BS ISO 12039:2019

BSI Standards Publication

Stationary source emissions — Determination of the mass concentration of carbon monoxide, carbon dioxide and oxygen in flue gas — Performance characteristics of automated measuring systems

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National foreword

This British Standard is the UK implementation of ISO 12039:2019.

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Stationary source emissions — Determination of the mass concentration of carbon monoxide, carbon dioxide and oxygen in flue gas — Performance characteristics of automated measuring systems

Émissions de sources fixes — Détermination de la concentration de monoxyde de carbone, de dioxyde de carbone et d'oxygène — Caractéristiques de fonctionnement et étalonnage de systèmes automatiques de mesure

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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

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For an explanation on the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT) see the following URL: www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 146, *Air quality*, Subcommittee SC 1, *Stationary source emissions*.

This second edition cancels and replaces the first edition (ISO 12039:2001), which has been technically revised. The main changes compared to the previous edition are as follows:

— The structure and the components are changed to be similar to the latest ISO standards; ISO 17179 (measurement of NH_3), ISO 13199 (measurement of total VOC), ISO 25140 (measurement of CH_4), ISO 21258 (measurement of N_2O) and others.

— Addition or deletion and change in terms and definitions.

— Addition of a new analytical technique (tuneable laser spectroscopy) for in-situ measurement of CO, CO_2 and O_2

— The performance characteristics and criteria as well as QA/QC procedures are changed to harmonize with latest ISO standards.

— Examples of performance test results and the results of uncertainty calculation are shown for CO, CO_2 and O_2 measurement.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

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Introduction

Carbon monoxide, carbon dioxide, and oxygen are gases found in the exhaust gases of combustion processes. Determination of the concentration of these gases is necessary to demonstrate compliance with local regulations and can assist the operator in the optimization of the combustion process. The determination of O_2 and/or CO_2 is also necessary to normalize the measured concentration of other gases and dusts to defined conditions. There are a number of ways to measure concentrations of CO, CO_2 and O_2 in stacks/ducts.

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Stationary source emissions — Determination of the mass concentration of carbon monoxide, carbon dioxide and oxygen in flue gas — Performance characteristics of automated measuring systems

1 Scope

This document specifies the fundamental structure and the most important performance characteristics of automated measuring systems for carbon monoxide (CO), carbon dioxide (CO_2) and oxygen (O_2) to be used on stationary source emissions. This document describes methods and equipment for the measurement of concentrations of these gases.

The method allows continuous monitoring with permanently installed measuring systems of CO, CO_2 and O_2 emissions. This international standard describes extractive systems and in situ (non-extractive) systems in connection with analysers that operate using, for example, the following principles:

— infrared absorption (CO and CO_2);

— paramagnetism (O_2);

— zirconium oxide (O_2);

— electrochemical cell (O_2);

— tuneable laser spectroscopy (TLS) (CO, CO_2 and O_2).

Other instrumental methods can be used provided they meet the minimum requirements proposed in this document.

Automated measuring systems (AMS) based on the principles above have been used successfully in this application for measuring ranges which are described in Annex G.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 14956, *Air quality — Evaluation of the suitability of a measurement procedure by comparison with a required measurement uncertainty*

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

3.1
analyser
analytical part in an extractive or *in situ AMS* (3.3)

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3.2
automated measuring system
AMS
measuring system interacting with the flue gas under investigation, returning an output signal proportional to the physical unit of the *measurand* (3.8) in unattended operation

[SOURCE: ISO 9169:2006, 2.1.2 modified]

Note 1 to entry: In the sense of this document, an AMS is a system that can be attached to a duct or stack to continuously or intermittently measure the mass concentration of CO, CO_2 and O_2 passing through the duct.

3.3
in situ AMS
non-extractive systems that measure the concentration directly in the duct or stack

Note 1 to entry: In situ systems measure either across the stack or duct or at a point within the duct or stack.

3.4
parallel measurements
measurements taken on the same duct in the same sampling plane for the same period of time with the *AMS* (3.2) under test and with the *reference method* (3.12) at points a short distance from each other, providing pairs of measured values

3.5
interference
cross-sensitivity
negative or positive effect upon the response of the measuring system, due to a component of the sample that is not the *measurand* (3.8)

3.6
interferent
interfering substance
substance present in the air mass under investigation, other than the *measurand* (3.8), that affects the response of *AMS* (3.2)

3.7
lack-of-fit
systematic deviation within the range of application between the measurement results obtained by applying the calibration function to the observed response of the measuring system, measuring *reference materials* (3.11) and the corresponding accepted value of such *reference materials* (3.11)

Note 1 to entry: Lack-of-fit may be a function of the measurement result.

