore, the use of BOD_n as a parameter has some disadvantages, such as:

• the analytical result depends on the local conditions at the laboratory, for instance the used seeding water (inoculum) for the test;

¹⁶¹ EN ISO 9562:2004 Water quality - Determination of adsorbable organically bound halogens (AOX) (ISO 9562:2004)

 BOD_n measurement does not allow for any prediction of the performance of the WWTP; it only provides an indication as to whether the waste water is easily degradable to a certain degree.

Total nitrogen (TN)

In general, there are three methods to determine total nitrogen:

- The measurement of total nitrogen as total nitrogen bound (TN_b) by thermal oxidation with subsequent detection according to EN 12260:2003¹⁶², where TN_b includes nitrogen in the forms of ammonia, ammonium, nitrite, nitrate and organic nitrogen compounds.
- The measurement of total nitrogen by wet chemical oxidation with subsequent detection according to EN ISO 11905-1:1998¹⁶³.
- The measurement of total nitrogen as the sum of Kjeldahl nitrogen¹⁶⁴, nitrate (NO₃)nitrogen and nitrite (NO₂)-nitrogen¹⁶⁵.

It has to be mentioned that these three analytical methods for total-nitrogen can lead to different results, depending on the characteristics of the sample. Dissolved nitrogen gas is not determined by these methods.

4.3.2 Continuous/periodic measurements

4.3.2.1 EN standards

The following EN standards or technical specifications (TS) deal, in general, with the measurement of emissions to water (Table 4.10). Most of them are related to periodic measurements and might be partly applied to continuous measurements of water emissions, such as EN ISO 5667-1:2006; whereas, EN ISO 15839:2006 deals specifically with continuous on-line monitoring. A list of the current (2013) EN standards for water emission measurements, sorted by pollutant, is included in Annex A.2.

For the general use of EN standards and other standard methods see Section 3.3.3.

Standard No	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 15839:2006	Water quality - On-line sensors/analysing equipment for water - Specifications and performance tests (ISO 15839:2003)
EN ISO/TS 13530:2009	Water quality – Guidance on analytical quality control for chemical and physicochemical water analysis

Table 4.10:	General EN standards or technical specifications (TS) dealing with the measurement
	of emissions to water

¹⁶² EN 12260:2003 Water quality - Determination of nitrogen - Determination of bound nitrogen (TN_b), following oxidation to nitrogen oxides

¹⁶³ EN ISO 11905-1:1998 Water quality - Determination of nitrogen - Part 1: Method using oxidative digestion with peroxodisulfate (ISO 11905-1:1997)

¹⁶⁴ EN 25663:1993 Water quality - Determination of Kjeldahl nitrogen - Method after mineralization with selenium (ISO 5663:1984)

¹⁶⁵ For the determination of nitrate and nitrite different EN standards are available.

In EN 1085:2007, a standardised terminology for the field of waste water treatment is established 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.

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

EN ISO 5667-3:2012 (Part 3) 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 pollutant and sum parameter.

EN ISO 15839:2006 specifies test procedures to be applied in the laboratory and in the field, to evaluate the performance characteristics of on-line sensors/analysing equipment used for the continuous measurements of water quality.

EN ISO/TS 13530:2009 provides comprehensive guidance for quality control of testing laboratories for ensuring the production of results with a known level of accuracy in the analysis of waters. This technical specification is applicable to the chemical and physico-chemical analyses of all types of water. Whilst sampling is an important aspect, this is only partly covered.

4.3.2.2 Different monitoring regimes

For the measurement of water parameters, different monitoring regimes are applied mainly differing in the sampling type. EN ISO 5667-1:2006 gives some guidance on sampling and distinguishes between continuous (on-line) measurement of specific parameters, periodic sampling, continuous sampling, composite sampling, and spot sampling.

An overview of the different sampling and measurements types are given in Table 4.11. More details are given in the following sections.

	Continuous sampling			
Sampling type	Sample type	Measurement type		
Directly positioned in the effluent flow				
Time-proportional	No discrete samples	Continuous on-line measurement		
Flow-proportional		incustrement		
Time-proportional	Discrete samples for specific time periods			
Flow-proportional	discrete samples for specific flow intervals	Periodic measurement (analysis of each discrete sample)		
Time-proportional	Composite samples for longer time intervals (e.g. 24 hours)			
Flow-proportional	Composite samples for longer time intervals (e.g. 24 hours)			
	Periodic sampling			
Sampling type	Sample type	Measurement type		
Time-proportional	Discrete samples for specific time intervals	\sim		
Flow-proportional	Discrete samples for specific flow intervals	Periodic measurement (analysis of each separate sample)		
Time-proportional	Composite samples for longer time intervals (e.g. 24 hours)			
Flow-proportional	Composite samples for longer time intervals (e.g. 24 hours)			
Spot sampling	Discrete samples			

Table 4.11: Overview of the different sampling and measurements types for emissions to water

- For **continuous (on-line) measurements,** the measurement devices are directly positioned in the effluent flow, or positioned separately, with the requisite that the sample of the effluent is taken continuously (time- or flow-proportional **continuous sampling**) and pumped to the device.
- For **continuous sampling**, the samples can be 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 or a sufficient number of discrete samples for the relevant time period to allow the determination of changes in waste water composition.

This method is most suitable for taking representative samples of 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.

• **Periodic (discontinuous) measurements** can be based on different sampling procedures. For periodic (discontinuous) sampling, The samples are taken at different intervals; the intervals may vary depending on time or waste water volume flow. One example is **flow-proportional sampling**, where a pre-defined amount of sample is taken for each pre-defined volume of discharge.

Order changed

The following main sampling types for periodic measurements can be distinguished.

Composite sampling is, by far, the most commonly used sampling method. Composite samples are obtained by mixing a proportional amount 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, or 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, and composite sampling is then mainly applied in order to reduce the amount of analytical work.

For **spot sampling**, discrete samples are taken at random time intervals and are generally not related to the volume of discharge. 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 4.3.2.4; for periodic measurements using composite and spot sampling; see Section 4.3.2.5.3.

4.3.2.3 When to measure continuously or periodically?

Several water parameters can be measured continuously as well as periodically. A number of parameters, such as pH, temperature and turbidity are typically usually measured continuously, because the results are used for process control and are important to run the waste water treatment plant properly.

To decide on the measurement regime for single substances and sum parameters, it might be helpful to evaluate the characteristics of the measuring method, including the advantages and disadvantages of continuous and periodic measurements, given as an overview in Table 4.12¹⁶⁶.

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¹⁶⁶ MCERTS Technical Guidance Note (Monitoring) M18 - Monitoring of discharges to water and sewer. Environment Agency, England and Wales, Version 3, 2012

Characteristic	Continuous measurement	Periodic measurement	
Sampling period	Measurement covers all or most of the period during which substances are discharged	Coverage depends on the sampling plan (for details see Section 4.3.2.5.2)	
Speed of results generation	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	
Applicability - status of standardisation	Limited applicability; restricted availability of standardised method	Generally applicable; standardised methods are available with defined performance requirements	
Averaging of results	Results continuously gathered and can be averaged typically e.g. over one hour or 24 hours	Results reported for a specified sampling period of most commonly 24 hours (daily average) or for spot samples of e.g. 2 hoursAccreditation of sampling and analysis according to EN ISO/IEC 17025:2005 ¹⁶⁷ Tends to be lower than the equivalent continuous measurement methodCertification of measurement equipment is only available in UK and only for a number of measurands	
Accreditation of sampling and analysis	Not applicable because of a lack of standardised methods		
Capital cost	Tends to be higher than the equivalent periodic measurement method		
Certification of equipment ¹⁶⁸	Certification of measurement equipment is only available in UK and only for a limited number of measurands		

Table 4.12:	Important characteristics of c	continuous and perio	dic measurements
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As mentioned in Table 4.12, continuous (on-line) measurements almost always provide a realtime output of results, and so the averaging period needs to be defined. Common averaging periods are e.g. 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, kept discrete or directly mixed over a pre-defined time period, e.g. an entire day, and then analysed afterwards. A typical example for 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 4.3.2.4.2).

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

- the need to control highly variable and/or excessive waste water emissions;
- the instability of the parameter during sampling, transportation and storage (e.g. volatile compounds);
- the expected impact of the waste water emission on the environment, taking local conditions into account;

¹⁶⁷ EN ISO/IEC 17025:2005 General requirements for the competence of testing and calibration laboratories (ISO/IEC 17025:2005)

¹⁶⁸ MCERTS Certification <u>http://www.siraenvironmental.com/mcerts/product.aspx?page=263</u>

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- 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 emission;
- the specific requirements of the industrial sector, and/or the specific circumstances of the installation;
- the costs of continuous measurements (economic feasibility).

A parameter that is almost always measured continuously is the volume flow of the waste water discharge (see Section 4.3.2.4.2).

In some Member States, (e.g. France, other MS ???), a mass flow threshold is used to decide the measurement regime and the measurement frequency. In France¹⁶⁹, for AOX, mercury, cadmium and several organic substances, mass flow thresholds in the discharge (kg/year) are implemented, when a daily sampling and daily analysis of water pollutants is required. In the Netherlands¹⁷⁰, in a limited number of permits, mass flow thresholds are used. The choice is determined by the specific discharge situation (i.e. short peak discharges, waste water diluted with cooling water). In general, it is assumed that below the specific mass flow threshold, a lower measurement frequency is sufficient, unless the conditions of the individual case require a different approach. Some mass flow thresholds for some water pollutants are given as examples in Table 4.13.

As mentioned in Table 4.12, certification of the measurement equipment is only available in the UK. 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.

Table deleted, because no further data was provided.

 Table 4.13: Mass flow thresholds in the discharge (kg/year) when a daily sampling and daily analysis of water pollutants is required.

Pollutant	Mass flow threshold (kg/year)		
	France ⁽¹⁾		
AOX	$\frac{2}{2}$		
Mercury	7.5		
Cadmium	10		
HCH (hexachlorocyclohexane, Lindane)	3		
CCl ₄ (carbon tetrachloride	30		
DDT (dichlorodiphenyltrichloroethane)	1		
PCP (phencyclidine)	3		
Aldrin, Dieldrin, Endrin	always		
HCB (hexachlorobenzene)	1		
HCBD (hexachlorobutadiene)	1		
CHCl ₃ (chloroform)	30		
EDC (1,2 dichloroethane)	30		
TRI (trichloroethane)	30		
PER (tetrachlorethen)	30		
TCB (trichlorobenzene)	30		
(1) -24 hour flow proportional <u>continuous</u> sampling and daily analysis is required.			
(2) kg/day			

 ¹⁶⁹ France: Arrêté du 2 février 1998 (2/2/98) relatif aux prélèvements et à la consommation d'eau ainsi qu'aux émissions de toute nature des installations classées pour la protection de l'environnement soumises à autorisation
 ¹⁷⁰ France: Arrêté du 2 février 1998 (2/2/98) relatif aux prélèvements et à la consommation d'eau ainsi qu'aux émissions de toute nature des installations classées pour la protection de l'environnement

¹⁷⁰ Email communication

Pollutant	Mass flow threshold (kg/year)
(3) If more than 80% of the halogenated organic co	mpounds are clearly identified and analysed
separately and if the unidentified fraction is not superior to 0.2 mg/l, a daily monitoring of	
this parameter is not necessary.	

4.3.2.4 Continuous measurements of water parameters

4.3.2.4.1 Continuous (on-line) measurements of water parameters (excluding flow)

In practice, continuous measurements in waste water are mainly done with sensors that are directly positioned in the effluent flow, or that are positioned separately and the sample of the effluent 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.

In EN ISO 15839:2006¹⁷¹, on-line sensors and on-line analysing equipment for water are defined as an automatic measurement device which continuously (or at a given frequency) gives an output signal proportional to the value of one or more measurands in a solution which it measures.

Some examples¹⁷² for different types of continuous measurements in waste water are:

- direct electrochemical measurement of e.g. pH, dissolved oxygen, conductivity;
- specific ion electrodes for the measurement of e.g. nitrate and ammonia;
- anodic stripping voltametry for the measurement of e.g. metals;
- colorimetric (spectrometry) for the measurement of e.g. ammonia, phosphate, total phosphorus, iron;
- measurement of TOC;
- measurement of turbidity.

EN ISO 15839:2006¹⁷³ describes for on-line sensors/analysing equipment for water:

- the determination of performance characteristics in the laboratory, such as linearity, limit 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, i.e. depending on the waste water characteristic, 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. It is useful to keep Records of all maintenance and calibration activities need to be kept as part of the quality assurance system, since they will be checked during accreditation and audit procedures.

¹⁷¹ EN ISO 15839:2006 Water quality - On-line sensors/analysing equipment for water - Specifications and performance tests (ISO 15839:2003)

 ¹⁷² MCERTS Technical Guidance Note (Monitoring) M18 - Monitoring of discharges to water and sewer. Environment Agency, England and Wales, Version 3, 2012

¹⁷³ EN ISO 15839:2006 Water quality - On-line sensors/analysing equipment for water - Specifications and performance tests (ISO 15839:2003)

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 directly install, commission and validate their devices.

As already mentioned in Table 4.12, in the UK, a certification system exists which also covers performance standards and test procedures for continuous water monitoring equipment¹⁷⁴.

4.3.2.4.2 Continuous measurements of waste water flow

As there was in the comments only the indication by France that these are not (or not all) the commonly used standards, it is proposed to delete the list and add a general statement (see below).

Note for the MEG:

EN standards dealing with flow and discharge measurements are EN ISO 748:2007, EN ISO 5167, and EN ISO 6416 prepared by TC 318 Hydrometry.

Standard No.	Title
EN ISO 748:2007	Hydrometry - Measurement of liquid flow in open channels
	using current meters or floats (ISO 748:2007)
EN ISO 5167:2003	Measurement of fluid flow by means of pressure differential
	devices inserted in circular cross section conduits running full
	- Part 1: General principles and requirements (ISO 5167-
	1:2003)
EN ISO 6416:2005	Hydrometry - Measurement of discharge by the ultrasonic
	(acoustic) method (ISO 6416:2004)

How these standards are used in the field of water emission measurements?

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 automatic sampling devices. Therefore, in almost all cases, waste water flows are measured continuously.

A wide range of flow measurement 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 these can be divided into three separate groups¹⁷⁵:

- open channel flow meters, which are commonly used for waste water flow measurement;
- pipe flow meters, for partly filled pipes; and
- pipe flow meters, for pipes which are completely filled and often pressurised.

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

¹⁷⁴ MCERTS Performance Standards and Test Procedures for Continuous Water Monitoring Equipment. Part 2 - Performance standards and test procedures for on-line monitors: Ammonia; COD; Conductivity; Dissolved Oxygen; Free Cyanide; Nitrates; Orthophosphate; pH; Temperature; TOC; Total Arsenic; Total Cadmium; Total Chlorine; Total Copper; Total Lead; Total Mercury; Total Nickel; Total Oxidised Nitrogen; Total Phosphorus; Turbidity. Environment Agency 2010

 ¹⁷⁵ Review on Danish Emission Control of Industrial Waste Water. Information sent to EIPPC Bureau.
 Danish Environment Agency, Technical Note, December 2012

cross-sectional area and the flow velocity. The flow area is determined by measuring the liquid level using a pressure transducer and then by calculating the area based on the diameter of the pipe. The average flow velocity is measured by means of a sensor emitting high frequency sound waves that are reflected by air bubbles and suspended particles in the waste water and then by using a change in frequency of the reflected sound waves ("Doppler effect") to calculate the average flow velocity.

