Performance Standards for Open Path Ambient Air Quality Monitoring Systems using Differential Optical Absorption Spectrometry (DOAS) and FTIR Spectroscopy

Environment Agency

Version 3

August 2017

MCERTS
THE ENVIRONMENT AGENCY'S MONITORING CERTIFICATION SCHEME

Foreword

The Environment Agency (the Agency) has established its Monitoring Certification Scheme MCERTS to deliver quality environmental measurements. The scheme is based on international standards and provides for the product certification of instruments, the competency certification of personnel and the accreditation of laboratories.

MCERTS performance standards are available for continuous ambient air quality monitoring systems (CAMS)[(1)]. This document builds on these by providing the performance standards for open path ambient air-quality monitoring systems (OPAMs) using differential optical absorption spectrometry (DOAS) and FTIR spectroscopy.

The MCERTS instrument performance standards described in this document are based on relevant sections of a number of international ISO and CEN standards. Close links have also been established with the CEN technical committee working group currently developing new standard on open path ambient air pollution monitoring. The typical applications covered include nitrogen monoxide (NO), nitrogen dioxide (NO_2), sulphur dioxide (SO_2), ozone (O_3), ammonia, formaldehyde, benzene, toluene, xylenes and methane for DOAS systems and methane, ethene, propene, ethane, benzene, toluene, m-xylene, p-xylene, o-xylene, carbon monoxide (CO), nitrous oxide, ammonia, formaldehyde, isobutene and 1,3- butadiene for FTIR systems. This list of applications is not exhaustive and many other gases can be measured. Specific other applications and the associated criteria are determined in each case by the Certification Committee.

MCERTS is a formal product certification scheme operating under the requirements of European Standard EN ISO/IEC 17065. Sira, the certification body in this document, runs this scheme for us.

The benefits of MCERTS are that it:

- makes available a certification scheme that is formally recognised within the UK and is accepted internationally
- gives confidence to regulatory authorities that instrumentation, once certified, is fit for purpose and capable of producing results of the required quality and reliability
- gives confidence to users of monitoring equipment that the instrumentation selected is robust and conforms to performance standards that are accepted by UK regulatory authorities
- supports the supply of accurate and reliable data to the public
- provides the instrument manufacturing companies with an independent authoritative endorsement of their products, which will facilitate their access to international markets and increase the take-up of their products in the UK

Laboratory and field testing under MCERTS must be carried out by laboratories and test organisations that are accredited to BS EN ISO IEC 17025 to carry out the MCERTS tests. The evaluation of the results obtained during the laboratory and field tests is carried out by Sira Certification Services of the CSA Group, using a group of independent experts known as the Certification Committee.

If you have any questions about the certification process or would like further information on how to make an application, please contact:

CSA Group Testing UK Ltd Tel: 01244 670900

Sira Certification Service

Unit 6 Hawarden Industrial Park

Hawarden, CH5 3US, United Kingdom

Email: mcerts@csagroup.com

Feedback

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

Email: enquiries@environment-agency.gov.uk

For more information on MCERTS and for copies of the performance standards and further guidance, see our website at:

www.mcerts.net

Contents

Record of amendments

Version number	Date	Amendment
2	Dec 2010	Minor updates of the performance standards and removal of CO from DOAS specification.
2	Dec 2010	Updating of the EU legislative references. Addition of the FTIR open-path instrumentation requirements.
3	Aug 2017	Minor update to provide for changes in standards and associated legislation for products.

This MCERTS document may be subject to review and amendment following publication. The latest version can be found on our website at www.mcerts.net

MCERTS performance standards for open path air quality monitoring systems

1. Introduction

1.1 The Environment Agency has established its Monitoring Certification Scheme MCERTS to promote quality monitoring based on international standards.

1.2 MCERTS performance standards are available for continuous ambient air quality monitoring systems (CAMS) [(1).]

1.3 This document builds on these by providing the performance standards for open path ambient air-quality monitoring systems (OPAMs). OPAMs are instrumental systems that continuously monitor ambient pollutant concentrations over an open path and automatically produce results.