Note 2 to entry: The expression “lack-of-fit” is often replaced in everyday language for linear relations by “linearity” or “deviation from linearity”.

[SOURCE: ISO 9169:2006, 2.2.9]

3.8
measurand
particular quantity subject to measurement

[SOURCE: ISO/IEC Guide 98 3:2008, B.2.9, modified — Example and Note removed.]

3.9
performance characteristic
one of the quantities assigned to equipment in order to define its performance

Note 1 to entry: Performance characteristics can be described by values, tolerances, or ranges.

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3.10
period of unattended operation
maximum interval of time for which the *performance characteristics* (3.9) remain within a predefined range without external servicing, e.g. refill, adjustment

[SOURCE: ISO 9169:2006, 2.2.11]

Note 1 to entry: The period of unattended operation is often called maintenance interval.

3.11
reference material
substance or mixture of substances with a known concentration within specified limits, or a device of known characteristics

Note 1 to entry: Normally calibration gases, gas cells, gratings or filters are used.

[SOURCE: ISO 14385-1:2014]

3.12
reference method
measurement method taken as a reference by convention, which gives the accepted reference value of the *measurand* (3.8)

3.13
transport time
<measuring system> time period for transportation of the sampled gas from the inlet of the probe to the inlet of the measurement instrument

3.14
response time
time interval between the instant when a stimulus is subjected to bring about a specified abrupt change and the instant when the response reaches and remains within specified limits around its final stable value, determined as the sum of the lag time and the rise time in the rising mode, and the sum of the lag time and the fall time in the falling mode

[SOURCE: ISO 9169:2006, 2.2.4]

Note 1 to entry: Lag time, rise time and fall time are defined in ISO 9169:2006.

3.15
span gas
gas or gas mixture used to adjust and check the span point on the response line of the measuring system

Note 1 to entry: This concentration is often chosen around 70 % to 90 % of full scale.

3.16
span point
value of the output quantity (measured signal) of the *automated measuring system* (3.2) for the purpose of calibration, adjustment, etc. that represents a correct measured value generated by reference gas

3.17
standard uncertainty
uncertainty (3.18) of the result of a measurement expressed as a standard deviation

[SOURCE: ISO/IEC Guide 98 3:2008, 2.3.1]

3.18
uncertainty (of measurement)
parameter associated with the result of a measurement, that characterizes the dispersion of the values that could reasonably be attributed to the *measurand* (3.8)

[SOURCE: ISO/IEC Guide 98 3:2008, 2.2.3, modified — Note 1,2 and 3 removed.]

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3.19
validation of automated measuring system
procedure to check the statistical relationship between values of the *measurand* (3.8) indicated by the *automated measuring system* (3.2) and the corresponding values given by *parallel measurements* (3.4) implemented simultaneously at the same measuring point

3.20
zero gas
gas or gas mixture used to establish the *zero point* (3.21) on a calibration curve within a given concentration range

3.21
zero point
specified value of the output quantity (measured signal) of the *AMS* (3.2) and which, in the absence of the measured component, represents the zero crossing of the calibration line. In case of O_2 monitoring *AMS* (3.2), the zero point is interpreted as the lowest measurable value.

4 Symbols and abbreviated terms

e_i	Residual (lack-of-fit) at level *i*
K	Coverage factor
N	Number of measurements
s_r	Standard deviation of repeatability
$u(\gamma_X)$	Combined uncertainty of *X* (CO, CO_2 or O_2) mass concentration
$U(\gamma_X)$	Expanded uncertainty of *X* (CO, CO_2 or O_2) mass concentration
M_x	Molar mass of *X* (CO, CO_2 or O_2, g/mol)
V_M	Molar volume (22,4 l/mol at standard conditions)
φ_X	Volume fraction of *X* (CO, CO_2 or O_2)
γ_X	*X* (CO, CO_2 or O_2) mass concentration in mg/m^3
γ_s	CO, CO_2 or O_2 mass concentration at standard conditions in mg/m^3 (273,15 K; 101,325 kPa)
γ_R	CO, CO_2 or O_2 mass concentration at reference conditions in mg/m^3 (273,15 K; 101,325 kPa; H_2O corrected)
$\bar{x}$	Average of the measured values x_i
x_i	*i*th measured value
$\bar{x}_i$	Average of the measured value at level i
$\dot{x}_i$	Value estimated by the regression line at level i
AMS	Automated measuring system
FTIR	Fourier transform infrared
GFC	Gas filter correlation

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NDIR	Non-dispersive infrared
QA	Quality assurance
QC	Quality control
TLS	Tuneable laser spectroscopy

5 Principle

This document describes automated measurement systems for sampling, sample conditioning, and determining CO, CO_2 and O_2 content in flue gas using instrumental methods (analysers).