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.

As mentioned in Table 4.12, in the UK, a certification system exists which also covers performance standards and test procedures for water flow meters¹⁷⁶. Also in the UK, a standard is in place for the inspection of flow monitoring structures¹⁷⁷.

4.3.2.5 Periodic measurements

4.3.2.5.1 General remarks

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 water emission measurements, it is often the case that the personnel responsible for sampling may not be the same as those responsible for the analysis, but both need to have a sound knowledge and experience in their respective field of responsibility. This is essential for obtaining reliable and comparable results. The testing laboratories should meet the requirements of EN ISO/IEC 17025:2005 and therefore, be accredited accordingly. This will be checked during accreditation and related audits (see Section 3.3.1).

The currently (2013) available general EN standards for the measurements of waste water are already mentioned in Section 4.3.2.1. 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 the available EN standards do not cover the whole range of necessary requirements for the measurement of specific parameters in waste water, for instance specific effects related to the waste water matrix. and Therefore, there is a broad range of other standards in use e.g. ISO, and/or national standards, and/or laboratory-

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¹⁷⁶ MCERTS: Performance Standards and Test Procedures for Continuous Water Monitoring Equipment. Part 3: Performance standards and test procedures for water flowmeters. Environment Agency 2013

¹⁷⁷ MCERTS: Minimum Requirements for the Self-Monitoring of Effluent Flow. Environment Agency 2013

developed and non-standard methods. In particular, laboratory-developed and non-standard methods need to be validated according to EN ISO/IEC 17025:2005 (see Section 3.3.3).

4.3.2.5.2 Measurement plan - Sampling plan

The objective of the measurement plan is to ensure a representative sampling and quantification of the effluent discharge from the industrial installation to the receiving water. Information is required over a period of time during which the water quality might vary and the samples need to be taken at times that adequately represent the quality and its variations.

The sampling plan design (or the related part of the measurement plan) considers these variations e.g. caused by Normal Operating Conditions (NOC) and Other Than Normal Operating Conditions (OTNOC), which may include seasonal and diurnal cycles, business week cycles, random or transient events, and long-term persistence or trends.

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

- measurement objective including specification of the water pollutants and sum parameters;
- collection of data to clearly describe NOC and OTNOC;
- collection of data related to the waste water flow and other parameters, if relevant, such as temperature, pH;
- volume of waste water that the sampling intends to represent;
- sampling method, including sampling equipment;
- necessary pretreatment and preservation of samples;
- sampling location, and sampling point;
- handling and storage of samples;
- sampling frequency;
- analytical parameters that have to be analysed in the samples at the laboratory;
- data treatment;
- quality assurance measures;
- documentation and reporting.

The measurement plan might be divided into a sampling plan or programme and an analysis plan, e.g. if the sampling and the analysis are done by the same laboratory. In any case, requirements, belonging to the applied analytic method, and constraints, resulting from sampling, need to be taken into account, respectively.

In the case of automatic sampling equipment to be permanently installed to cover longer time periods, it may be sufficient to elaborate 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 sampling, the plan may need to be updated for each sampling campaign.

In the following paragraphs, some examples¹⁷⁸ are given for conditions that can affect the final effluent discharge and that, therefore, need to be reflected in the measurement plan.

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

¹⁷⁸ Review on Danish Emission Control of Industrial Waste Water. Information sent to EIPPC Bureau. Danish Environment Agency, Technical Note, December 2012

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

Batch production might require (spot) sampling of the waste water discharge, or (spot) sampling after the batch has passed through an equalisation tank if the discharge pollution follows these batches. If sampling takes place in a tank, good mixing is necessary to ensure that the entire volume is homogenised. If mixing is difficult and un-mixed zones are inevitable, e.g. the tank is very big, than it is advisable to take several sub-samples and to mix them before analysis.

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

Outdoor areas and stocks (e.g. metal industry, wood-based panel industry), where storage may be uncovered, can result in a contaminated run-off, in particular under exceptional weather conditions (e.g. heavy rainfalls). It is recommended to take flow-proportional samples of run-off, even if it might be difficult, to properly determine the load coming from these areas.

When **accidents or breakdowns** occur at an industrial site and an unforeseen discharge of polluted waste water happens, it is advisable to have a contingency plan for measurements and documentation of the water pollutants, in terms of concentration and loads, to allow an estimation of the possible impact on the water environment. The sampling plan and the information included are 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).

In some cases, there might be special demands to cope with the **concentrations and/or loads of some pollutants in the influent**¹⁷⁹ of a waste water treatment plant. In particular, when a central waste water treatment plant is receiving different waste water streams from different sources or installations, fluctuations of the influent need to be controlled (e.g. by temporary storage of waste water), since they can affect the performance of the waste water treatment plant.

4.3.2.5.3 Sampling methods for waste water

For the periodic sampling of waste water, there are basically two sampling methods:

- composite sampling, where the samples are taken periodically, during a specific time period (one day), and combined into one composite sample before analysis; and
 - spot (or grab) sampling, where discrete samples are taken and analysed separately.

Composite sampling and spot sampling will be described in more detail in the following sections.

4.3.2.5.3.1 Composite sampling

There are two types of composite samples, where sub-samples with a defined volume of waste water are taken from the discharge: flow-proportional and time-proportional. For the flow-proportional sample, a fixed sample amount is taken for each pre-defined volume (e.g. every

¹⁷⁹ CWW BREF

 10 m^3). For time-proportional samples, a fixed sample amount is taken for each time unit (e.g. every 5 minutes).

When targeting representative results, flow-proportional composite samples are generally preferred and are most commonly applied. The applicability of time-proportional composite sampling has some restrictions, because variations in concentrations and flow may not be measured correctly. There might be some cases, depending on the parameter to be measured and/or the industrial sector, where time-proportional or spot sampling can be applied, but in BAT conclusions, the associated monitoring is preferably based on 24-hour flow-proportional composite sampling, to guarantee a generally applicable monitoring regime.

With time-proportional and flow-proportional composite sampling, the interval between each sub-sample should preferably be between 3 minutes (the shortest time that the sampler needs to go through a complete cycle) and 10-12 minutes. The maximum recommended time interval between two sub-samples is 20 minutes, to enable the composite sample to be representative of the observed time period.¹⁸⁰

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 give a daily average. Shorter times might also be used in exceptional cases (see below), for example two hours, or half an hour.

Composite sampling 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 volume of the total sample is as large as is it 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 sitting in the automatic sampling device. This may lead to shorter sampling collection and storage times (see Section 4.3.2.5.5)

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, ammonia, even when auto samplers are refrigerated.¹⁸¹

For weekly, monthly or annual averages, it is good practice to collect a reasonable number of 24-hour flow-proportional composite samples (see Section 4.3.2.5.6), to analyse them separately, and then to average the measurement results (see Section 4.3.2.6).

It is generally not advisable to mix e.g. 24-hour flow-proportional composite samples to obtain average concentrations for longer time periods (such as weekly and monthly), 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 done in individual cases, where concentrations remain stable and where longer storage times will not lead to changes in the sample composition.

As mentioned in Table 4.12, in the UK, a certification system exists which also covers performance standards and test procedures for automatic water sampling equipment.¹⁸²

¹⁸⁰ Review on Danish Emission Control of Industrial Waste Water. Information sent to EIPPC Bureau. Danish Environment Agency, Technical Note, December 2012

¹⁸¹ MCERTS Technical Guidance Note (Monitoring) M18 - Monitoring of discharges to water and sewer. Environment Agency, England and Wales, Version 3, 2012

¹⁸² MCERTS Performance Standards and Test Procedures for Continuous Water Monitoring Equipment Part 1 - Performance standards and test procedures for automatic water sampling equipment. Environment Agency 2009

4.3.2.5.3.2 Spot sampling

Spot samples can be taken at random moments and are not necessarily related to the volume discharged. Spot samples can be used, for example, in the following situations:

- where the composition of the waste water is relatively constant;
- when the quality of the discharged waste water needs to be checked at a particular moment, e.g. for inspection purposes;
- when separate phases are present in the discharge, and therefore, automatic sampling is not applicable, e.g. when it contains mineral oil, or volatile or aliphatic substances;
- when the target substances are not stable in the sample, e.g. due to decomposition, evaporation or coagulation;
- when the discharge is not continuous (from batch or hold-up tanks or special weather conditions), but only when the effluent is well mixed;
- when the discharge caused by plant failure or accidental release needs to be evaluated.

When water flows and/or substance concentrations vary significantly, spot sampling is generally not suitable. However, specific parameters – for instance oil components, grease, volatile compounds, dissolved oxygen, bacteriological parameters, chlorine and sulphide – might only be determined in spot samples¹⁸³, or with continuous on-line measurement, if available for the parameter.

4.3.2.5.4 Sampling location, sampling point

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.

To select the sampling point for automatic sampling devices, the following recommendations might be helpful^{184,185}.

- 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 sampling point should have a water level higher than 50 mm.
- The suction hose and suction head should be installed in such a way that the suction head is placed at a depth of approximately one-third dry weather water depth at the sampling point.
- Sampling points in channels should be placed away from the sides and the bottom of the channel, to avoid contamination of the sample with sediment or biological growths.
- The waste water at the sampling point should be well mixed (turbulent flow), in order to avoid the sedimentation of particles.
- Cleaning around the sampling point should be performed with (at least) a frequency set in advance.
- Up-damming behind the sampling point should be avoided, because it might be followed by intermittent load.
- The sampling points should not be affected by the recirculating internal flows.

¹⁸³ Review on Danish Emission Control of Industrial Waste Water. Information sent to EIPPC Bureau. Danish Environment Agency, Technical Note, December 2012

¹⁸⁴ see previous reference (Review on Danish Emission Control of Industrial Waste Water)

¹⁸⁵ MCERTS Technical Guidance Note (Monitoring) M18 - Monitoring of discharges to water and sewer. Environment Agency, England and Wales, Version 3, 2012

• Stratification requires special sampling and makes it almost impossible to take representative samples.

In addition to the items mentioned above, the following hints for spot sampling might be helpful.

- When sampling an outfall, samples should be taken from the regions of high turbulence and good mixing, usually at the centre of the discharge, where solid materials have little chance to settle.
- When sampling from chambers (e.g. manholes), contaminations of the sample with deposits from the cover (when the cover is lifted), from the chamber walls, and any bottom deposits should be avoided.
- When samples from the effluent are taken at a tap, care should be taken to ensure that any dead space is flushed out with effluent before the sample is collected.

4.3.2.5.5 Handling and storage of samples

To preserve pollutants that may change during sample storage, the following measures may be necessary:

- keeping the sample in the dark;
- cooling of the sample;
- filtration of the sample;
- stabilisation of the sample with acid or bases or other chemicals;
- avoiding precipitation during storage; and
- re-dissolving precipitation in the laboratory, if it occurs.

According to EN ISO 5667-3:2012¹⁸⁶, the container and its contents need to be stored in the dark at cool temperatures (5 ± 3 °C), also during the sampling, and it is recognised that some time may be required to bring the sample temperature to within this range. Cooling of the sample during the sampling period minimises any changes in the composition, for example with regards to organic matter or the ratio of the different nitrogen fractions (ammonium, nitrate, nitrite and total nitrogen).

In the relevant EN standards for the analysis of waste water (see Annex A.2), detailed information is given for each waste water parameter regarding e.g. the analytical method, the required sample volume, the required type of container, the pretreatment of containers, the recommended preservation techniques, such as filtration, storage temperature, and the sample durability. General information on the preservation and handling of water samples, including maximum storage times, is provided by EN ISO-5667-3:2012.

The allowed storage time also depends on the matrix of the waste water to be sampled, but it is a fundamental recommendation that the transport and storage time should be as short as possible. Efforts should be made to start the examination within 24 hours from sample collection. Where logistics do not allow this, samples may be examined up to 48 hours after collection.

The storage also depends on the expected concentrations. If the detection of low concentrations is required, the analysis may need to be done 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,

¹⁸⁶ EN ISO 5667-3:2012 Water quality - Sampling - Part 3: Preservation and handling of water samples (ISO 5667-3:2012)
nutrients, metals). But when the analysis of 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 interval between sampling and analysis.

It is important to take into account laboratory instructions on the use of sampling containers and sample preservation before and while sampling. For example, some measurements will require no air space to be left after filling, to stop the loss of volatile components, while others need space left in the bottle to allow the addition of extraction solvents when reaching the laboratory. Often sampling containers may be treated beforehand, e.g. preservatives may be added to sample containers before they are dispatched from the laboratory.

Not taking laboratory instructions into account while sampling may lead to invalid analytical results. In particular, when sampling and analysis is done by different laboratories, a procedure has to be established to assure quality of the measurement results. The audit of these procedures is part of accreditation according to EN ISO/IEC 17025:2005¹⁸⁷ (see also Section 3.3.1).

4.3.2.5.6 Sampling frequency

Depending on the numbers of samples taken, 24-hour flow-proportional composite sampling allows a representative characterisation of the long-term discharge profile.

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

- every day (daily);
- once per week (weekly);
- twice per month;
- once per 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 4.3.2.6), whereas with other frequencies, depending on the stability of the conditions, the calculated average, technically speaking, only represents the sampled days. Therefore, it is more accurate to call it an 'average of samples obtained during one year' (see Sections 3.3.4.2 and 4.3.2.6) than a yearly average. For spot sampling, the frequencies might be the same but the samples only represent the sampling period, e.g. one or two hours.

Higher frequencies imply a higher work load and higher costs. In the case of automatic sampling devices, the work load might not be as relevant but the additional analyses will cause significant additional costs. Therefore, the measurement (sampling) frequency should reflect criteria, such as:

- emission profile or emission pattern;
- amount of pollutant released;
- variability of the concentration of the parameter in the discharge;
- 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 sampling frequency while other than normal operating conditions (OTNOC) occur, e.g. during process plant start-up or during unexpected low or high

¹⁸⁷ EN ISO/IEC 17025:2005 General requirements for the competence of testing and calibration laboratories (ISO/IEC 17025:2005)

amounts of incoming water. In calculating averages, results obtained from these samples should be used only if allowance is made for the increased frequency, and these samples are weighted in time, so that a period of intense sampling receives the appropriate weight.

As already stated in Section 4.3.2.3, it is good practice to measure continuously the waste water flow of the effluent discharge to the receiving environment. This is to allow, at any time, a calculation of the amount of emissions released.

Spot samples, on the contrary to 24-hour flow-proportional composite samples, only allow a snapshot of the long-term discharge profile. This might be sufficient in individual cases, but if it is necessary to provide representative data for longer time periods, then a higher number of spot samples are required or and 24-hour flow-proportional composite sampling is advisable.

4.3.2.5.7 Analysis of samples

The currently (2013) available EN standards for the analysis of pollutants and sum parameters are listed in Annex A.2, together with additional information. In general, these EN standards also contain requirements on how to treat the sample to avoid any losses during storage, transportation and measurement.

Some recommendations for equipment used for water analysis are given in the following paragraphs¹⁸⁸. These points are regularly checked during accreditation of the laboratory according to EN ISO/IEC 17025:2005:

- Instrument operating instructions, calibration procedures and performance checks need to be fully documented and available to the personnel, as part of the quality management system.
- Instrument performance checks and calibration procedures need to be carried out at appropriate intervals and a record kept showing that calibration is maintained.
- All instruments need to be correctly maintained and records of the maintenance need to be kept, whether or not carried out by a third party, such as the instrument manufacturer.
- 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 need to be clearly labelled and identifiable by the personnel.