1.4 OPAMs covered by these MCERTS performance standards operate on two different principles:

DOAS (differential optical absorption spectrometry) measures the concentration of gaseous pollutants by using their characteristic absorption of electromagnetic radiation. The radiation spectrum analysed for this purpose ranges from near ultraviolet to near infrared (250 nm to 2500 nm). Reference spectra are fitted to the measured spectra by the least squares method. Superimposed absorption structures of multiple constituents can be separated.

FTIR (Fourier transform infrared) spectroscopy is based on measurement of long path absorption of infrared radiation between an artificial source and an infrared spectrometer and calculation of the integrated concentration. By performing a Fourier transform of the interferogram across a wide range of wavelengths a spectrum is obtained that is characteristic of the gases within the monitoring path.

1.5 The following air pollutants are covered by this standard: nitrogen monoxide (NO), nitrogen dioxide (NO_2), sulphur dioxide (SO_2), ozone (O_3), ammonia, formaldehyde, benzene, toluene, xylene, and methane for DOAS, and methane, ethene, propene, ethane, benzene, toluene, m-xylene, p-xylene, o-xylene, carbon monoxide, nitrous oxide, ammonia, formaldehyde, isobutene and 1,3-butadiene for FTIR. Many other gases can also be measured.

1.6 EN reference methods for gaseous ambient pollutants specify testing procedures and performance criteria. Individual performance characteristics which contribute to the combined uncertainty of the method are defined. The EN standards also provide procedures to determine the expanded uncertainty of the method from individual performance criteria. To ensure consistency of approach and comparability of the test results non-reference methods such as OPAMs are treated as “ black box” systems and the same criteria, testing methodologies and uncertainty calculations are applied following the procedures specified in the Guide to the demonstration of equivalence of ambient air monitoring methods[(7)].

1.7 Therefore main instrument performance characteristics against which OPAMs will be assessed by a combination of laboratory and field testing are:

Laboratory tests

- response time
- laboratory repeatability standard deviation, detection limit
- short term zero and span drift
- averaging of short term fluctuations in measurand concentrations;
- linear fit
- cross-sensitivity to interfering substances
- influence of surrounding air temperature and pressure
- effect of supply voltage variations
- susceptibility to physical disturbances (where required)
- assessment of maximum path length for equivalence with a point analyser (based on the existing comparative studies)

Field tests

- field performance of two identical OPAMs analysers against the relevant standard method (if applicable) to determine whether systematic differences occur in the measured results
- field repeatability of two OPAMs analysers
- long-term zero and span drift
- availability (maintenance interval)

The definitions of the performance characteristics (and other terms used in this document) are given in Section 4.

1.8 The general requirements and the performance standards to be met by OPAMs are presented in this document in Sections 5 and 6, respectively. The main published and draft international and national standards on which these performance standards are based are presented in Appendix 1.

1.9 The MCERTS performance standards have been defined so that MCERTS-certified OPAMs operating over a specified maximum path length will be capable of meeting the requirements of the Directive 2008/50/EC of the European Parliament and of the Council of 21 May 2008 an Ambient Air Quality and Cleaner Air for Europe (2). Total allowable uncertainties at the specified limit values for instruments monitoring regulated air pollutants are now published in the new EC Air Quality Directive(2). These uncertainties specified as data quality objectives are given in Table 1.1. Compliance with the data quality objectives for regulated pollutants is mandatory and recommended as targets for unregulated pollutants. The Ambient Air Quality CEN Standards define the standard reference methods for monitoring of the pollutants covered by the Directive.