There are two types of automated measuring systems:

— extractive systems;

— in situ systems.

With extractive systems, the representative gas sample is taken from the stack with a sampling probe and conveyed to the analyser through the sampling line and sample gas conditioning system.

In situ systems do not require any sample processing. For the installation of these systems, a representative place in the stack is to be chosen.

The systems described in this document measure CO, CO_2 and O_2 concentrations using instrumental methods that shall meet the minimum performance specifications given.

This document specifies performance characteristics and criteria for AMS.

6 Description of the automated measuring systems

6.1 Sampling and sample gas conditioning systems

Sampling and sample gas conditioning systems for extractive and in situ methods shall conform to ISO 10396.

In extractive sampling, these gases are conditioned to remove aerosols, particulate matter and other interfering substances before being conveyed to the instruments. Three kinds of extractive systems:

a) Cold-dry,

b) Hot-wet, and

c) Dilution,

as well as non-extractive systems, are described in ISO 10396. In non-extractive sampling, the measurements are made in situ; therefore, no sample conditioning other than filtering of filterable materials at the probe tip is required.

The details of the extractive sampling and sample gas conditioning systems as well as analyser equipment are described in Annex A and Annex B. In Annex C, two kinds of in situ systems are illustrated.

6.2 Analyser equipment

Examples of the typical analytical methods available are described in the Annex A, Annex B and Annex C.

AMS shall meet the performance characteristics described in Clause 7.

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7 Performance characteristics and criteria

7.1 Performance criteria

Table 1 gives the performance characteristics and performance criteria of the analyser and measurement system to be evaluated during performance tests, by means of ongoing QA/QC in the laboratory and during field operation. Test procedures for the performance test are specified in Annex E.

Table 1 — Performance characteristics and criteria of AMS for measurement of CO, CO_2 and O_2

Performance characteristic	Performance criterion		Test procedure
	CO and CO_2	O_2	
Response time	≤200 s	≤200 s	E.2
Standard deviation of repeatability at zero point	≤2,0 % of the upper limit of the lowest measuring range used[a]	≤0,2 % for O_2 volume concentration[b]	E.3.2
Standard deviation of repeatability at span point	≤2,0 % of the upper limit of the lowest measuring range used	≤0,2 % for O_2 volume concentration	E.3.3
Lack-of-fit (linearity)	≤2,0 % of the upper limit of the lowest measuring range used	≤0,2 % for O_2 volume concentration	E.4
Zero drift within 24 h	≤2,0 % of the upper limit of the lowest measuring range used	≤0,2 % for O_2 volume concentration	E.8
Span drift within 24 h	≤2,0 % of the upper limit of the lowest measuring range used	≤0,2 % for O_2 volume concentration	E.8
Zero drift within the period of unattended operation	≤3,0 % of the upper limit of the lowest measuring range used	≤0,2 % for O_2 volume concentration	E.9
Span drift within the period of unattended operation	≤3,0 % of the upper limit of the lowest measuring range used	≤0,2 % for O_2 volume concentration	E.9
Sensitivity to sample gas pressure, for a pressure change of 2 kPa	≤3,0 % of the upper limit of the lowest measuring range used	≤0,2 % for O_2 volume concentration	E.11
Sensitivity to sample gas flow for extractive AMS	≤2,0 % of the upper limit of the lowest measuring range used	≤0,2 % for O_2 volume concentration	E.12
Sensitivity to ambient temperature, for a change of 10 K in the temperature range specified by the manufacturer	≤3,0 % of the upper limit of the lowest measuring range used	≤0,3 % for O_2 volume concentration	E.13

[a] Percentage value as percentage of the upper limit of the lowest measuring range used.

[b] Percentage value as oxygen volume concentration (volume fraction).

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Table 1 *(continued)*

Performance characteristic	Performance criterion		Test procedure
	CO and CO_2	O_2	
Sensitivity to electric voltage in the voltage range specified by the manufacturer	≤2,0 % of the upper limit of the lowest measuring range used per 10V	≤0,2% for O_2 volume concentration	E.14
Cross-sensitivity	≤4,0 % of the upper limit of the lowest measuring range used	≤0,4 % for O_2 volume concentration	E.5
Losses and leakage in the sampling line and conditioning system	≤2,0 % of the measured value		E.6 for loss and E.7 for leakage
Excursion of the measurement beam of cross-stack in situ AMS	≤2,0 % of the measured value of the lowest measuring range used		E.10

[a] Percentage value as percentage of the upper limit of the lowest measuring range used.