Other methods used for screening the waste water pollution are **test kits or rapid tests**. The majority of appropriate test kits involve colorimetric methods. They come in two main formats, those using visual comparators and those using portable or bench top spectrometers.

Generally, the use of visual comparators is not recommended, as these systems are very dependent on the user and environmental conditions. They often lack the accuracy required for assessing regulatory permits and for the definition of associated emissions levels for the elaboration of BAT conclusion. But they may help the operator of a waste water treatment plant to collect actual performance data.

Test kit methods using spectrometers have increased in sophistication and quality in recent years, and many are based on standard laboratory methods, and traceability of the data can be achieved due to electronic result storage capabilities. They are available for many parameters, such as COD, ammonia, phosphate and iron.

¹⁸⁸ MCERTS Technical Guidance Note (Monitoring) M18 - Monitoring of discharges to water and sewer. Environment Agency, England and Wales, Version 3, 2012

Test kits or rapid tests offer some advantages, as the methods may benefit from reagents being pre-packaged, ease and convenient use, and as they may have built in calibration procedures. However, they should undergo a full evaluation before use, ensuring appropriate performance characteristics and matrix suitability, in order to be treated in the same way as a standard method in terms of documentation and quality assurance and regular control procedures.

The analytical results of test kits or rapid tests need to prove that they are of an equivalent scientific quality than the one 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 permit conditions or to be referred to in elaborate BAT conclusions; in addition, the equivalent scientific quality needs to be checked regularly.

4.3.2.6 Data treatment

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

Results of **continuous measurements** as described in Sections 4.3.2.3 and 4.3.2.4 may refer to very short time periods, as well as to long averaging periods, and, in addition, quality checks need to be established in advance. Common averaging periods are e.g. one hour, two hours or 24 hours, depending on the objective of the measurement. If the task is to derive a daily average, 24 hours may be the right averaging period. If, in addition, the performance of the plant over the day is of interest, shorter averaging periods, e.g. one hour averages may be shown as well. Furthermore, the same averaging period is applied for the results of the flow measurements.

In the case **periodic measurement** with 24-hour flow-proportional composite sampling, no additional calculations are required to derive representative daily averages, as the sampling method already considers the waste water flow. Other sampling methods, such as time-proportional composite sampling, may require additional calculations to be representative of e.g. the discharge of a pollutant for the entire day.

To calculate a **representative concentration over a longer time period**, the results for a single substance or a sum parameter need to be averaged and weighted by the related waste water flow, as given in the following equation:



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

The **calculation of the specific load** (e.g. monthly, yearly) based on a daily measurement frequency can be done according to Equation 4.2:

Equation 4.2

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

where l _{specific}	=	specific load over all measurement results of the parameter during the required time period (e.g. month, year)
$egin{array}{c_i} q_i \ p_i \ n \end{array}$	= = =	concentration of the parameter during i th time period (day) flow rate during i th time period (day) production output during i th time period (day) number of measurements.

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

In the case of a BAT-AEL or ELV given as a specific yearly load based on 24-hour flowproportional composite sampling, this means that the measurement result of each 24-hour flowproportional composite sample obtained during the observed time period (e.g. month, year) is multiplied with the corresponding daily flow and then divided by the daily production output to calculate the **specific daily load**. The specific daily loads are summed up and divided by the number of measurements to calculate the **specific load** for e.g. a month or a year. Some example calculations are given in Annex A.6.

When the daily production is more or less stable over the year, the average yearly load can be calculated and divided by the average yearly production to calculate the specific yearly load.

The calculation of specific loads based on a measurement frequency less than daily can be done in a similar way, but it needs to be ensured that the measurement results are representative for the examined time period. However, the average should be called an average over the samples obtained during one year or during one month, to avoid any confusion with yearly or monthly averages based on a daily measurement frequency (see Section 3.3.4.2).

In cases, where the concentration values of the parameter are below the limit of quantification, assumptions need to be made, how to treat these data and how to calculate the load. For further information see Section 3.3.4.4 'Limit of detection/limit of quantification'.

There might be cases, such as batch production, where no daily measurements or discharges are not available. Another for example are for seasonal companies that discharge the most during a short period in the year (e.g. the harvest period). To estimate the load, a particular day or number of days might be considered as being representative for a particular period and the calculation is based on this/these day(s).

4.3.2.7 Reporting of measurement results

In the measurement report, it is described in a transparent and traceable way, where and how the measurements were carried out, and also sufficient detail to enable the results to be traced back through the calculations to the collected raw data and process operating conditions. Each EN standard (see Annex A.2), specifying the determination of a single substance or sum parameter, contains a section on reporting and on the expression of results. In general, the measurement report should at least contain the following information:

- a reference to the EN standard(s) applied;
- information which allows the complete identification of the sample;
- expression of results as indicated in the EN standard(s);
- sampling method and method for sample pretreatment, if appropriate;
- any deviations from the standardised method; and

• any details of all circumstances which could have affected the result.

Further information might be needed, in particular, for assessing regulatory permits and for the definition of associated emissions levels for the elaboration of BAT conclusions, to present the complete picture about the operating conditions and the responsible laboratory, and to ensure a sound and well-founded interpretation of the results, such as:

- name and address of laboratory carrying out the sampling and the analysis;
- reference to the sampling plan indicating deviations, if any occurred;
- information on operating conditions (NOC, OTNOC) before and during sampling;
- identification of the sampling site (e.g. unit, plant, installation);
- identification of the sampling location(s) and sampling point(s);
- identification of the sampling method (e.g. spot sample, 24-hour flow-proportional composite sample) and any sample pretreatment and sample preservation method;
- sampling date and time (for composite sampling start/stop dates and times);
- further sampling details and observations necessary to evaluate the measurement results;
- 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;
- measurement results and related measurement uncertainties.

4.3.2.8 Elaboration of BREFs

The provided data are the basis for the elaboration of BAT conclusions and, where appropriate and reasonable, for BAT-AELs. In association with BAT-AELs, the monitoring regime needs to be established. The sampling method for waste water predominantly applied in Europe is **24-hour flow-proportional composite sampling.** This sampling method guarantees, to a great extent, representative daily measurement results, even if the concentrations and the flows are varying. Therefore, 24-hour flow-proportional composite sampling is the sampling method to which BAT conclusions generally refer to.

For the elaboration of BAT conclusions, it is important might be advisable not only to report e.g. aggregated yearly data, but also the measurement result of each single 24-hour flowproportional composite sample, to ensure a sound data basis for the derivation of BAT-AELs.

Furthermore, in order to allow a correlation between the data and **NOC or OTNOC**, it is necessary purposeful to report measurement uncertainties, sampling methods and sampling conditions (e.g. flow, temperature, pH), the measurement frequencies, together with unambiguous information on the operating conditions and the related waste water discharge flows. Usually, there is no need to submit complete measurement reports for periodic measurements during the elaboration of BREFs.

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. For the sake of clarity, it is advisable to use the terms mentioned in Section 4.3.2.5.6, such as once per week or month. Other frequencies, e.g. lower or higher, might be applied in special cases, taking into account e.g. local conditions.

Data of waste water flows are essential for the elaboration of BAT conclusions and the derivation of BAT-AELs, independently of whether if they are expressed as concentrations or as loads. To get the complete right picture of the pollutant released, the waste water flow needs to be taken into account (see Section 4.3.2.6). Therefore, as already mentioned above, water flows need to be provided together with the measurement results.

In general, as already mentioned, BAT-AELs are based on 24-hour flow-proportional composite sampling and established as daily, weighted monthly or weighted yearly concentrations or as daily, monthly or yearly specific loads, e.g. per unit of product.

It seems appropriate to set BAT-AELs as a concentration value:

- if the measured concentrations of water parameters mainly depend on the design and operation of the waste water treatment plant rather than on the production process or process-integrated techniques; and
- if water saving techniques and other process-integrated techniques for the reduction of emissions do not significantly affect the final concentration levels of these parameters.

Examples might be the parameters TSS, BOD_n, and P, because the achieved concentration levels of these parameters will be relatively stable after biological waste water treatment, with only small variations within predictable ranges. Defining (specific) loads in these cases may lead to very wide ranges for BAT-AELs, because of the varying flow, while the concentration values stay at the same level.

It seems appropriate to set BAT-AELs as a specific load value, e.g. per unit of product, if the measured concentrations of water parameters mainly depends on the production process and applied process-integrated measures, and on the design and operation of the waste water treatment plant.

In this case, water saving measures will normally lead to higher measurable concentrations in the discharge, because the same amount of pollutants is then dissolved or suspended in a lower water volume. Since water saving measures should not be discredited, BAT-AELs for those parameters are better set as specific load values. This is common practice in a number of Member States for some industrial sectors and for parameters, such as COD and AOX.

For further information on data gathering and reference information accompanying emission data, see the 'BREF guidance'¹⁸⁹

4.3.3 Indirect monitoring of emissions using surrogate parameters

Examples for the different categories of surrogate parameters 4.3.3.1

As pointed out in Section 3.2.3.3.1, surrogate parameters are measurable or calculable parameters which may be used instead of the direct measurements of specific pollutant concentration for some practical purposes and/or for economic reasons. A distinction can be made between quantitative, qualitative and indicative surrogates.

The determination of emissions to water is covered to a large extent by the measurement of sum parameters representing a group of substances containing the same chemical element or showing similar characteristics, which can be seen as a **quantitative surrogate** for the specific group of substances. Examples, representing a group of substances containing the same chemical element, are:

Total Organic Carbon (TOC), instead of the individual organic compounds; Total Nitrogen (TN), instead of the individual nitrogen compounds;

¹⁸⁹ COMMISSION IMPLEMENTING DECISION of 10 February 2012 laying down rules concerning guidance on the collection of data and on the drawing up of BAT reference documents and on their quality assurance referred to in Directive 2010/75/EU of the European Parliament and of the Council on industrial emissions (2012/119/EU).

- Adsorbable Organically bound halogens (AOX), instead of the individual halogenated organic compounds;
- Total Hydrocarbon Oil Index content (HOI), instead of the individual hydrocarbon compounds; or
- Phenol index, instead of the individual phenolic compounds.

Quantitative surrogate parameters or sum parameters representing a group of substances showing similar characteristics are e.g.:

- in the case of for the Chemical Oxygen Demand (COD), the oxidisability by dichromate instead of the individual organic compounds; or
- in the case of Biochemical Oxygen Demand (BOD_n), the mass of oxygen consumed by a seed of aerobic microorganisms.

Qualitative surrogate parameters provide reliable qualitative information of the emission and can substitute for direct emission measurements. Examples of their use may include:

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

Indicative surrogate parameters provide information about the operation of the waste water treatment process and therefore give an indication of potential emissions. Examples may include:

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

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

4.3.3.2 Elaboration of BREFs

Whenever emissions to water are addressed in BAT conclusions and BAT-AELs 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 environmental and economic reasons, the sum parameter COD is increasingly replaced by TOC, which also has the advantage that it can be measured continuously. Furthermore, there is a tendency no longer to use to not define BAT-AELs for BOD_n but rather to use it as a parameter to describe the efficiency of the biological treatment of a waste water treatment plant, because of the long time period (five or seven days) required to carry out the measurement (for more details see Section 4.3.1).

For further information on data gathering and reference information accompanying emission data, see the 'BREF guidance'¹⁹⁰.

¹⁹⁰ COMMISSION IMPLEMENTING DECISION of 10 February 2012 laying down rules concerning guidance on the collection of data and on the drawing up of BAT reference documents and on their quality assurance referred to in Directive 2010/75/EU of the European Parliament and of the Council on industrial emissions (2012/119/EU).

4.3.4 Indirect monitoring of emissions using toxicity tests

4.3.4.1 General remarks

Biomonitoring data measured with toxicity tests represent a valuable tool for the assessment of the toxicity of waste water, in particular of complex effluents. It is possible to assess the possible hazardous character of waste water discharges in an integrated manner and to assess synergistic/antagonistic effects of a mix of pollutants. The toxicity test results provide the basis for measures to control pollution and to minimise the ecotoxic impact of waste water effluents.

Complex effluents can be characterised as effluents containing complex mixtures of known and unknown chemicals and/or where the adverse effects caused by the effluent cannot be explained by the chemical properties of the single components, including any combined effects¹⁹¹. In these cases, the assessment of toxicity might be quicker and less expensive than extensive chemical characterisation associated with ecotoxicological characteristics, and this thereby simplifies the control of the effluent.

Apart from the possibility of using the toxicity tests to estimate the overall potential hazardous effects on the receiving water, these tests biomonitoring can also be used to protect or to optimise biological waste water treatment plants.

For the toxicity assessment of complex waste water effluents, different methods are available, such as the fish egg test, *Daphnia* test, algae test and luminescent bacteria test, which will be covered in more detail in Section 4.3.4.2, and have to adhere to the 3R (replacement, reduction, refinement) principle/approach as outlined in Directive 2010/63/EU¹⁹². These methods are often used to obtain additional information to that related to single substances and/or sum parameter measurements (e.g. TOC, AOX).

The advantages of using toxicity tests can be summarised as follows:

- All waste water compounds are considered, regardless of their origin and detection by chemical analysis. The compounds do not necessarily need to be identified. By-products and metabolites are also assessed.
- Toxic effects on aquatic organisms are directly obtained; the combined/synergistic effects of several compounds are also considered.
- The sources of hazardous effluents (production steps or hot spots) inside industrial areas can often be identified by backtracking, if unknown synergistic effects of pollutants are negligible.
- The assessment of toxicity might be quicker and less expensive than the extensive chemical characterisation associated with the investigation of ecotoxicological characteristics of complex effluents.

Toxicity tests are an integral part of any Whole Effluent Assessment¹⁹³ (WEA) strategy. WEA includes a variety of (biological) tests to determine persistency, bioaccumulation and toxicity (PBT-criteria) and covers effects of known, as well as unknown substances present in the effluent; therefore, it is particularly suitable for complex effluents. The Whole Effluent Assessment (WEA) strategy is described in more detail in Section 4.3.4.4.

¹⁹¹ OSPAR Commission 2007; Practical Guidance Document on Whole Effluent Assessment. Publication Number: 316/2007

¹⁹² DIRECTIVE 2010/63/EU OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 22 September 2010 on the protection of animals used for scientific purposes

¹⁹³ OSPAR Commission, 2005, Whole Effluent Assessment Report

In Europe, national waste water control is mainly based on the single substance approach, i.e. setting ELVs for single substances or sum parameters. However, the assessment of the toxicity of waste water effluents is a well-established method and has been successfully employed to indicate the potential for environmental impacts from chemicals.¹⁹⁴ Several Member States (e.g. Austria, Belgium, Denmark, Estonia, Finland, France, Germany, Ireland, Latvia, Lithuania, Netherlands, Poland, Portugal, Sweden, UK) have experience in applying toxicity tests for the monitoring of industrial discharges. Some Member States also use toxicity tests in specific permits, or at least their use is regulated by general provisions¹⁹⁵.

4.3.4.2 EN standards

Toxicity tests 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 performance. 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 receiving water type (fresh or salt water). It is advisable to combine tests with organisms of different trophic levels.

Toxicity tests or bioassays 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. It has to be mentioned that the application of toxicity tests requires different skills (ecotoxicological) than those required for the measurement of emissions to water as described in Sections 4.3.2 and 4.3.3.