Table 1.1 Data quality objectives for ambient air quality assessment

Parameter	Sulphur dioxide, nitrogen dioxide, and carbon monoxide	Benzene	Ozone and related NO and NO_2
Fixed measurements			
Uncertainty	15%	25 %	15%
Minimum data capture	90%	90%	90%
Minimum time coverage			
-urban background and traffic	N/A	35%	N/A
- industrial sites	N/A	90%	N/A
Indicative measurements			
Uncertainty	25%	30%	30%
Minimum data capture	90%	90%	90%
Minimum time coverage	14%	14%	> 10% during summer

1.10 Two EN standards provide procedures and guidance on the use of DOAS and FTIR-based systems for monitoring campaigns. These two standards are BS EN 16253 for DOAS and BS EN 15483 for FTIR (see Appendix 1).

1.11 Throughout this document the terms “MCERTS certificate” and “certificate” refer to the MCERTS product-conformity certificate.

2. European Union and United Kingdom legislative requirements for continuous ambient air-quality monitors

2.1 Air quality limit values

2.1.1 Tables 2.1a and 2.1b give the standards from the Air Quality Standards Regulations and the European Union air-quality limit values in absolute concentration units. The EU limit values are, in general, very similar to the concentrations given in the Air Quality Standards Regulations (3). The limit values used to derive the performance characteristics specified in this document are given in Table 2.2. EU limit values have been chosen where these are available.

2.1.2 Where certification of an OPAM is required in scenarios where no limit value is specified, 80% of the certification range shall be used as the value at which the performance characteristics are defined.

2.1.3 The UK currently requires fifteen-minute average values for SO_2 ambient air-quality concentrations to be reported, whereas the current EU Directive specifies ten-minute averaging times. It is possible that the UK will propose a procedure that shows equivalence with the EU requirements but continue to report fifteen-minute SO_2 average concentrations. The MCERTS Certification Committee will take this into account if it arises.

Table 2.1a European Union air quality limit values

Pollutant	NAQS averaging time	NAQS standard	Number of permissible exceedances	Date to be met
SO_2	15-min. mean	100 ppb	max of 35 exceedances	end 2005
	1-hour mean	132 ppb[4]	max of 24 exceedances	end 2004
	24-hour mean	47 ppb	max of 3 exceedances	end 2004
	calendar year & winter	8 ppb	rural areas	2000
NO_2	1-hour mean	105 ppb	max of 18 exceedances	end 2005
	annual mean	21 ppb		end 2004
NO_x	annual mean	16 ppb		end 2000
Benzene	running annual mean	5 ppb 1 ppb	None	end 2003 end 2005
CO	running 8-hour mean	10 ppm 8.6 ppm	None	end 2003 end 2004
O_3	running 8-hour mean	50 ppb	max of 10 exceedances	end 2005

Table 2.1b European Union air quality limit values

Pollutant	Period	Limit	Number of permissible exceedances	Date to be met
SO_2	1 hour[4]	131 ppb	not to be exceeded > 24 x per calendar year	1 Jan 2005[2]
	24 hours	48.6 ppb	not to be exceeded > 3 x per calendar year	1 Jan 2005
	calendar year & winter	7 ppb	rural areas	E.I.F + 24 months
NO_2	1 hour	104.6 ppb	not to be exceeded > 18 times per calendar year	1 Jan 2010[2]
	calendar year	21 ppb		1 Jan 2010 [2]
NO_x	calendar year	15.7 ppb	rural areas	E.I.F + 24 months
Benzene	calendar year	1.66 ppb [1]	None	1 Jan 2010 [2]
CO	rolling 8-hour mean	8.6 ppm [1]	None	1 Jan 2005
O_3	hourly mean	120 ppb	20 exceedances	1 Jan 2005

E.I.F. = entry into force (of EU Directive).

[1] currently proposed values

[2] a decreasing margin of tolerance is applicable until this date.

[3] or 2010 at industrial sites contaminated with lead.