[b] Percentage value as oxygen volume concentration (volume fraction).

The measuring range is defined by two values of the measurand, or quantity to be supplied, within which the limits of uncertainty of the measuring instrument are specified. The upper limit of the lowest measuring range used should be set suitable to the application such that the measurement values lie within 20 % to 80 % of the measuring range.

7.2 Determination of the performance characteristics

7.2.1 Performance test

The performance characteristics of the AMS shall be determined during the performance tests described in Annex E. The values of the performance characteristics determined shall meet the performance criteria specified in Table 1.

The ambient conditions applied during the performance tests shall be documented.

The measurement uncertainty of the AMS measured values shall be calculated in accordance with ISO 14956 on the basis of the performance characteristics determined during the performance test and shall meet the level of uncertainty appropriate for the intended use. These characteristics may be determined either by the manufacturer or by the user.

7.2.2 Ongoing quality control

The user shall check specific performance characteristics during ongoing operation of the measuring system with a periodicity specified in Table 2.

The measurement uncertainty during field application shall be determined by the user of the measuring system in accordance with applicable international or national standards. For process monitoring (non-regulatory application), the level of uncertainty shall be appropriate for the intended use. It can be determined by a direct or an indirect approach for uncertainty estimation as described in ISO 20988. The uncertainty of the measured values under field operation is not only influenced by the performance characteristics of the analyser itself but also by uncertainty contributions due to:

— the sampling line and conditioning system,

— the site-specific conditions, and

— the calibration gases used.

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8 Selection and installation procedure

8.1 Choice of the measuring system

To choose an appropriate analyser, sampling line and conditioning unit, the following characteristics of flue gases should be known before the field operation:

— ambient temperature range;

— temperature range of the flue gas;

— water vapour content of the flue gas;

— dust loading of the gases;

— expected concentration range of CO, CO_2 and O_2;

— expected concentration of potentially interfering substances;

To avoid long response time and memory effects, the sampling line should be as short as possible. If necessary, a bypass pump should be used. If there is a high dust loading in the sample gas, an appropriate heated filter shall be used.

Before monitoring emissions, the user shall verify that the necessary QA/QC procedures have been performed.

NOTE Information on QA/QC procedures is provided in ISO 14385-1 and ISO 14385-2.

8.2 Sampling

8.2.1 Sampling location

The sampling site shall be in an accessible location where a representative measurement can be made. In addition, the sampling location shall be chosen with regard to safety of the personnel.

8.2.2 Representative sampling

It is necessary to ensure that the gas concentrations measured are representative of the average conditions inside the flue gas duct.

NOTE The selection of sampling points for representative sampling is described e.g. in ISO 10396, where gas stratification, fluctuations in gas velocity, temperature and others are mentioned.

8.3 Calculation

8.3.1 Conversion from volume to mass concentration for CO

Results of the measurement for CO shall be expressed as mass concentrations at reference conditions.

If the CO concentration is provided as a volume fraction, Formula (1) shall be used to convert volume fraction of CO (10^{-6}), ϕ_{CO}, to CO mass concentrations, γ_{CO}:

$$\gamma_{CO} = \varphi_{CO} \cdot M_{CO} / V_M \tag{1}$$

where

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γ_{CO} is the CO mass concentration in mg/m^3;

φ_{CO} is the volume fraction of CO (by volume, 10^{-6});

M_{CO} is the molar mass of CO (=28,010 g/mol);

V_M is the molar volume (= 22,4 l/mol at standard conditions).

8.3.2 Conversion from wet to dry conditions for CO, CO_2 and O_2 concentrations

The CO concentration measured in the wet gas shall be corrected to the CO concentration at standard conditions, using Formula (2):

$$\gamma_s = \gamma_{CO} \cdot \frac{T}{273,15} \cdot \frac{101,325}{101,325 + p} \tag{2}$$

where

γ_{CO} is the CO mass concentration measured in the wet gas (mg/m^3);

γ_s is the CO mass concentration in the wet gas at standard conditions in mg/m^3 (273,15 K; 101,325 kPa);

T is the temperature (K);

p is the difference between the static pressure of the sample gas and the standard pressure (kPa).