The toxicity tests and sampling procedures are standardised in EN, ISO or National standards, and applied in several Member States. The OECD also provides in its 'OECD Guidelines for the Testing of Chemicals'¹⁹⁶ tests to assess the effects on biotic systems, including toxicity tests.

A list of all EN standards currently (2013) available for the sampling of waste water for biotesting and for toxicity tests in waste water are given in Annex A.7. Because of the huge amount of methods available, this list only covers EN standards.

In the following paragraphs, a brief overview of some EN standards is given following an ascending order of the trophic levels.

EN ISO 11348:2008, Parts 1-3 specify a method for the determination of the inhibitory effect of water samples on the light emission of a **marine bacterium**. Therefore, it is also called the 'luminescent bacteria test'. Specified volumes of the test sample or 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 (e.g. 5, 15 or 30 minutes). **EN ISO 10712:1995** also uses bacteria as a test organism, but for a growth inhibition test.

EN ISO 8692:2012 and **EN ISO 10253:2006** specify growth inhibition tests with **fresh water algae** or **marine unicellular algae**. An inoculum of exponentially growing monospecies algal strains are cultured for several generations in defined mediums containing a range of

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 ¹⁹⁴ ECETOC 2011, TR 111: Development of guidance for assessing the impact of mixtures of chemicals in the aquatic environment
 ¹⁹⁵ COURA 2010 Wheth Effluent Account (WEA) – Present environment for the use of

¹⁹⁵ COHIBA 2010 Whole Effluent Assessment (WEA) - Proposed recommendations for the use of toxicity limits. (COHIBA Control of Hazardous Substances in the Baltic Sea Region

¹⁹⁶ OECD 2013 Guidelines for the Testing of Chemicals, Section 2 Effects on Biotic Systems <u>http://www.oecd-ilibrary.org/environment/oecd-guidelines-for-the-testing-of-chemicals-section-2-effects-on-biotic-systems_20745761</u>

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.

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. Inhibition of growth is measured after seven days relative to control cultures grown under identical conditions.

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 growthinhibiting 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 compared with that of the controls.

EN ISO 6341:2012 uses the water flea *Daphnia magna* (Cladocera, Crustacea), representing a **primary consumer and a major component of the zooplankton** in aquatic ecosystems. The test specifies the determination of the immobilisation of the water flea after 24 h or 48 h exposure to the test sample under specified conditions.

EN ISO 15088:2008 uses the eggs of the zebrafish (*Danio rerio* Hamilton-Buchanan former *Brachydanio rerio*) as test material. This standard specifies a method for the determination of the degrees of dilution or of concentrations, as a measure of the acute toxic effect of waste water to **fish eggs** within 48 hours. Fish, as **high-order consumers**, are a confirmed part within test concepts regarding aquatic organisms from different trophic levels.

EN ISO 15088:2008 has been elaborated 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 7346:1997.

EN ISO 7346:1997, Part 1-3, describe the determination of the acute lethal toxicity of substances under specified conditions to a **fresh water fish** (zebrafish *Danio rerio*). In some Member States, fish bioassays are replaced by other methods (e.g. EN ISO 15088:2008) for ethical reasons.

In addition, there are several other biotest methods using different organisms which are standardised by ISO or at a national level, and frequently applied by different Member States.

4.3.4.3 Assessment of the toxicity of waste water

Toxicity tests of waste water effluents are generally applicable to identify situations where a production site has an inherent toxicity problem which is not easily identified by the observation of other parameters or where other parameters indicate variations in the performance of the biological WWTP.

Toxicity tests are rarely carried out on-line. The time needed to obtain the results, typically between 24 and 96 hours, does not allow directly controlling the waste water treatment.

Extensive experience exists in several Member States with the application of biological systems for the assessment of the toxicity of industrial waste water effluents. In the COHIBA-project¹⁹⁷, involving eight Member States, the results show, among others, that

Order of bullet points changed.

- the results of a ring-test with different laboratories, applying three tests (i.e. *Daphnia magna* acute toxicity, algae growth inhibition, and luminescent bacteria tests) did not differ largely;
- the variability of the test results can be reduced to a certain extent by improved quality control, using standardised and validated methods, and by ring-testing;
- the bioassays used in different countries differ from each other in respect of e.g. organisms, end points, expression of results;
- to assess toxicity of an effluent, it is recommended to conduct several tests using relevant end points and at least 2-3 organisms from several trophic levels;
- 24-hour flow-proportional composite samples are favoured, since the composition of waste water can vary significantly over time.

In any case, it is important to communicate the toxicity test results with an adequate report of the effluent sampling, the applied test methods, the known matrix effects, and the statistical analyses applied to the data; for reporting see also Section 4.3.2.7.

As mentioned above, the expression of toxicity results can vary from country to country. In the following list¹⁹⁸, the most commonly used units are represented:

• 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 EC₅₀ of 20 % means that 50 % of the test organisms were affected when the effluent concentration was 20 %. The smaller the effective concentration, the more toxic the effluent is. The EC values are point estimates and are based on concentration/response-relationships. They can be determined statistically or graphically with at least five data pairs of concentration/response between 0 and 100 % responses. On the basis of the EC data, error terms can be calculated, but, for moderate 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.7 use this unit.

The EC_x methodology is usually applied to single substances, and results are expressed as concentration values (e.g. mg/l). However, dilution values for a waste water sample representing a given response level can, in principle, also be obtained from an approach using dilutions (see LID below).

No Observed Effect Concentration (NOEC): NOEC is the highest concentration of the effluent where no observable adverse effects are detected. NOECs are used in many countries, especially when determining chronic toxicity. However, the results of different NOEC measurements might not be comparable, due to the selection of different dilution series.

¹⁹⁷ COHIBA 2010 Whole Effluent Assessment (WEA) - Proposed recommendations for the use of toxicity limits. (COHIBA Control of Hazardous Substances in the Baltic Sea Region) (Denmark, Finland, Estonia, Germany, Ireland, Latvia, Lithuania, Poland, Sweden)

¹⁹⁸ COHIBA 2010 Whole Effluent Assessment (WEA) - Proposed recommendations for the use of toxicity limits. (COHIBA Control of Hazardous Substances in the Baltic Sea Region)

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• **Lowest Ineffective Dilution (LID):** The LID approach is used to monitor the toxicity of the waste water by means of dilution series. uses dilutions of the original waste water, as the concentration of the substance(s) is generally not known. The sample will be diluted with defined ratios of dilution water until the defined effects is no longer are 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 test control).

Procedures on how to calculate LID values are given in all the EN standards listed in Annex A.7.

The LID value gives the ratio of the volume of the diluted sample in relation to the original sample; the higher the LID value (respective the necessary dilution), the higher the toxicity of the original waste water samples.

• **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, also other definitions for TU are used (e.g., $TU_C = EC_{10}^{199}$), which makes the comparison between TUs difficult.

The use of toxicity tests is less comprehensive than whole effluent assessment (WEA, see Section 4.3.4.4), which, in addition, includes persistency and liability to bioaccumulation.

4.3.4.4 Whole effluent assessment (WEA)

In addition to only assessing the toxicity of the waste water effluent, WEA methods also aim at estimating the persistency (degradability) and bioaccumulation potential. By applying the so called PBT-criteria (**P**ersistency, **B**ioaccumulation potential and **T**oxicity assessment), the possible hazardous character of effluents is assessed, which would otherwise be insufficiently controlled when relying only on the physico-chemical and chemical indications provided by the analysis of conventional waste water parameters. Additionally, genotoxic effects and endocrine disruptive effects may be studied using WEA protocols, but so far, these are less common.

In particular, in the case of complex effluents, WEA might be quicker and less expensive than the extensive chemical characterisation associated with ecotoxicological characteristics and can be used, as well as for assessing toxicity, as a tool within an environmental management system.

Degradability (persistency) can be is typically studied in 28 day biological tests over several days, and gives information on whether the biotreatment already given is adequate or whether such treatment should be considered for the untreated waste water. It is often quantified e.g. by Dissolved Organic Carbon (DOC) measurements, or by CO_2 evolution. A method to measure biodegradability is the Zahn-Wellens test as described in EN ISO 9888:1999²⁰⁰. Furthermore, if followed by toxicity tests, an indication of the potential for the reduction of toxicity is given. Although preferably called degradability, the established abbreviation in the WEA systematic is 'P' for persistency.

¹⁹⁹ OSPAR Commission 2007; Practical Guidance Document on Whole Effluent Assessment. Publication Number: 316/2007

²⁰⁰ EN ISO 9888:1999 Water quality – Evaluation of ultimate aerobic biodegradability of organic compounds in aqueous medium – Static test (Zahn-Wellens method) (ISO 9888 : 1999); German version EN ISO 9888 : 1999

Liability to bioaccumulate 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 a liquid extraction method. Quantification is done by gas or liquid chromatography.

The toxicity in WEA is measured with the same biological test methods, or bioassay methods, used for the toxicity assessment, e.g. bacteria, algae, crustacean and fish bioassays (see Sections 4.3.4.2 and 4.3.4.3).

The application of WEA presents some difficulties, including:

- There is a lack of agreement on standardised test methods for bioaccumulation and persistency.
- It might be difficult to find laboratories that are competent 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.

In any case, it is important to communicate the results of WEA testing with an adequate report of the effluent sampling, applied test methods, and the statistical analyses applied to the data; for reporting, see also Section 4.3.2.7.

Some examples for the applicability of the WEA approach, or of the assessment of toxicity if applied alone, are listed below:

- ranking the environmental risk of discharges to an aquatic system;
- toxicity identification/reduction evaluations;
- prioritisation of waste water treatment measures;
- judging effectiveness of treatment improvements;
- backtracking effects observed in receiving environments.

4.3.4.5 Elaboration of BREFs

Although BAT conclusions and BAT-AELs normally address specific substances and sum parameters. In specific industrial sectors, in particular where complex waste water effluents can be expected and where the analysis of specific substances or sum parameters was shown to be inadequate, it may be advantageous to derive BAT conclusions and associated BAT-AEL ranges for waste water toxicity. it would be impossible to derive BAT conclusion and associated BAT-AEL ranges for waste water toxicity in specific industrial sectors where complex waste water effluents can be expected.

Biomonitoring data measured with toxicity tests represent a valuable tool for the assessment of toxicity, in particular of complex effluents. If sufficient data are available, they can provide the basis for measures to control pollution and to minimise the ecotoxic impact of waste water effluents. Therefore, depending on the industrial sector, it may be a viable option is advisable to use information provided by toxicity measurements, and if available, by persistency and bioaccumulation measurements, in the elaboration of BAT conclusions.

However, there may be some limitations on the use of the results of biological testing for the elaboration of BAT conclusions, because possible effects on the environment also depend on variables present in the receiving water (e.g. salinity) are taken into account while testing. These details are of interest in every individual case, and therefore, belong to the permit conditions.

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OSPAR²⁰¹ pointed out that since the complexity of substances in effluents is increasing and the methods for assessing the effects are improving at the same time, it seems obvious that WEA parameters will be used regularly for the benchmarking of BAT performance. In practice, toxicity or WEA data are only rarely used in Europe.

So far, there is the only one BREF, the 'Manufacture of Organic Fine Chemicals' (OFC 2006), where for the protection and performance of the biological waste water treatment part, BAT-AELs are defined in terms of toxicity of the effluent. BAT-AELs are given as LID values for fish, *Daphnia*, algae, and luminescent bacteria; the expression as EC_{50} levels is also possible. According to In the OFC BREF, it is BAT to carry out regular biomonitoring of the total effluent after the biological WWTP if substances with ecotoxicological potential are handled or produced with or without intention. Monitoring is defined as toxicity monitoring in combination with on-line TOC measurement.

In the 'Common Waste Water and Waste Gas Treatment/Management Systems in the Chemical Sector' (CWW 2011) BREF, the assessment of toxicity, persistency and bioaccumulation is mentioned in detail. Currently (2013), it is not clear if it will be a part of the BAT conclusions on the environmental management system, dealing with waste water to be discharged into the receiving water.

In the 'Surface Treatment using Organic Solvents' (STS 2007) BREF, it is BAT to monitor raw materials and effluent to minimise the discharge of materials with aquatic toxicity, and reducing their effects where there is a risk of contact with water (...).

In the 'Pulp and Paper Industry' (PP 2013) BREF, it is mentioned that regarding paper making, for example sites, the whole effluent toxicity has been assessed for single mills (e.g. in Germany: toxicity to duckweed) or as parameters in an ordinance for paper mill waste water (e.g. Austria: toxicity to fish), because of the complexity of effluents containing a wide range of substances.

In other BREFs, such as 'Iron and Steel Production' (IS 2012), the 'Large Volume Organic Chemical Industry' (LVOC 2003) and 'Industrial Cooling Systems' (ICS 2001), data on toxicity were collected for some subsectors and are included in the related sections, or as in 'Tanning of Hides and Skins' (TAN 2013), it is mentioned in the recommendations for future work that the exchange of information on toxicity and whole effluent assessment including biodegradability tests would be beneficial for the next review of the BREF and for all regulatory authorities.

To summarise the experience gained during the elaboration of BREFs, depending on the industrial sector, it might be worthwhile to take into account results obtained by the application of toxicity tests, e.g. in the case of the production of fine chemicals, pharmaceuticals, pesticides and co-treated waste water from different plants.

4.3.5 Monitoring costs aspects of emissions to water connected with monitoring

The costs of monitoring emissions to water, in general, are mentioned several times in Section 4.3, in particular, when different monitoring regimes (Sections 4.3.2.2 and 4.3.2.3) or different sampling frequencies (Section 4.3.2.5.6) are mentioned.

However, no data on the costs of monitoring emissions to water (like for air) were provided during the elaboration of this document. Therefore, detailed information based on current data cannot be provided, neither for sampling nor for analysing.

²⁰¹ OSPAR Commission, 2005, Whole Effluent Assessment Report

Some very general information is available in a report provided by CONCAWE²⁰², which serves as a guidance to 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, but only as a minor feature. The focus is clearly on analytical capability of the analytical method, rather than on the more subjective feature of the indicative costs of the method.

In the method assessment programme, the indicative cost for each method is placed in one of three specific bands, based on sample preparation, treatment and analytical method used for the determination. Usually the more complex the analysis, the more the cost of this analysis, and the higher the cost, the higher the ranking score assigned to it. This indicative cost is given as low, medium or high cost, represented as $\mathcal{E}, \mathcal{E}\mathcal{E}$ and $\mathcal{E}\mathcal{E}\mathcal{E}$, respectively.

As already mentioned above, the variation of the indicative cost feature in the report is very limited. Almost all water parameters are categorised as 'high cost' ($\in \in \in$).

²⁰² CONCAWE 2013 Refinery effluent analysis methodologies for relevant parameters from EU – regulatory regimes

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5 CONCLUDING REMARKS AND RECOMMENDATIONS FOR FUTURE WORK

Timing of the review process

The work for the review of the Reference Document on the General Principles of Monitoring, the MON REF (originally adopted by the Commission in 2003), began with the reactivation, in December 2009, of the group of experts that participated in the elaboration of the original document. This was followed, in April 2010, by a call to the experts to express their wishes for the review of the document.

At the meeting of the Industrial Emissions Directive (IED) Article 13 forum on 12-13 September 2011, the review of the MON REF and its format was discussed.