[4] formed from 10-minute averages or 15-minute averages (UK)

Table 2.2 Limit values (certification ranges) used for MCERTS performance standards

Pollutant	Limit value or certification range
Sulphur Dioxide	131.0 ppb
Nitrogen Dioxide	104.6 ppb
Ozone	120.0 ppb
Carbon Monoxide	8.6 ppb
Benzene	1.66 ppb
Ammonia	350 ppb
Formaldehyde	100 ppb
Toluene	100 ppb
Methane	10 ppm
Nitrous oxide	350 ppb
1.3 Butadiene	5 ppb
Ethane	500 ppb
Ethene	250 ppb
Propene	50 ppb
Toluene	50 ppb
o-xylene	50 ppb
m-xylene	50 ppb
p-xylene	25 ppb
Isobutene	10 ppb

2.2 Combined performance characteristic

2.2.1 MCERTS includes an overall measure of the performance of OPAMs by combining together statistically all the relevant performance characteristics. This is known as a combined performance characteristic U_c. Only those performance characteristics that influence directly the uncertainty of the measurements produced by the OPAM will be used to derive the combined performance, which shall be expressed as an expanded uncertainty with the level of confidence of 95%. The methodology used is based on the ISO Guide to the Expression of Uncertainty in Measurement (GUM)[(6)] and on ISO Standard 14956[(5)]. It is calculated by summing, in quadrature, the individual standard uncertainties u_i, determined for each relevant performance characteristic. The standard uncertainty u is determined by measurement and in the case of a normal distribution is usually taken as the standard deviation of the mean X_{bar}, as shown in Figure 1. The expanded uncertainty U is defined by multiplying the standard uncertainty u by a coverage factor to obtain a 95% confidence level. Therefore the 95% confidence interval for X lies within the limits defined by ±U. The performance standards are defined in terms of measurement results and should be understood as being ± values. The numbers included in relevant tables are given as absolute values.

$$u_c = \sqrt{\sum_{i=1}^{n} u_i^2} \qquad 2.1$$

The combined performance characteristic U_c, expressed at the 95% confidence level is derived from the combined standard uncertainty u_c by multiplying it by a coverage factor dependent on the total number of the degrees of freedom.