If necessary, the CO concentration measured in the wet gas should be corrected to the CO concentration at reference conditions (dry gas), using Formula (3):

$$\gamma_r = \gamma_{CO} \cdot \frac{T}{273,15} \cdot \frac{101,325}{101,325 + p} \cdot \frac{100\ \%}{100\ \% - h} \tag{3}$$

where

γ_{CO} is the CO mass concentration measured in the wet gas (mg/m^3);

γ_r is the CO mass concentration at reference conditions in mg/m^3 (273,15 K; 101,325 kPa; H_2O corrected);

T is the temperature (K);

p is the difference between the static pressure of the sample gas and the standard pressure (kPa);

h is the absolute water vapour content (volume fraction) (%).

The concentration of CO_2 or O_2 measured in the wet gas can be corrected to the CO_2 or O_2 concentration at reference conditions (dry gas), by using the Formula (3) by substituting CO_2 or O_2 for γ_{CO}.

9 Quality assurance and quality control procedures

9.1 General

Quality assurance and quality control (QA/QC) are important in order to ensure that the uncertainty of the measured values for CO, CO_2 and O_2 is kept within the limits specified for the measurement task. The results of the QA/QC procedures shall be documented.

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9.2 Frequency of checks

AMS shall be adjusted and checked after the installation and then during continuous operation. Table 2 shows the minimum required test procedures and frequency of checks. The user shall implement the relevant procedures for determination of performance characteristics or procedures described in this paragraph and Annex E. The results of the QA/QC procedures shall be documented.

Table 2 — Minimum checks and minimum frequency of checks for QA/QC during the operation

Check	Minimum frequency for permanently installed AMS	Test procedure
Response time	Once a year	E.2
Standard deviation of repeatability at zero point	Once a year	E.3.2
Standard deviation of repeatability at span point	Once a year	E.3.3
Lack-of-fit	Once a year and after any major changes or repair to the AMS, which will influence the results obtained significantly	E.4
Sampling system and leakage check	Once a year or after any major changes or repair to the sampling system	E.7
Beam alignment (in situ AMS only)	Once a year	According to manufacturer's manual
Light intensity attenuation through cleanliness and dust load (in situ AMS only)	According to manufacturer's requirements	According to manufacturer's manual
Cleaning or changing of particulate filters at the sampling inlet and at the monitor inlet	The particulate filters shall be changed periodically depending on the dust load at the sampling site. During this filter change the filter housing shall be cleaned.	According to manufacturer's manual
Zero drift[a]	Once in the period of unattended operation or period specified by national standards	E.8
Span drift[a]	Once in the period of unattended operation or period specified by national standards	E.8
Regular maintenance of the analyser	According to manufacturer's requirements	According to manufacturer's manual

[a] Analysers can be checked with internal gas cells or optical filters for this determination.

The user shall implement a procedure to guarantee that the reference materials used meet the uncertainty requirement specified in Annex E, e.g. by comparison with a reference gas of higher quality.

9.3 Calibration, validation and measurement uncertainty

The calibration and validation of the AMS shall be performed annually and after repair of the analyser in accordance with applicable national or international standards.

Permanently installed AMS for continuous monitoring shall be calibrated by comparison with

a) an independent method of measurement, or

b) a certified reference material.

In either case, the validation shall include the determination of uncertainty of the measured value obtained by calibrating the AMS. The AMS shall be subject to adjustments and functional tests according

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to 9.2 before each calibration. This ensures that the measurement uncertainty is representative of the application at the specific plant.

The validation shall include the determination of the uncertainty of measured values obtained by comparison between reference gas or reference material with the AMS.

NOTE The determination of the uncertainty of measured values obtained by permanently installed AMS for continuous monitoring on the basis of a comparison with an independent method of measurement is described, e.g. in ISO 20988.

The uncertainty of the measured values shall meet the uncertainty criterion specified for the measurement objective.

10 Test report

It is presupposed that the test report satisfies applicable legal requirements. If not specified otherwise, it shall include at least the following information:

a) a reference to this document, e.g. ISO 12039:2019;

b) a description of the measurement objective;

c) the principle of gas sampling;

d) information about the analyser and description of the sampling and conditioning line;

e) identification of the analyser used, and the performance characteristics of the analyser, listed in Table 1;

f) operating range;

g) sample gas temperature, sample gas pressure and optical path length through an optical cell (it is needed for only in situ measurement);

h) details of the quality and the concentration of the span gases used;

i) description of plant and process;

j) the identification of the sampling plane;

k) the actions taken to achieve representative samples;

l) a description of the location of the sampling point(s) in the sampling plane;

m) a description of the operating conditions of the plant process;

n) the changes in the plant operations during sampling;

o) the sampling date, time, and duration;

p) the time averaging on relevant periods;

q) the measured values;

r) the measurement uncertainty;

s) the results of any checks;

t) any deviations from this document.

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