In March 2012, the Commission decided, after considering the work programme for the exchange of information required under Article 13(3)(b) of the IED and after further discussion and reflection, not to draw up a horizontal BAT reference document (BREF) on Monitoring, but rather to develop a JRC Reference Report on Monitoring (ROM).

This change of process implied that the Technical Working Group (TWG) for the revision of the MON REF was no longer be active. However, to gather information on monitoring and to utilise the expertise of the IED Article 13 forum members, a Monitoring Expert Group (MEG) was set up instead to develop the ROM.

In March 2012, a background paper (BP), which also included wishes expressed during the reactivation of the TWG, was sent to the MEG providing more information about the expected content of the ROM. This was followed by a draft structure in April 2012 and a draft Scope of the ROM in June 2012.

Developing a reference report required some changes to the work process compared to the development of a BREF, and so requests for additional clarification were raised during this time period to clarify the process and document parameters. In September 2012, further clarification was provided by the Commission about the status of the document, stating that 'the ROM will not be a legally binding interpretation of the IED - the legally binding text is that of the Directive itself. However, the ROM will represent a reference for enhancing consistent application of the Directive by those involved'.

During the work process to develop the ROM, the three main sections: 'General aspects of monitoring', Monitoring of emissions to air' and 'Monitoring of emissions to water' were sent to the MEG as stand-alone documents in April 2013, May 2013 and August 2013 respectively, together with the associated annexes. The consultation period for the MEG to comment on these stand-alone documents ended in September 2013.

The EIPPCB merged all the individual parts of the ROM together, after assessing and taking into consideration the comments received, and prepared the final draft of the ROM, which was sent to the MEG in October 2013.

Before finalising, this section has to be completed.

Sources of information

The ROM summarises the commonly available information collected by the EIPPCB from various sources, such as internet pages, international and national standards, and publications. Some Member States also provided special contributions summarising their monitoring practises. Altogether, more than 150 references are included in the ROM. All the information gathered was made available to the MEG, unless protected by copyright.



Furthermore, the Technical Committee CEN/TC 230 'Water analysis' and CEN/TC 264 'Air quality' of the European Committee for Standardisation provided the Annexes: A.1 'EN standards for air measurements' and A.2 'EN standards for water measurements'. Annex A.5 'Monitoring costs of emissions to air' was provided by the UK.

Recommendations for future work

The current document only covers the monitoring of emissions to air and to water. But it is recognised that monitoring is also of interest for other topics, such as noise, soil, groundwater, waste, energy, and greenhouse gases, which can also be relevant for the elaboration of BAT conclusions or for permitting IED installations. It may be helpful to summarise available information on these topics in the future.

In addition, in some sections of the ROM several different possibilities are mentioned, e.g. for sampling duration, for the measurement frequency or for the treatment of data, which reflect the current situation in Europe, but which may lead to different results. For the future, it is recommended collecting more information on these subjects in order to give further recommendations.

6 ANNEXES

A.1. EN standards for the measurement of the emissions to air

	Environmental Medium	Component(s)	Monitoring Method for SRM	EN or ISO standard for SRM	Limit of Detection
	Stack gas	O ₂	Paramagnetism	EN 14789	\leq 0.20 % of the range
	Stack gas	Temperature	Thermocouples	IEC Publication 584-2	
	Stack gas	Flow rate	Differential pressure, vane anemometer et al	EN ISO 16911-1	Not applicable
	Stack gas	Water vapour	Adsorption or condensation/adsorption method; Temperature method	EN 14790	Not specified
	Stack gas	СО	Non-dispersive infrared spectrometry	EN 15058	$\leq \pm 2.0$ % of the range
	Stack gas	SO ₂	Absorption in liquid phase	EN 14791	Ion chromatography method: 0.1 mg/m ³ ; titration method: 2.2 mg/m ³
	Stack gas	NO _X	Chemiluminescence	EN 14792	\leq +/-2.0 % of the range
	Stack gas	Dust	Gravimetric	EN 13284-1	For dry gases: 0.3 mg/m ³ ; for water saturated gases: 2 mg/m ³
	Stack gas	NH ₃		-	
	Stack gas	HCl (gaseous chloride content)	Absorption in liquid phase	EN 1911	0.2 mg/m ³ with a sample volume of 0.5 m ³
	Stack gas	HF (gaseous fluoride content)	Absorption in liquid phase	ISO 15713	0.1 mg/m ³ with a sample volume of 0.1 m ³
	Stack gas	TOC	Continuous flame ionisation detector method	EN 12619 EN 13526	EN 12619: 0.4 mg/m ³ EN 13526: 5 % of the emission limit value
	Stack gas	Individual gaseous organic compounds	Solid adsorbent/solvent extraction or thermal desorption	EN 13649	Not specified
	Stack gas	PCDD/F	Filter, a condensate flask and a solid or liquid adsorbent	EN 1948 part 1, 2 and 3	Not specified
	Stack gas	РСВ	Filter, a condensate flask and a solid or liquid adsorbent	EN 1948 part 4	Depending on method: WHO-TEQ 0.11 to 0.57 pg/m ³)
11	Stack gas	Hg (Total)	Filtration and absorption in liquid phase	EN 13211	2.6 μg/m ³ (gas volume of 0.05 m ³)
	Stack gas	As, Cd, Tl, Sb, Pb, Cr, Co, Cu, Mn, Ni, V (total emission of specific elements)	Filtration and absorption in liquid phase	EN 14385	\leq 5 µg/m ³ (for each element)

 Table 6.1:
 Periodic Monitoring of Stack Emission

RB/BS/EIPPCB/ROM_Final_Draft

Environmental Medium	Component(s)	Monitoring Method for SRM	EN or ISO standard for SRM	Limit of Detection
Stack gas	N ₂ O	Non-dispersive infrared spectrometry	EN 21258	\leq 2 % of upper limit of the lowest measuring range used
Stack gas	CH ₄	Continuous flame ionisation detector method/gas chromatography	EN 25140 EN 25139	\leq 2 % of upper limit of the lowest measuring range used
Stack gas	Odour	Olfactometry	EN 13725	Not specified
Stack gas	Particles PM ₁₀ /PM _{2.5}	Impactor, gravimetric	ISO 23210	PM ₁₀ : 0.4 mg/m ³ (sample volume: 1 m ³) PM _{2.5} : 0.3 mg/m ³ (sample volume: 1 m ³)

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	Environmental Medium	Component(s)	Examples for Monitoring Methods for AMS	EN or ISO standard for SRM	Certification Standard for AMS / Calibration Standard	Limit of Detection
	Stack gas	O ₂	Paramagnetism, electrochemical cell, ZrO ₂	EN 14789	EN 15267 EN 14181	\leq 0.40 Vol %
	Stack gas	Temperature	Thermocouples	IEC Publication 584-2		6
	Stack gas	Flow rate	Ultrasonic, differential pressure, mass flow	EN ISO 16911- 1	EN 15267 EN 14181 EN ISO 16911-2	\leq 4.0 % of range at lower reference point
	Stack gas	Water vapour	TDL, FTIR, NDIR with GFC	EN 14790	EN 15267 EN 14181	\leq 4.0 % of the upper limit of the certification range
	Stack gas	SO ₂	NDIR, FTIR, NDUV, DOAS	EN 14791	EN 15267 EN 14181	\leq 4.0 % of the upper limit of the certification range
	Stack gas	СО	NDIR, FTIR	EN 15058	EN 15267 EN 14181	\leq 4.0 % of the upper limit of the certification range
	Stack gas	NO _X	Chemiluminescence, NDIR, FTIR, NDUV, DOAS	EN 14792	EN 15267 EN 14181	\leq 4.0 % of the upper limit of the certification range
	Stack gas	Dust	Optical, triboelectric	EN 13284-1	EN 15267 EN 14181 EN 13284-2	\leq 4.0 % of the upper limit of the certification range
	Stack gas	NH ₃	NDIR with gas filter correlation, FTIR, TDL	-	EN 15267 EN 14181	\leq 4.0 % of the upper limit of the certification range
	Stack gas	HCl (gaseous chloride content)	NDIR with gas filter correlation, FTIR, TDL	EN 1911	EN 15267 EN 14181	\leq 4.0 % of the upper limit of the certification range
	Stack gas	HF (gaseous fluoride content)	FTIR, TDL	ISO 15713	EN 15267 EN 14181	\leq 4.0 % of the upper limit of the certification range
	Stack gas	тос	Continuous flame ionisation detector method	EN 12619 EN 13526	EN 15267 EN 14181 EN 12619	\leq 4.0 % of the upper limit of the certification range
	Stack gas	Hg (Total mercury)	Atomic absorbance spectroscope, cold vapour atomic fluorescence spectroscopy	EN 13211	EN 15267 EN 14181 EN 14884	\leq 4.0 % of the upper limit of the certification range
	Stack gas	N ₂ O	NDIR, FTIR	EN ISO 21258	EN 15267 EN 14181	\leq 4.0 % of the upper limit of the certification range
11	Stack gas	CH ₄	Continuous flame ionisation detector method, NDIR, FTIR	EN ISO 25140	EN 15267 EN 14181	\leq 4.0 % of the upper limit of the certification range
	([*]) two times the r	epeatability standar	d deviation at zero accordin	ng to EN 15267-3 in t	field test	

 Table 6.2:
 Continuous Monitoring of Stack Emission

A.2. EN standards for the measurement of emissions to water

Table 6.3: Monitoring of water pollutants

Environmental medium	Substance(s)	EN or ISO standard	Monitoring frequency	Monitoring Method	Limit of detection (LoD) Limit of quantification (LoQ) Limit of application Application range	Additional comments
Water	Flow rate	Several EN or ISO standards	Continuous/periodic	R		In addition to EN and ISO, several Member States use national standards for regulatory purposes
Water	Temperature		Continuous/periodic			
Water	рН	EN ISO 10523:2012	Continuous/periodic	Measurement of the potential difference of an electrochemical cell		
Water	Oxygen content	EN ISO 5814:2012	Continuous/periodic	Determination by means of an electrochemical cell		
Water	Conductivity	EN 27888:1993	Continuous/periodic	EC		All types of water
Water	Turbidity	EN ISO 7027:1999	Continuous/periodic	 a) Transparency testing tube b) Transparency testing disk c) Measurement of diffuse radiation d) Measurement of the attenuation of a radiant flux 		
Water	BOD ₅	EN 1899-1:1998	Periodic	Dilution and seeding method with allylthiourea acid addition	Applicable to waters with $BOD \ge 3 \text{ mg/l} (LoD)$	
Water	BOD_5	EN 1899-2:1998	Periodic	Method for undiluted samples	Applicable to waters with $BOD \ge 0.5 \text{ mg/l} (LoD)$	
Water	BOD ₅	ISO 5815-1:2003	Periodic	Dilution and seeding method with allythiourea addition	Applicable to waters with $BOD \ge 3 \text{ mg/l} (LoD)$	In Europe, EN 1899-1 is applied
Water	BOD ₅	ISO 5815-2:2003	Periodic	Method for undiluted samples	Applicable to waters with BOD $\geq 0.5 \text{ mg/l (LoD)}$	In Europe, EN 1899-2 is applied
Water	BOD ₇	EN 1899-1 and EN 1899-2, ISO 5815-1 and ISO 5815-2				

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Environmental medium	Substance(s)	EN or ISO standard	Monitoring frequency	Monitoring Method	Limit of detection (LoD) Limit of quantification (LoQ) Limit of application Application range	Additional comments
Water	COD	ISO 15705:2002	Periodic	1.) Photometric detection at 600 nm 2.) Titrimetric	1.) LoD: 6 mg/l 2.) LoD: 15 mg/l	ISO 15705 specifies a sealed tube method. Several Member States use national standards for regulatory measurements of COD in waste water (e.g. NEN 6633 in NL or DIN 38409-41 in DE)
Water	COD	ISO 6060:1989	Periodic	Reduction of oxidisable substances with potassium dichromate in strong sulphuric acid; titration	Application range: 30 mg/l and 700 mg/l	
Water	ТОС	EN 1484:1997	Periodic	Oxidation of organic carbon by combustion, addition of oxidants, UV-radiation or other high energy radiation	Application range: 0.3 mg/l to 1 000 mg/l (lower end is for special cases, e.g. drinking water)	
Water	ТОС	ISO 8245:1999	Periodic	Oxidation of organic carbon by combustion, addition of oxidants, UV-radiation or other high energy radiation		In Europe, EN 1484 is applied
Water	TSS	EN 872:2005	Periodic	Determination of suspended solids in raw waters, waste waters and effluents by filtration through glass fibre filters	LoD: approx. 2 mg/l	
Water	TSS	ISO 11923:1997	Periodic	Determination of suspended solids in raw waters and waste waters by filtration though glass-fibre filters.	LoD: approx. 2 mg/l	In Europe, EN 872 is applied
Water	TN_b	EN 12260:2003	Periodic	Quantification by combustion and detection of nitrogen oxides using chemiluminescence	Application range: approx. 1 mg/l to 200 mg/l; LoD: approx. 0.5 mg/l	
Water	TN (as inorganic N) sum of nitrate-N, nitrite-N and ammonium-N	ISO 29441:2010	Periodic	Determination of total nitrogen after UV digestion - Method using flow analysis (CFA and FIA) and spectrometric detection	Application range: 2 mg/l to 20 mg/l; (0.2 mg/l to 2 mg/l are possible)	

Environmental medium	Substance(s)	EN or ISO standard	Monitoring frequency	Monitoring Method	Limit of detection (LoD) Limit of quantification (LoQ) Limit of application Application range	Additional comments
Water	Ammoniacal N	EN ISO 11732:2005	Periodic	FIA or CFA	LoQ: 0.05 mg N/l	
Water	Ammoniacal N	ISO/FDIS 15923-1:2013	Periodic	Discrete analysis	LoQ: 0.05 mg N/l	At the time of the development of this report (2013) the standard was under publication
Water	Nitrogen	EN 25663:1993	Periodic	Kjeldahl-N	Up to 10 mg in the test portion	
Water	Nitrogen	EN ISO 11905-1:1998	Periodic	Digestion with oxidative digestion with peroxodisulphate	Followed by FIA (EN ISO 13395)	
Water	Nitrogen	EN ISO 13395:1996	Periodic	FIA and CFA	From 0.01 mg/l to1 mg/l for nitrite(N) From 0.2 mg/l to 20 mg/l for nitrite/nitrate(N)	
Water	Nitrogen	EN ISO 14402:1999	Periodic	FIA and CFA	From 0.01 mg/l to 1.0 mg/l	
Water	Nitrogen	EN ISO 6878:2004	Periodic	Ammonium molybdate spectrometric method	0.005 mg/l to 0.8 mg/l	
Water	AOX	EN ISO 9562:2004	Periodic	Determination of organically bound chlorine, bromine and iodine (expressed as chloride) adsorbable on activated carbon	LoQ: 15 μg/l	
Water	EOX	No European or international standard exists	Periodic			
Water	Cd	EN ISO 11885:2009	Periodic	ICP-OES	LoQ: approx. 0.2 µg/l	
Water	Cd	EN-ISO 17294-2:2004	Periodic	ICP-MS	Lower LoD: approx. 0.3 µg/l	
Water	Total Cr	EN ISO 11885:2009	Periodic	ICP-OES	LoQ: approx. 2 µg/l	
Water	Total Cr	EN-ISO 17294-2:2004	Periodic	ICP-MS	Lower LoD: approx. 1 µg/l	
Water	Cu	EN ISO 11885:2009	Periodic	ICP-OES	LoQ: approx. 2 µg/l	
Water	Cu	EN-ISO 17294-2:2004	Periodic	ICP-MS	Lower LoD: approx. 1 µg/l	
Water	Pb	EN ISO 11885:2009	Periodic	ICP-OES	LoQ: approx. 5 µg/l	
Water	Pb	EN-ISO 17294-2:2004	Periodic	ICP-MS	Lower LoD: approx. 0.1 µg/l	
Water	Ni	EN ISO 11885:2009	Periodic	ICP-OES	LoQ: approx. 2 µg/l	
Water	Ni	EN-ISO 17294-2:2004	Periodic	ICP-MS	Lower LoD: approx. 1 µg/l	