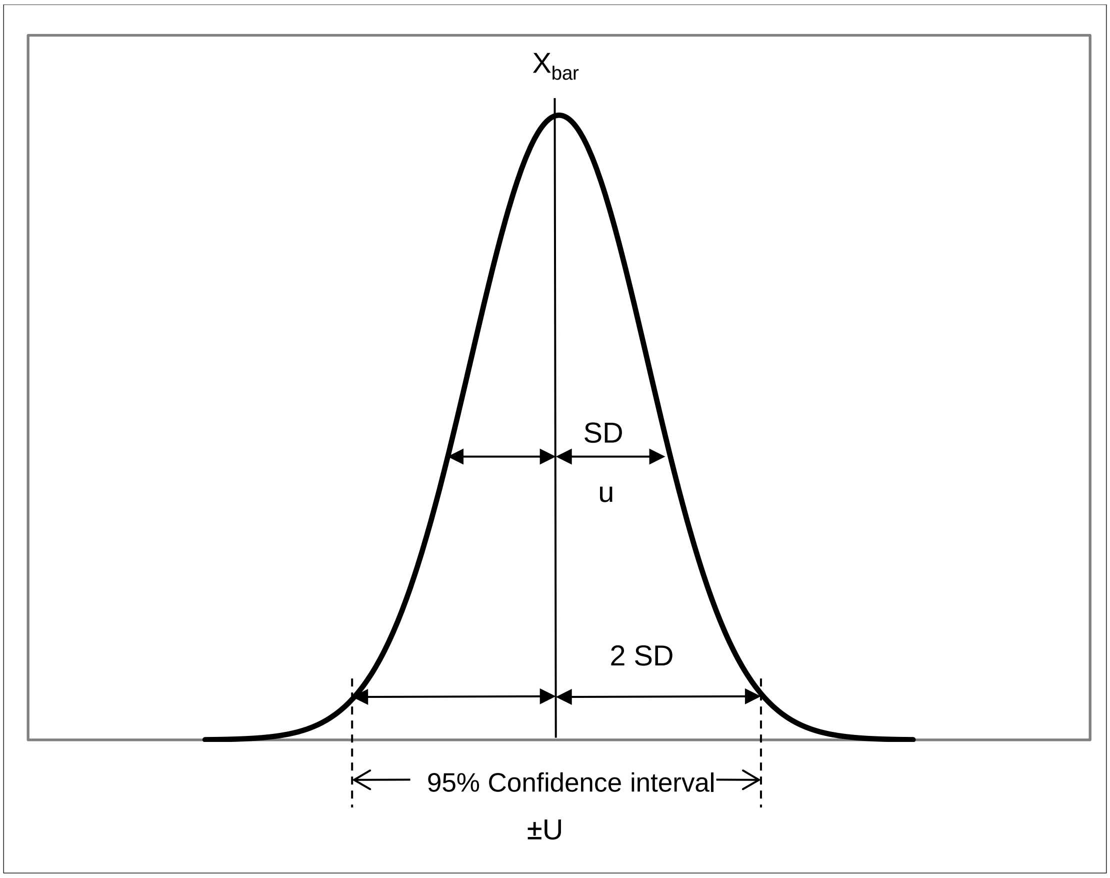

Figure 1

2.2.2 The combined expanded uncertainties are compared against the MCERTS combined performance standard. The OPAM must satisfy this requirement as well as meeting the performance standards specified for all individual performance characteristics. The combined performance standard will not be met if all individual performance characteristics contributing to the combined standard uncertainty are at their individual limits specified by MCERTS. Some of the individual performance characteristics have to be better than the corresponding performance standards if the combined performance standard requirement is to be met. On average, an OPAM should have individual performance characteristics equal to half of the corresponding MCERTS performance standards, in order to meet this combined performance characteristic. Combined performance characteristic for OPAMs monitoring CO, NO_x, SO_2, and O_3 shall be calculated for an averaging period of one hour. Individual performance characteristics are determined over fifteen-minute periods. Therefore the uncertainty due to the repeatability standard deviation is divided by 2 to calculate its contribution to the hourly uncertainty budget.

2.3 Operational conditions

2.3.1 OPAMs should be assessed under conditions where good agreement can be expected between point analysers and open path integrated samples, the conditions expected in a well-mixed environment. OPAMs are not typically used in rural and remote areas where very low concentration levels may be encountered. In urban locations, including measurements across street canyons OPAMs are expected to provide averaged results where rapidly changing pollutant concentrations are smoothed out due to spatial integration. Such locations are likely to have higher levels of cross-interferent species that could have an effect on the OPAM. As OPAMs are generally expected to be used under urban or industrial complex conditions they will be tested against the challenging criteria appropriate for such sites. Typical applications of the OPAMs are:

- measurements in the vicinity of industrial complexes
- measurements at airports
- in tunnel measurements based on multiple reflection systems
- measurements close to urban areas
- studies of pollution in street canyons
- measurements at refineries and filling stations

2.3.2 Typical levels of pollutant concentrations measured in the UK are given in Table 2.3.

Table 2.3 Typical concentration values of the determinands covered in this document