						Annexes
Environmental medium	Substance(s)	EN or ISO standard	Monitoring frequency	Monitoring Method	Limit of detection (LoD) Limit of quantification (LoQ) Limit of application Application range	Additional comments
Water	Zn	EN ISO 11885:2009	Periodic	ICP-OES	LoQ: approx. 1 µg/l	
Water	Zn	EN-ISO 17294-2:2004	Periodic	ICP-MS	Lower LoD: approx. 1 µg/l	
Water	Hg	EN ISO 17852:2008	Periodic	AFS method without enrichment	Application range: approx. 1 ng/l to 100 µg/l; LoQ: < 1 ng/l	
Water	Hg	EN ISO 17294-1:2006	Periodic	ICP-MS	Lower LoD: approx. 5 μg/l	
Water	Hg	EN ISO 12846:2012	Periodic	AAS method with enrichment	Application range: approx. 0.01 μg/l to 1 μg/l; LoQ 0.008 μg/l (with enrichment)	
Water	Hg	EN ISO 12846:2012	Periodic	AAS method without enrichment	Lower limit of application: approx. 0.05 µg/l; LoQ 0.024 µg/l (without enrichment)	
Water	Phosphorus	EN ISO 10695:2000	Periodic	GC	LoD: 0.5 µg/l	
Water	Phosphorus	EN ISO 15681-1:2004	Periodic	FIA	Orthophosphate from 0.01 mg/l to 1.0 mg/l (P) total phosphorus from 0.1 mg/l to 10 mg/l (P)	
Water	Phosphorus	EN ISO 15681-2:2004	Periodic	CFA	Orthophosphate from 0.01 mg/l to 1.0 mg/l (P); total phosphorus from 0.1 mg/l to 10 mg/l (P)	
Water	Hydrocarbons	EN ISO 9377-2:2000	Periodic	Solvent extraction and gas chromatography	Above 0.1 mg/l	
Water	Complexing agents	EN ISO 16588:2003	Periodic	GC	From 0.5 µg/l to 200 µg/l	
Water	Complexing agents	EN ISO 16588:2003/A1:2005	Periodic	GC	From 0.5 µg/l to 200 µg/l	Validation data improved
Water	Chlorine	EN ISO 7393-1:2000	Periodic	Titrimetric method using N, N- diethyl-1.4-phenylenediamine	Application range 0.03 mg/l to 5 mg/l	

Environmental medium	Substance(s)	EN or ISO standard	Monitoring frequency	Monitoring Method	Limit of detection (LoD) Limit of quantification (LoQ) Limit of application Application range	Additional comments
Water	Chlorine	EN ISO 7393-2:2000	Periodic	Colorimetric method using N, N- diethyl-1, 4-phenylenediamine, for routine control purposes	Application range 0.03 mg/l to 5 mg/l	
Water	Chloride	EN ISO 15682:2001	Periodic	CFA and FIA and photometric or potentiometric detection	1 mg/l to 1 000 mg/l	
Water	Anions	EN ISO 10304-1:2009	Periodic	Liquid chromatography of ions: Determination of bromide, chloride, fluoride, nitrate, nitrite, phosphate and sulphate	LoD: ≥ 0.05 mg/l for bromide, nitrite LoD: ≥ 0.1 mg/l for chloride, fluoride, nitrate, phosphate, sulphate (lower LoD possible with special pretreatments)	
Water	Anions	EN ISO 10304- 1:2009/AC:2012	Periodic	Liquid chromatography of ions: determination of bromide, chloride, fluoride, nitrate, nitrite, phosphate and sulphate	Corrigendum, see EN ISO 10304-1	
Water	Anions	EN ISO 10304-3:1997	Periodic	Liquid chromatography of ions: determination of chromate, iodide, sulphite, thiocyanate and thiosulfate (ISO 10304-3:1997)	\geq 0.05 mg/l to 50 mg/l (depending on the ion)	
Water	Anions	EN ISO 10304-4:1999	Periodic	Liquid chromatography of ions: determination of chlorate, chloride and chlorite in water with low contamination	\geq 0.01 mg/l (depending on the ion)	
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Pollutant	Mass flow threshold (kg/h)										
	IED	Germany 203	France 204,205 (¹)	Belgium ²⁰⁶ (Flanders)	Denmark 207						
Dust		3	$5-50(^2)$ > 50(^3)	5	200						
Sulphur dioxide		30	150	50	200						
Nitrogen oxides, as NO ₂		30	150	30	200						
Carbon monoxide, for evaluating the efficiency of combustion		5									
Carbon monoxide, all other cases		100	50								
Inorganic gaseous fluoride compounds, expressed as HF		0.3	5								
Inorganic gaseous chloride compounds, expressed as HCl		1.5	20								
Ammonia			10								
Chlorine		0.3									
Hydrogen sulphide		0.3									
Total organic carbon (TOC)	10 (4)	2.5 1 (⁶)	15 10 (⁵) 2 (⁶)	r	25						
Mercury and its compounds, expressed as Hg		2.5 g/h ⁽⁷⁾									
Cd and Hg			10 g/h (⁸)								
As and Se and Te			$50 \text{ g/h} (^8)$								
Pb			$100 \text{ g/h}(^8)$								
Sb and Cr and Co and Cu and Sn and Mn and Ni and V and Zn			500 g/h (⁸)								
HCN or Br HBr or Cl HCr or H ₂ S			1								
Heavy metals					2						

A.3. Mass flow thresholds for continuous measurement of emissions to air

(from all relevant sources).

A continuous measurement of total suspended particles dust with at least an optical instrument (e.g. opacimeter) is required.

A continuous measurement of dust based on a gravimetric method is required.

IED, Annex VII (Technical provisions relating to installations and activities using organic solvents), Part 6 (Emission monitoring).

If specific equipment for VOC abatement is implemented.

According to a list of organic substances with a higher environmental risk.

Continuous determination of mercury mass concentrations, unless it has been reliably proven that the mass concentrations are less than 20 % of the ELVs given in the German TA Luft.

A daily periodic measurement of the emissions is carried out on a 'continuously taken' representative sample.

- 203 Germany: First General Administrative Regulation Pertaining the Federal Immission Control Act (Technical Instructions on Air Quality Control - TA Luft) of 24 July 2002
- 204 France: Arrêté du 2 février 1998 (2/2/98) relatif aux prélèvements et à la consommation d'eau ainsi qu'aux émissions de toute nature des installations classées pour la protection de l'environnement soumises à autorisation
- 205 French contribution to the elaboration of ROM, Contribution to the chapter 3 dealing with the general aspects of monitoring, INERIS-DRC-12-126076-13244A, 06/12/12 - K.Adam
- 206 Email communication
- 207 Email communication

A.4. Monitoring of odours using survey and electronic noses

A.4.1. Odour surveys

There are several odour monitoring or survey methods which are standardised at national levels and applied for odour monitoring in ambient air in some Member States. Examples are:

<u>NF X43-103:1996</u>: Qualité de l'air - Mesurage olfactométriques - Mesurage de l'odeur d'un effluent gazeux - Méthodes supraliminaires (Air quality - Olfactometric measurements - Measurement of gaseous odour release - Suprathreshold methods).

This method of olfactory equivalencies²⁰⁸ (or a comparative method) consists of comparing the odour intensity of a determined sample with a reference scale based on different intensities. This reference scale establishes an orderly series of concentrations of a pure substance, for example, of n-butanol.

The NF X43-103 standard is used for different applications, such as materials selection and environmental studies. The measurement methodology is based on the comparison of the odour perception with a standard substance scale, in order to determine the intensity of the odour. The panel constitutes six to eight members. For field measurements in the vicinity of industrial installations, measuring points are defined according to 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).

<u>VDI 3940 Part 3:2010</u>: Measurement of odour impact by field inspection - Determination of odour intensity and hedonic odour tone.

The document describes a method which allows the determination of odour intensity and hedonic tone in the field. It is mainly applied together with grid or plume measurements (see above). The method uses selected and trained panel members.

VDI 3940 Part 4:2010: Determination of the hedonic odour tone - Polarity profiles.

The document describes a 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 e.g. pleasant odours ('fragrance') or unpleasant odours ('stench'). The method uses selected and trained panel members.

<u>VDI 3883 Part 1:1997:</u> Effects and assessment of odours - Psychometric assessment of odour annoyance - Questionnaires (under revision).

The document 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.

<u>VDI 3883 Part 2:1993:</u> Effects and assessment of odours - Determination of annoyance parameters by questioning - Repeated brief questioning of neighbour panellists.

The document describes a survey method for determining the existing odour annoyance by using local volunteers. They have to answer repeatedly the question of a momentary sensation

²⁰⁸ ADEME 2009: Summary on the topic 'odour pollution' (contribution to CWW)

of smell and their annoyance rating. This can be done 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.

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

<u>Other types of odour surveys</u>, such as 'Odour diaries', register and analyse the odour complaints of residents in a specific area, together with additional information on the perceived odour. Information from odour complaints may be a direct indication of odour annoyance, but the interpretation of the information collected should be done carefully. On the one hand, the absence of odour complaints does not necessarily mean that there is no odour nuisance. On the other hand, the driving force for odour complaints might not be the perceived odour but rather another reason.

In Ireland; a procedure is in place²⁰⁹, which offers a consistent and systematic approach to the assessment of odours on and in the local area of facilities and installations that are licensed by the Irish EPA, using a special 'Odour Investigation Record Sheet'.

A.4.2. Electronic sensor systems

Electronic sensor systems, also called 'electronic noses' or 'e-noses', are multi-gas sensor systems with sensors intended to detect gaseous substances²¹⁰. Because the sensors cannot smell like the human olfactory system, these substances may be both odorous and non-odorous gases. It is more a broad-spectrum sensitivity depending on the sensor types used.

Specific training of the sensors creates the possibility of identifying substance types, by comparing the 'fingerprint' of the sample with one of the substances from a database. These fingerprints may be comparable to specific odour emissions, but electronic sensors need to be calibrated for the odour to be measured. After calibration and training, electronic sensors are can be primarily suitable for semi-qualitative or semi-quantitative analyses. But There is no European standardised method available which describes how to apply electronic sensor systems. In the Netherlands, the Netherlands Technical Agreement (NTA) 9055²¹¹ is available which sets out requirements for the use of electronic ambient air monitoring.

Electronic sensors include three major parts: a sample delivery system, a detection system, and a data processing system^{212,213}.

The **sample delivery system** enables the generation of the headspace (volatile compounds) of a sample, which is the fraction analysed to create a 'fingerprint'. The system then injects this headspace into the detection system, where the sensor array is located. The An efficient sample handling system is essential to guarantee the quality of the analysis.

²⁰⁹ Irish EPA 2010 Air Guidance Note 5 (AG5) Odour Impact Assessment Guidance for EPA Licensed Sites

 ²¹⁰ Netherlands technical agreement NTA 9065:2013 Air quality - Odour measurements - Odour measurement and calculation

²¹¹ Netherlands Technical Agreement NTA 9055 Luchtkwaliteit – Elektronische luchtmonitoring – Geur(overlast) en veiligheid [Air quality – Electronic air monitoring – Odour (nuisance) and safety]

²¹² INERIS 2009: Monitoring of odour emissions Electronic noses. (contribution to CWW)

²¹³ Peris, Miguel, Laura Escuder-Gilabert 2009: A 21st century technique for food control: Electronic noses. Analytica Chimica Acta 638 (2009) 1–15

The **detection system**, which consists of an array of sensors, is the 'reactive' part of the instrument. Each sensor is more or less sensitive to all volatile molecules but each in their specific way. Mostly sensor arrays are used that react to volatile compounds on contact: the adsorption of volatile compounds on the sensor surface causes a physical change of the sensor.

Commonly used sensors are metal oxide semiconductor, conducting polymers, quartz crystal microbalance, and surface acoustic wave. An electronic sensor array is equipped with several sensors. A commonly used number of sensors is six.

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. These fingerprints need to be interpreted in relation to the measurement objective.

The possibility to correlate the electronic sensors results with those obtained by odour measurements depends on the efforts taken to train the system and to calibrate the system with odour concentrations measurements.

To train electronic sensor systems, qualified samples are needed to build up a database of reference for odours. These samples are taken on site and analysed by olfactometry. The samples are then presented to the electronic sensor system, in order to: first, create a qualitative fingerprint database to recognise the gas composition (i.e. the odour), and second to develop a mathematical model that is able to convert the raw sensor data into odour concentrations. It is necessary to perform a reasonable number of parallel measurements with the electronic sensor system and via olfactometric measurements according to EN 13725:2003.

An electronic sensor system can be 'trained' for a certain application to detect different fingerprints and for a range of odour concentrations. That is to say, that an electronic sensor system 'trained' for specific sources cannot be used to monitor other sources or another plant without a new adapted 'learning programme'.

According to 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 could only be established with a great uncertainty.

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

- conformity of raw materials, intermediate and final products;
- batch to batch consistency;
- detection of contamination, spoilage, adulteration;
- monitoring of storage conditions;
- qualitative control of abatement systems.

A.5. Monitoring costs of emissions to air

Industry sector		Power (LCPD)						Incineration and co incineration								
Type of process	Gas tur	bines	Coal-fii generati	red power ion 4 units	Coal-fire FO	d without FD	hout Cement (example site 1)		Cement (example Lime site 2)		Inciner	ator	WID Power	r generation	Power	plant
AMS installations																
Pollutants monitored	NO _X , CO, O ₂		Particulate, NO, SO ₂ , H ₂ O, CO, O ₂		Particulate, NO _X , SO ₂ , O ₂		H ₂ O, O ₂ , TOC, NO, NO ₂ , N ₂ O, NH ₃ , HCl, CO, SO ₂ , CO ₂		Particulate, NO _X , SO _X , CO, VOCs, HCl, O ₂	Particulate (multiple stacks)	NA		$\begin{array}{c} HCl, CO,\\ NO_X, SO_2,\\ O_2, H_2O,\\ VOCs,\\ particulate \end{array}$		HCl, CO, NO _X , SO ₂ , O ₂ , H ₂ O, VOCs	
Technology employed	IR, UV, electrochemical		Light scatter, <i>in</i> <i>situ</i> NDIR, zirconia		Extrative IR, opacity		FTIR, FID, zirconia detector		FTIR	Tribolectric	NA		FTIR, FID, zirconia cell, triboelectric		FTIR	
Costs																
System purchase cost	£175k	For 5 systems, with 3-years warranty	Existing AMS £25.5k. This is for upgrade of one existing system.	Upgrade to existing systems - gaseous approx. £10k/unit, particulate £12k, O ₂ £3k per unit	£257k	Price for 4 systems	£70k	Per system	£136k	£40k	NA		£115k		£160k	Full system price
Installation cost	£21k	For 5 systems, including commissioning	NA	Minimal retro fit to existing system	NA		£6.5k		£20k	£15k	NA		£5k	Estimated	£32k	
Other significant cost	£24k	Spares	£9k	Instrument air compressor plant	£16k	Software	£14k		NA	NA	NA		£4.5k		£20k £141k	Data acquisition back-up system
	£3.5k	Training	£20k £3.5k	Reporting software, software licence	£3k	Training					NA				NA	
Ongoing maintenance, service and calibration costs per year	£9k	Servicing	£7k		£16.5k		£10k		£20k	£10k	NA		£10k		NA	

Table 6.4: Installed AMS systems and compliance monitoring costs for different sectors regulated under the IED

RB/BS/EIPPCB/ROM_Final_Draft

Industry sector		Р	ower (LCP	D)						Inci	neration and c	o incinera	tion			
Type of process	Gas tur	bines	Coal-fi generat	red power ion 4 units	Coal-fire F(d without SD	Cement (exan	nple site 1)	Cement (example site 2)	Lime	Inciner	ator	WID Powe	er generation	Power	plant
Total cost	£232.5k	For 5 systems	Unknown		£292.5k	For 4 systems	£100.5k	For 1 system.	£176k	£65k	NA		£134.5k		£353k	
EN 14181 calibration costs											<u> </u>					
QAL2 costs	£22k	For 5 systems	£7.5k	For 1 system	£24k	For 4 systems	£5k £4k	Gases, particulate	£6.5k	NA	£12.5k-£20k		£18k	initial QAL2	NA	
AST cost	£7k	For 5 systems	£3k	For 1 system	£18k	For 4 systems	£3.2k £1.6k	Gases	£1.7k	£0.9k	£6k-£12k		NA		NA	
Periodic compliance monitoring								F		2						
Pollutants monitored	NO _X , CO, O ₂		Particulate. NO, SO ₂ , H ₂ O, CO, O ₂		NA		SO ₂ , NO _x , VOC, CO ₂ , CO, HCl, HF, NH ₃ , N ₂ O, group 1, 2, 3 metals, PCBs, PAHs, O ₂ , H ₂ O, flow, C ₆ H ₆ , C ₈ H ₈ , CH ₃ Cl, C ₄ H ₆ , C ₄ H ₄ , C ₂ H ₆ , C ₂ H ₄ , C ₃ H ₈ , NM VOCs, PCDDs, PCDFs,		HF, heavy metals, dioxins, furans, PCBs, PAHs, ammonia, methane,	Particulates, SO _X , NO _X , CO	Dioxins and WID suit		Full WID suit		NA	
Frequency of tests	Annual		NA				Bi-annual		Bi-annual	3 monthly	Quarterly and bi-annual		Annual			
Costs Cost per set of tests	£7k	For 5 systems	NA		3		£4.5k £0.2k	Per test, particulate test	£26.5k	£26k/yr	£23k £47k	Quarterly, bi-annual	£27k			
128			24										RB/RS/J	TIPPCB/PO	M Final	Draft

Industry sector				Meta	ls	Chemical						Food			
Type of process	Foundry furnace	Metal finishing	Batteries (finishing)	Aluminium recycling/re- melting	Metal refining and chemical		Steel works		Rubber	Pigments	Chemical (example site 1)		Chemical (example site 2)		Sugar beet drying (animal feed)
AMS installations															
Pollutants monitored	Particulate (silica)	2 x Particulate	Particulate	Particulate	Particulate, VOCs, chlorine, NO _X		Large number of process and emission points	Overall costs for the complete works, which includes many plants	2 x Particulate	10 x Filter leak	Not applicable to this process		NO _x , CO		3 x Particulate
Technology employed	Probe electrification	Probe electrification	Probe electrification	Probe electrification	In situ particulate, extractive chemiluminescence, chlorine		NA	, V	Probe electrification	Probe electrification			Extractive IR		Probe electrification
Costs	For 1 stack	For 2 stacks	For 1 stack	For 1 stack					For 2 stacks	For 10 silos					For 3 stacks
System purchase cost	£4k	£10k (£5k/stack)	£7.2k	£5k	£15k £20k £24k £18k-£26k	Particulate, FID, chlorine, NO _X	NA		£8.5k (£4.25k/stack)	£15k (£1.5k/silo)			Old system installed 1997		£12k (£4k/stack)
Installation cost	£4.5k	£3k	£2.5k	£1k	£1.5k £1.5k £6k £10k	Particulate FID chlorine NO _X	NA		£4k	£6k			NA		£4.3k
Other significant cost	None	None	None	None	£20k	NO _x initial spares	NA		£4k	None			NA		£4.3k
0					£0.9k/day	Training	NA						NA		
maintenance, service and calibration costs per year	£2k	£4.5k	£6k	£2k	£4.5k £1.8k £11k £22k	Particulate FID chlorine NO _X	£250k		£3k	£3.5k			£2.5k £1.5k	Annual, weekly calibration	£4.5k
Total cost	£10.5k	£17.5k	£15.7k	£8k	Varies depending on above		Unkown		£19.5k	24.5k			NA		£25.1k
EN 14181 calibration costs															
QAL2 costs	Not applicable to this process	Not applicable to this process	Not applicable to this process	Not applicable to this process	Not applicable to this process		£170k	Combined cost estimate per annum	Not applicable to this process	Not applicable to this process			£8.4k		Not applicable to this site

Industry sector	Metals									Chemical						
Type of process	Foundry furnace	Metal finishing	Batteries (finishing)	Aluminium recycling/re- melting	Metal refining and chemical		Steel works Rubber		Rubber	Pigments	Chemical (exam	ple site 1)	Chemical site	l (example e 2)	Sugar beet drying (animal feed)	
AST cost	Not applicable to this process	Not applicable to this process	Not applicable to this process	Not applicable to this process	Not applicable to this process				Not applicable to this process	Not applicable to this process			£6.5k		Not applicable to this site	
Periodic compliance monitoring																
Pollutants monitored	Particulate (silica)	Particulate (Zn, Cu, Ni)	Particulate	VOCs, Metals (Pb, Cd), HCl	NA		Large number of process and emission points	Overall costs for the complete works which includes many plants	Particulate (kaolin)	None	Batch chemical process involving reflux, distillation and drying solvents (e.g. chloroform, dichloromethane), ammonia, HCl		NO _x , CO		Particulate	
Frequency of tests	Annual	Annual	Annual	Annual					Annual	Not required	Annual				Annual	
Costs																
Cost per set of tests	£2k	£2k	£2k	£1k	S	29	£410k		£3k		£1.5k	This is for analysis of the data only, as the monitoring is carried out by the operator (the equipment is owned by process operator ±110k for two FTIR systems).	NA		£4.5k	

NA: No information available

Source: This survey was conducted by the UK Source Testing Association, www.s-t-a.org, whose members comprise Test Laboratories, Process Operators, Instrument Manufacturers and Regulators. The examples show the cost of stack emissions monitoring for different industrial processes and sites. They were provided by industrial operators and relate to actual sites. December 2012

Costs: Costs are given as 1000 £. In December 2012, 1 £ was equivalent to 1.20 - 1.25 Euros.

1) For multicomp	onent gas requiren	nents			Initial costs	Lifeti	me	Annual	Periodic		
Typical application	Compound(s) to be measured	Instrument technology	Approvals and certification range	System purchase ex works	Any significant option	Price of significant options	Typical life of instrument	Period between calibration	service contracts	manual sampling costs	
Coal-fired power plant combustion	SO ₂ , NO, NO ₂ , O ₂	Extractive UV and IR	MCERTS	£25k-£40k	Analyser house or shelter	£6k-£40k	10-15 years	12 months	£4k		
		In situ IR	MCERTS	£20k	Acid gas protection, compressor air	£5k £4.5k	NA	NA	NA	£3k	
gases		Extractive IR and Paramagnetic	MCERTS	£40k-£50k incl. analyser housing	Automated QAL3	£7.5k	NA	Weekly	NA		
		Extractive UV and IR	MCERTS	£30k-£50k	Analyser house or shelter	£6k-£40k	10-15 years	ars 12 months £4k			
	SO ₂ NO NO ₂ O ₂	FTIR and Zirconia	MCERTS	£82k	Automated QAL3	£7.5k	NA	NA	NA		
Coal with SCR	NH ₃ , CO, CO ₂	Extractive IR, paramagnetic and across stack TDLA for NH ₃	MCERTS	£50k and £28k for laser and purge panel	Laser purge panel	£2.5k	10 years (min for lasers)	6-12 months for laser	NA	£4k	
Cement main kiln	CO, NO _x , SO ₂ . O ₂	Extractive UV and IR	MCERTS	£30k-£50k	Analyser house or shelter, water cooled probe	£6k-£40k £10k	10-15 years	12 months	NA	£4.5k	
		Extractive IR and paramagnetic	MCERTS	£40k-£50k	Automated QAL3	£7.5	NA	NA	NA		
Incinerator		Extractive FTIR and FID	MCERTS	£80k-£110k	Analyser house or shelter, automated QAL3	£30k-40k £7.5k	10-15 years	12 months	£7k		
AMSs) including co- incineration	HCL, VOC	Extractive IR, paramagnetic and across stack TDLA for HCl	MCERTS	£50k and £28k for laser and purge panel	Laser purge panel	£2.5k	10 years (min for lasers)	6-12 months for laser	NA	£12k-£20k	
Incinerator applications (Gas	CO, NO _X , SO ₂ O ₂ HCL,	Extractive FTIR and zirconia	MCERTS	£82k	Automated QAL3	£7.5	10-15 years	12 months	£7k	671-	
AMSs) including co- incineration		Extractive IR and paramagnetic	MCERTS	£56k	Automated QAL3	£7.5	10 years (min for lasers)	6-12 months for laser	NA	£/K	
	NO, NO ₂ , CO, O ₂	Extractive UV and IR	MCERTS	£25k-£40k	Analyser house or shelter	£6k-£30k	10-15 years	12 months	NA		
Gas turbine AMS	NO, NO ₂ ,CO ₂ , CO, O ₂	Extractive NDIR, chemiluminescence and paramagnetic	MCERTS	£43k	Automated QAL3	£7.5	NA	NA	NA	£4k	
ATEX area applications	SO ₂ , NO, NO ₂ , O ₂ , NH ₃ , CO, CO ₂	Extractive UV and IR	MCERTS	£40k-£60k	Analyser house or shelter	£30k-£80k	10-15 years	12 months	£4k	NA	

Table 6.5: Range of costs for supply of AMSs for sites regulated under the IED

2) Single compone	ent: Gas				Initial costs	Lifetin	ne		Periodic	
Typical application	Compound(s) to be measured	Instrument technology	Approvals and certification range	Instrument purchase ex works	Any significant option	Price of significant options	Typical life of instrument	Period between calibration	Annual service contracts	manual sampling costs
Aluminium, chemical, incineration	HCl or HF	Across stack TDLA	MCERTS	£18k-28k						£3k - £5k
Combustion	O_2	In situ zirconia probe, across stack TDLA	MCERTS/TUV	£5k-12k	NA	NA	3-10 years	3-6 months	NA	£1k
Crematoria	O ₂ , CO	Electrochemical	MCERTS/TUV	£5k-8k			2-6 years	3-6 months		£1k-£2k
Chemical, solvent, incineration	TOC	FID	MCERTS/ TUV	£24k	NA	NA	NA	NA	NA	£1k-£3k
Cashan antan	Single stream			£100k	NA	NA	7-10 years	NA	NA	NA
Carbon capture	Multi steam (4)			£150k	NA	NA	7-10 years	NA	NA	NA
Main stack	Mercury	Semi continuous		£38k-£57k	NA	NA	5-10 years	3-6 months	£1k	£3k-£15k
Incineration	Long term dioxin	Semi continuous		£100k	NA	NA	7-10 years	NA	NA	£3k-£15k
Ammonia slip for SCR	NH ₃	TDLA	None	£25k	Purge	£2k	10-15 years	6 months	£2k	£3k
3) For single com	ponent: Dust				Initial costs	Lifetiı	ne	Annual	Periodic	
Typical application	Compound(s) to be measured	Instrument technology	Approvals and certification range	Instrument purchase ex works	Any significant option	Price of significant options	Typical life of instrument	Period between calibration	service contracts	manual sampling costs
Incinerator/cement kiln	Particulate	In situ scatter probe	MCERTS/TUV 0-15 0- 100 mg/m ³	£8.5k including blower	Extended probe length	£1k	10 years	12 months	£2k	£1.5k
Combustion plant and large stack with electrostatic precipitator	Particulate	Cross stack: transmission	MCERTS/TUV 0-150 mg/m ³	£7.5k and £1k blower	NA	NA	10 years	12 months	£2k	£1.5k
Combustion plant with dry FGD	Particulate	In situ back scatter	0-50 mg/m ³	£6k and £1k blower	NA	NA	10 years	12 months	£2k	£1.5k
Stack with wet collector (e.g. wet FDD, lime kiln)	Particulate	Extractive system with heating chamber and scatter probe	TUV 0-15 mg/m ³	£32k (complete system including blower)	Corrosion resistance against SO ₂	£10k	10 years	12 months	£7k	£1.5k
Large stack	Particulate	In situ laser/scatter light	MCERTS	£8k-12k	Dual range	£5k-8k	5-15 years	3-6 months	NA	£2k
Stack with bag filter (e.g. steel, non- ferrous, chemical industries)	Particulate	In situ probe electrification	MCERTS/TUV 0-15 mg/m ³	£6k	Additional sensors for multiple stack applications	£4k	10 years	12 months	£1.4k	£1.5k
Dust monitoring in explosive zone	Particulate	In situ scatter probe	MCERTS/TUV ATEX category 1, 2, 3	£9.5k	NA	NA	10 years	12 months	£1.4k	£2k
	N)`								
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4) Single compone	ent: Filter leak				Initial costs	Lifetin	ne	Annual	Periodic	
Typical application	Compound(s) to be measured	asured Instrument technology Approvals and Instrument certification range works Approvals and Instrument purchase ex works		Any significant option	Any significant option Price of significant options		Period between calibration	service contracts	manual sampling costs	
Leak of bag filter in all industries	Filter leak	<i>In situ</i> probe electrification	TUV EN 15859	£3k	250- 800 °C operating range (for ceramic filters)	£1k	10 years	12 months	£0.7k	Not required
Leak of compartment in multichamber bag filter	Chamber leak	<i>In situ</i> probe electrification		£1.5k	£1.5k NA NA 10 years 12 months		£0.6k	Not required		
5) Single compone	ent: Flow rate				Initial costs		Lifetin	ne	Annual	Periodic
Typical application	Compound(s) to be measured	Instrument technology	Approvals and certification range	Instrument purchase	Any significant option	Price of significant options	Typical life of instrument	Fypical life of instrumentPeriod between calibration		manual sampling costs
Coal-fired power plant and large stacks	Flow	Cross stack ultrasonic	MCERTS	£15k	NA	NA	NA	NA	NA	£1k-£3k
		Averaging pitot	MCERTS	£10k-£15k	NA	NA	NA	NA	NA	£1k-£3k
	Flow	Probe ultrasonic	MCERTS/TUV	£5k-12k	NA	NA	NA	NA	NA	£1k-£3k
Point measurement		Thermal mass	MCERTS/TUV	£5k	NA	NA	NA	NA	NA	£1k-£3k
for smaller stacks	1°10 w	Pitot	MCERTS/TUV	£3k	Purging if high dust	£2k	NA	NA	NA	£1k-£3k
		Vane anemometer	MCERTS/TUV	£4k	NA	NA	NA	NA	NA	£1k-£3k
6) Data Acquisitio	n:				Initial costs		Lifetiı	ne	Annual	Periodic
Typical application	Compound(s) to be measured	Instrument technology	Approvals and certification range	Instrument purchase	Any significant option	Price of significant options	Typical life of instrument	Period between calibration	service contracts	manual sampling costs
DAHS for AMS	DAHS	Data recording	MCERTS	£10k-£20k	Annual licence, no of pollutants to be recorded	£3.5k	NA	NA	NA	NA
DAHS for particulate	Particulate	Recording from multiple dust monitors	MCERTS/TUV	£1k-£5k	NA	NA	3-10 years	3-6 months	NA	NA
NA: No information ava	ailable	`		r .					· ·	· · · ·

Source: This survey was conducted by the UK Source Testing Association, www.s-t-a.org, whose members comprise Test Laboratories, Process Operators, Instrument Manufacturers and Regulators – December 2012 *Costs:* Costs are given as 1 000 £. In December 2012, 1 £ was equivalent to 1.20 – 1.25 Euros.