Pollutant	**Rural**		**Kerbside**	
	Short Term	Long Term	Short Term	Long Term
Benzene	N/A	0.5 ppb annual average	N/A	2 ppb annual average
Nitrogen dioxide	25 ppb hourly average	15 ppb annual average	55 ppb hourly average	40 ppb annual average
Ozone	70 ppb hourly average	35 ppb annual average	40 ppb hourly average	15 ppb annual average
Sulphur dioxide	10 ppb hourly average	5 ppb annual average	30 ppb hourly average	15 ppb annual average
Ammonia	35 ppb hourly average	15 ppb annual average	15 ppb hourly average	5 ppb annual average
Formaldehyde	1.5 ppb hourly average	1 ppb annual average	80 ppb hourly average	8 ppb annual average
Toluene	1 ppb hourly average	0.5 ppb annual average	25 ppb hourly average	15 ppb annual average
m-xylene	50 ppb hourly average	10 ppb annual average	250 ppb hourly average	50 ppb annual average
o-xylene	5 ppb hourly average	1 ppb annual average	100 ppb hourly average	10 ppb annual average
p-xylene	5 ppb hourly average	1ppb annual average	25 ppb hourly average	5 ppb annual average
Methane	15 ppm hourly average	5 ppm annual average	5 ppm hourly average	2 ppm annual average
Carbon monoxide	200 ppb hourly average	100 ppb annual average	4 ppm hourly average	2 ppm annual average
Nitrous oxide	50 ppb hourly average	25 ppb annual average	350 ppb hourly average	100 ppb annual average
1.3 butadiene	0.5 ppb hourly average	0.25 ppb annual average	1.5 ppb hourly average	0.5 ppb annual average

Ethane	100 ppb hourly average	50 ppb annual average	500 ppb hourly average	200 ppb annual average
Ethene	20 ppb hourly average	10 ppb annual average	100 ppb hourly average	25 ppb annual average
Propene	10 ppb hourly average	5 ppb annual average	50 ppb hourly average	15 ppb annual average
Isobutene	2 ppb hourly average	1 ppb annual average	10 ppb hourly average	2 ppb annual average

3. References

1 MCERTS Performance Standards for Continuous Ambient Air Quality Monitoring Systems, Environment Agency.

2 Directive 2008/50/EC of the European Parliament and of the Council of 21 May 2008 on ambient air quality and cleaner air for Europe.

3 Statutory Instruments 2007 No.64, Environmental Protection, The Air Quality Standards Regulations, 2007.

4 The Air Quality Strategy for England, Scotland, Wales and Northern Ireland, DETR, January 2000.

5 CR 14377(2002) Air Quality Approach to Uncertainty Estimation for Ambient Air Reference Measurement Methods.

6 ISO Guide to the Expression of Uncertainty in Measurements ENV 13005-1999, Geneva, Switzerland.

7 Guide to the demonstration of equivalence of ambient air monitoring methods-Report by an EC Working Group on Guidance for the Demonstration of Equivalence, January 2010.

4. Definitions of performance characteristics and other terms

Accuracy: The closeness of agreement between a single measured value of the determinand and the true value (or an accepted reference value).

Availability: Fraction of the total monitoring time for which data of acceptable quality have been collected (excluding servicing and calibrations).

Averaging time: Period of time over which an arithmetic or time weighted average of concentrations is calculated. [T_a – is the averaging period used by the OPAM. T_{ra} – Required data averaging period, e.g. prescribed by legislation].

Combined performance characteristic: Expanded combined uncertainty calculated by summing the results of the relevant performance tests in accordance with the law of propagation of uncertainty i.e. taking a square root of the sum of squares of the individual components.

Cross sensitivity: Response of the OPAM to determinands other than those that it is designed to measure.

Detection limit: The concentration value of determinand gas above which there is at least a 95 percent degree of confidence that the measured value is different from zero.

Short term drift – zero and span: Short term zero and span drift is a measure of the drift in the output signal over the time period during which other performance characteristics are to be determined.

Expanded uncertainty: An interval about the measurement result that is expected to encompass a specific fraction of the distribution of values attributable to the determinand.

Field repeatability: Expanded uncertainty calculated from the standard deviation of differences between measurements made by two co-located identical analysers over the test period.

Linearity: Measure of fit of the instrument's response across its measurement range to a straight line using a number of samples of approximately equally distributed concentrations of a pollutant and a zero concentration.

Maintenance interval: Time in the operating environment in the field over which the OPAM's zero and span drifts remain within specific limits.

Repeatability: Repeatability is a measure of the variation between successive measurements made maintaining the input span gas and all influence variables as constant as practical.

Response time: A measure of the dynamic response of the OPAM to a step change in the pollutant concentration.

5. General instrument requirements

5.1 General requirements for OPAMs submitted for testing

5.1.1 Manufacturers are required to submit the following:

- two identical, complete air quality monitoring systems (OPAMs)
- calibration gases (where appropriate)
- a set of appropriate calibration cells and auxiliary equipment
- all necessary components for operation under field conditions

5.1.2 The OPAM submitted for testing shall have analogue or digital outputs that allow the provision of negative readings with respect to zero of at least 15% of the certification range (see section 5.4). This is to ensure that the instrument performance tests carried out around the zero reading are valid (e.g. tests of zero drift, detection limit and cross-interference), and not truncated at the OPAM's zero reading.

5.1.3 The determinand concentrations measured by an OPAM are generally expressed either in density units (mass of determinand per unit volume of the ambient atmosphere) or in volume fraction units (volume of determinand per unit volume of the ambient atmosphere), although other units may also be used. The first of these units (density) is directly dependent on the temperature and pressure of the ambient atmosphere, while the second (volume fraction) may also have a weak dependence. Nationally traceable calibration gas mixtures, however, are generally defined in units of mole fraction, which are independent of gas temperature and pressure. Conversion factors between these different units may be calculated, but there may be uncertainties in some of the parameters in the conversion calculations. The OPAM manufacturer or supplier shall inform the relevant MCERTS Certification Committee and the test house(s) as to which concentration units are being used, and the test house shall take these conversion calculations and any uncertainties into account when carrying out relevant tests (e.g. the accuracy test). The test house and the Certification Committee shall, where required, provide comments on the validity of any such algorithm employed by the OPAM supplier or manufacturer, to ensure its proper subsequent use. It is therefore essential that the measurement units used by the OPAM and any conversions to reference conditions applied (e.g. gas pressure and temperature) are clearly and unambiguously identified by the manufacturer. Results reported in units of mass per unit volume shall be expressed at standard temperature and pressure (temperature of 293 K, pressure of 101.3 kPa).

5.1.4 OPAMs that have output readings sensitive to ambient air temperature and/or pressure shall be able to make corrections for changes in these parameters. These corrections may be carried out by using in-built pressure and temperature sensors or by using external sensors. The manufacturer or supplier of the OPAM shall provide the test house with information as to whether any in-built temperature and pressure corrections are being applied. Where no internal corrections are applied, the manufacturer or supplier shall provide the test house with any algorithms that are required for the conversion of the OPAM readings to different ambient temperatures and pressures.

5.1.5 The OPAMs submitted for testing shall conform to all applicable EC Directives. These include: the Electro-magnetic Compatibility Directive 2014/30/EU (formerly 2004/108/EC); the Low Voltage Directive 2014/35/EU (formerly 2006/95/EC), covering electrical equipment designed for use within certain voltage limits, and; the Directive on the restriction of the use of certain hazardous substances in electrical and electronic equipment (2011/65/EU). Equipment within the scope of the Hazardous Atmospheres Directive, 2014/34/EU (formerly 94/9/EC) falls outside the scope of this MCERTS document. OPAM manufacturers or suppliers shall supply declarations of conformity to all relevant Directives applicable to the equipment.

5.2 Response times

5.2.1 The response times shall be determined as a part of the performance tests. The response times should be determined in single gas operation mode. When they become a part of the instrument cycle in a multiple gas operation mode the total cycle duration should be assessed against the averaging time requirements. A minimum performance requirement is that the OPAM shall have response times less than 25% of the required averaging period. Table 5.1 provides examples of the averaging times used in the UK for collecting ambient air quality information.