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Table 6.6: Periodic stack emission monitoring costs for sites regulated under the IED

		Costs	
Compound(s)	Single test	Triplicate tests	QAL2
Particulate EN 1384-1	£0.6k -£3k	£1k-£4k	£5k-£15k
Combustion gases EN 14789, EN 14790, EN 14791, EN 14792 and EN 15058	Add up to £3k	Add up to £1-£4k	Add up to £5k
TVOC EN 1219	Add up to £2k	Add up to £1k-£4k	Add up to £5k
HCI EN 1911	Add up to £2k	Add up to £1k to £4k	Add up to £5k
Dioxins EN 1948	Add up to £3k	Add up to £3k-£6k	NA
Metals EN 14385	Add up to £3k	Add up to £3k-£5k	NA

NA: No information available

Source: This survey was conducted by the UK Source Testing Association, www.s-t-a.org, whose members comprise Test Laboratories, Process Operators, Instrument Manufacturers and Regulators – December 2012.

The costs are based on a test site that is within 100 miles of the monitoring organisation's main office/laboratory. The cost of particulate test(s) includes all the travel and set up costs. Each subsequent compound is in addition to the particulate test(s).

Costs: Costs are given as 1 000 £. In December 2012, 1 £ was equivalent to 1.20 - 1.25 Euros

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A.6. Examples for the calculation of flow-weighted average concentrations and the specific load in waste water (see Section 4.3.2.6)

Date	Flow rate (daily)	Production (daily)	COD concentration (daily average)	COD specific load (daily average)
	\mathbf{q}_{i}	p_{i}	c _i	$l_{specific} = \frac{\sum_{i=1}^{n} \frac{c_i q_i}{p_i}}{n}$
	[m ³]	[t]	[mg/l]	[kg/t]
01/03/2011	7 950	1 530	269	1,40
02/03/2011	8 503	1 4 3 2	265	1.57
03/03/2011	7 364	1516	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 2 2 8	1 546	254	1.35
22/03/2011	7 095	1 527	248	1.15
23/03/2011	8 0 2 6	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 1 5 6	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 1 4 1	1 520	245	1.31
Monthl (wei	ly average ighted)	$c_w = \frac{\sum_{i=1}^n c_i q_i}{\sum_{i=1}^n q_i}$	244	38.59
Monthl (not w	ly average veighted)		244	

 Table 6.7:
 Calculation of monthly averages for a parameter measured daily - flow-weighted average concentrations and specific load for COD for a month with relatively stable flow rates

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Table 6.8:Calculation of monthly averages for a parameter measured daily - flow-weighted
average concentrations 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	Pi	Ci		$l_{specific} = \frac{\sum_{i=1}^{n} \frac{C_i q_i}{p_i}}{n}$, S
	[m ³]	[t]	[mg/l]		[kg/t]	
01/05/2011	7 6 5 6	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 0 3 8	1 345	219		1.31	
07/05/2011	7 275	1 585	233		1.07	
08/05/2011	8 0 2 8	1 224	244		1.60	
09/05/2011	8012	1 291	235		1.46	
10/05/2011	6453	1 465	235		1.03	
11/05/2011	8 566	1 4 3 4	232		1.39	
12/05/2011	8 0 8 5	1 478	276		1.51	
13/05/2011	7 1 4 1	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	6904	1 071	184	_	1.19	
21/05/2011	6172	1454	189		0.80	
22/05/2011	7 242	1 422	194		0.99	
23/05/2011	6585	1 504	201		0.88	
24/05/2011	7083	1536	217	-	1.00	
25/05/2011	7 0 6 8	1 294	230		1.26	
26/05/2011	/ 30/	1 554	229		1.08	
27/05/2011	65//	1 504	224		0.98	
28/05/2011	(717	1 460	241		1.18	
29/05/2011	0/1/	1 5 3 0	239		1.05	
30/05/2011	7449	1 541	240	-	1.16	
31/05/2011	/ 069	1 325 n	251		1.34	
Monthly a (weight	verage ted)	$c_w = \frac{\sum_{i=1}^n c_i q_i}{\sum_{i=1}^n q_i}$	223		37.64	
Monthly a (not weig	verage (hted)		 219			

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Table 6.9: Calculation of averages of samples obtained during one year for a parameter measured periodically - flow-weighted average concentrations and specific load for AOX for relatively stable flow rates

Date	Flow rate (daily)	Production (daily)		AOX concentration		AOX Specific load
				(daily average)		(daily average)
						$\sum_{i=1}^{n} \frac{c_i q_i}{c_i q_i}$
	q_i	p_i		c _i		$\sum_{i=1}^{n} p_i$
						$l_{specific} = \frac{n}{n}$
	[m ³]	[t]		[mg/l]		[kg/t]
04/01/2011	7 857	1413		0.13		0.00072
11/01/2011	8 405	1 552		0.28		0.001 52
19/01/2011	7 445	1 378		0.24		0.001 30
27/01/2011	7 642	1 526		0.15		0.00075
02/02/2011	8 3 5 1	1 411		0.13		0.00077
10/02/2011	8 2 1 8	1 576		0.20		0.001 04
14/02/2011	6764	934		0.12		0.00087
20/02/2011	6517	1 393		0.14		0.00066
08/03/2011	7 035	1 508		0.22		0.00103
16/03/2011	7764	1575		0.35	P	0.00173
24/03/2011	/ 442	1 541		0.32		0.001.02
03/04/2011	0 141 7 /61	1 520		0.30		0.00193
12/04/2011	7401	1 4 2 4		0.24		0.00119
19/04/2011	8 3 3 1	1 388		0.10		0.00034
27/04/2011	8038	1 327		0.28		0.00170
05/05/2011	7 474	1534		0.06		0.00029
24/05/2011	7 083	1 536		0.68		0.00314
08/06/2011	7 493	1 366		0.24		0.001 32
16/06/2011	7 790	1 524		0.22		0.00112
24/06/2011	7 868	1 476		0.30		0.001 60
27/06/2011	7 873	1 554		0.18		0.00091
04/07/2011	8 2 5 8	1 581		0.21		0.001 10
12/07/2011	7.704	1 4 4 6		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	8512	1 498		0.23		0.00131
06/09/2011	7 527	1 397		0.32		0.00172
19/09/2011	/ 881	933		0.29		0.00245
04/10/2011	8 4 8 5	1 361		0.25		0.00136
11/10/2011	7 402	1 432		0.22		0.00113
25/10/2011	7 371	1 298		0.19		0.00097
02/11/2011	6873	1 565		0.20		0.00105
07/11/2011	7 858	1 537		0.25		0.00128
16/11/2011	8.591	1070		0.23		0.001 85
01/12/2011	8 3 1 8	1 550		0.34		0.001 82
07/12/2011	8418	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
Average of samples obtained during one year (weighted)		$c_w = \frac{\sum_{i=1}^n c_i q_i}{\sum_{i=1}^n q_i}$	_	0.24		0.001 33
Average of sam during o (not wei			0.24		I	

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Annexes

A.7. EN standards for sampling of waste water for biotesting and for toxicity tests in waste water

The toxicity tests and sampling procedures are standardised in EN, ISO or National standards applied in several Member States. The OECD also provides in 'OECD Guidelines for the Testing of Chemicals²¹⁴ tests to assess the effects on biotic system, including toxicity tests. In the following only the current (2013) EN standards are listed.

Sampling	Standard No	Title	5
Sampling	EN ISO 5667-3:2012	Water quality - Sampling - Part 3: Preservation and handling of water samples (ISO 5667-3:2012)	
Sampling	EN ISO 5667-16:1998	Water quality - Sampling - Part 16: Guidance on biotesting of samples (ISO 5667-16:1998)	
Test organism	Standard No	Title	
Bacteria	EN ISO 11348-1:2008	Water quality - Determination of the inhibitory effect of water samples on the light emission of <i>Vibrio fischeri</i> (Luminescent bacteria test) - Part 1: Method using freshly prepared bacteria (ISO 11348-1:2007)	
Bacteria	EN ISO 11348-2:2008	Water quality - Determination of the inhibitory effect of water samples on the light emission of <i>Vibrio fischeri</i> (Luminescent bacteria test) - Part 2: Method using liquid-dried bacteria (ISO 11348-2:2007)	
Bacteria	EN ISO 11348-3:2008	Water quality – Determination of the inhibitory effect of water samples on the light emission of <i>Vibrio fischeri</i> (Luminescent bacteria test) - Part 3: Method using freeze-dried bacteria (ISO 11348-3:2007)	
Bacteria	EN ISO 10712:1995	Water quality – <i>Pseudomonas putida</i> growth inhibition test (Pseudomonas cell multiplication inhibition test) (ISO 10712:1995)	
Microorganism	EN ISO 9509:2006	Water quality - Toxicity test for assessing the inhibition of nitrification of activated sludge microorganisms (ISO 9509:2006)	
Microorganism	EN ISO 8192:2007	Water quality - Test for inhibition of oxygen consumption by activated sludge for carbonaceous and ammonium oxidation (ISO 8192:2007)	
Algae	EN ISO 8692:2012	Water quality – Fresh water algal growth inhibition test with unicellular green algae (ISO 8692:2012)	
Algae	EN ISO 10253:2006	Water quality — Marine algal growth inhibition test with <i>Skeletonema costatum</i> and <i>Phaeodactylum tricornutum</i> (ISO 10253:2006)	
Algae	EN ISO 10710:2013	Water quality - Growth inhibition test with the marine and brackish water macroalga <i>Ceramium tenuicorne</i> (ISO 10710:2010)	

²¹⁴ OECD 2013 Guidelines for the Testing of Chemicals, Section 2 Effects on Biotic Systems <u>http://www.oecd-ilibrary.org/environment/oecd-guidelines-for-the-testing-of-chemicals-section-2-</u> <u>effects-on-biotic-systems_20745761</u>

Test organism Standard No		Title		
Higher plants	EN ISO 20079:2006	Water quality – Determination of the toxic effect of water constituents and waste water on duckweed (<i>Lemna minor</i>) – Duckweed growth inhibition test (ISO 20079:2005)		
Crustacean EN ISO 6341:2012;		Water quality – Determination of the inhibition of the mobility of <i>Daphnia magna Straus</i> (<i>Cladocera, Crustacea</i>) - Acute toxicity test (ISO 6341:2012)		
Fish eggs EN ISO 15088:2008		Water quality – Determination of the acute toxicity of waste water to zebrafish eggs (<i>Danio</i> <i>rerio</i>) (ISO 15088:2007)		
Fish	EN ISO 7346-1:1997	Water quality – Determination of the acute lethal toxicity of substances to a freshwater fish <i>Brachydanio rerio Hamilton-Buchanan</i> (<i>Teleostei, Cyprinidae</i>) - Part 1: Static method (ISO 7346-1:1996)		
Fish	EN ISO 7346-2:1997	Water quality - Determination of the acute lethal toxicity of substances to a freshwater fish (<i>Brachydanio rerio Hamilton-Buchanan</i> (Teleostei, Cyprinidae)) - Part 2: Semi-static method (ISO 7346-2:1996)		
Fish	EN ISO 7346-3:1997	Water quality - Determination of the acute lethal toxicity of substances to a freshwater fish (<i>Brachydanio rerio Hamilton-Buchanan</i> (Teleostei, Cyprinidae)) - Part 3: Flow-through method (ISO 7346- 3:1996)		

RAMCORAT

NORMAGORAFINAPROGRESS

GLOSSARY

AMS	Automated Measuring System	
AST	Annual Surveillance Test	
ATEY	Directive 94/9/EC on equipment and protective systems intended	
AILA	for use in potentially explosive atmospheres (ATEX)	
BAT	Best Available Technique	(
BAT-AEL	Best Available Technique-Associated Emission Level	
BREF	Best Available Techniques Reference Document	
CEN	European Committee for Standardisation	
CEN/TC	European Committee for Standardisation/Technical Committee	
CEN/TR	CEN Technical Report	
CEN/TS	CEN Technical Specification	
DAHS	Data Acquisition and Handling System	
DIAL	Differential Infrared Absorption LIDAR	
DOAS	Differential Optical Absorption Spectroscopy	
EA	European co-operation for Accreditation	
ECx	Effective Concentration	
EIPPCB	European Integrated Pollution Prevention and Control Bureau	
ELV	Emission Limit Value	
	European Monitoring Evaluation Programme/European	
EMEP/EEA	Environment Agency	
EN	European Standard	
EPA	Environment Protection Agency	
FGD	Flue-Gas Desulphurisation	
FID	Flame Ionization Detector	
FprEN	Final draft European pre-Standard	
FTIR	Fourier Transform Infrared Spectroscopy	
GUM	Guide to the expression of Uncertainty in Measurement	
IFC	International Electrotechnical Commission	
IEC	Industrial Emissions Directive	
ILD ID	InfraPad spectroscopy	
	International Organization for Standardization	
	Leek Detection and Renair Programme	
	Lowest Ineffective Dilution	
	Limit of Detection	
	Limit of Quantification	
MCERTS	Monitoring Certification Scheme	
MEG	Monitoring Export Group	
	NonDispersive InfraPad sensor	
NOC	NonDispersive initiated sensor	
	Normal Operating Condition	
	No Observed Effect Concentration	
	Optical Gas Imaging techniques	
UMA	Operator Monitoring Assessment	
UTNUC	Other Than Normal Operating Condition	
PR I	Persistency, Bioaccumulation, Toxicity	
prEN	European pre-Standard	
QAL	Quality Assurance Level	
RDM	Reverse Dispersion Modelling	
RM	Reference Method	
ROM	JRC Reference Report on Monitoring	
SCR	Selective Catalytic Reduction	
SOF	Solar Occultation Flux	
SRM	Standard Reference Method	

SRU	Sulphur Recovery Unit	
TDLA	Tunable Diode Laser Analyzer	
TU	Toxicity Unit	
TUV	TÜV Technischer Überwachungsverein (Technical inspection body)	
TWG	Technical working Group	
UBA	German Federal Environment Agency	
UV	UltraViolet spectroscopy	
VDI	The Association of German Engineers (Verein Deutscher	
VDI	Ingenieure)	
WEA	Whole Effluent Assessment	
WID	Waste Incineration Directive	
	MCDRAFT	

REFERENCES

Footnotes will be removed and converted to references according to the BREF format.