5.3 Averaging times

5.3.1 Most of the performance requirements given in this document apply to results produced by OPAMs that are averaged values of the pollutant concentration over a period defined as the averaging time T_a. In cases where the OPAM internally produces averaged results and where the averaging time T_a is selectable, then it shall be selected by the OPAM manufacturer or supplier, in consultation with the MCERTS Certification Committee and the test house(s). In most cases the averaging times specified for air quality monitoring given in Table 5.1 should be used. The averaging times actually used will be stated on the MCERTS certificate.

Table 5.1 Examples of averaging times used for sampling and reporting in the UK

Pollutant	Typical Averaging Time (T_a)	Reporting Time
Benzene	1 hour	Annual average
Carbon Monoxide	15 minutes	Eight hour average
Nitrogen Dioxide	15 minutes	Hourly average
Ozone	15 minutes	Eight hour average
Sulphur Dioxide	15 minutes	Hourly average Daily average
Ammonia	Not specified	Hourly average
Formaldehyde	Not specified	Hourly average
Toluene	Not specified	Hourly average
Xylenes	Not specified	Hourly average
Methane	Not specified	Hourly average
Ethane	Not specified	Hourly average
Ethene	Not specified	Hourly average
1,3 butadiene	Not specified	Hourly average
Nitrous oxide	Not specified	Hourly average
Isobutene	Not specified	Hourly average
Propene	Not specified	Hourly average

5.4 Certification range

5.4.1 The OPAM manufacturer or supplier shall specify and agree with the MCERTS Certification Committee, for each pollutant concentration to be measured, a certification range of concentrations over which the OPAM is to be tested for each determinand.

5.4.2 Each certification range shall be generally between zero and a maximum value of the pollutant concentration. These values shall be agreed by the MCERTS Certification Committee as being fit for the intended purpose. The certification ranges may be expressed as a product of optical path length and concentration or in concentration units for a fixed path length.

5.4.3 Typical values of the certification range for OPAMs are given in Table 5.2. These ranges are recommended unless the OPAM manufacturer or supplier and the Certification Committee agree that there is a strong justification for selecting different ranges. Where no limit value is given, the compliance with the performance standards shall be verified at 80% of the certification range. If a manufacturer or supplier wishes to demonstrate performance over different ranges, additional testing will be required for each range.

Table 5.2 Typical certification ranges for OPAMs (expressed in concentration units)

Pollutant	Urban background/centre, suburban, kerbside, roadside and industrial sites	
	Scale min	Scale max
NO	0.0 ppb	2000 ppb
NO_2	0.0 ppb	1000 ppb
SO_2	0.0 ppb	2000 ppb
O_3	0.0 ppb	300 ppb
Ammonia	0.0 ppb	350 ppb
Formaldehyde	0.0 ppb	100 ppb
Toluene	0.0 ppb	50ppb
Xylenes	0.0 ppb	50 ppb
Benzene	0.0 ppb	50 ppb
Methane	0.0 ppm	30 ppm
Ethane	0.0 ppb	500 ppb
Ethene	0.0 ppb	250 ppb
Propene	0.0 ppb	50 ppb
1,3 Butadiene	0.0 ppb	10 ppb
Isobutene	0.0 ppb	10 ppb

5.4.4 Where the OPAM has user-selectable settings range for example, these would be chosen by the OPAM manufacturer or supplier and agreed with the Certification Committee in conjunction with the test house(s), to be appropriate for the certification range. In practice, the OPAM range selected is likely to be similar to the certification range, although this is not essential. However, the OPAM will be tested only over the certification range. The OPAM settings, once chosen, will not be altered during the tests. The settings used will be stated on the certificate.

5.4.5 Auto-ranging OPAMs will not have their ranges adjusted in any way by the test house(s) during the tests. The certificate will state that the performance tests have been carried out in auto-range mode. The certificate will show only the certification range tested and will not mention any internal range settings to which the OPAM may have switched during the tests. If the OPAM manufacturer or supplier wishes to certify the OPAM at specific internal range settings, separate tests shall be performed, using agreed certification ranges. Where the output of an auto-ranging OPAM is not converted to air quality units, or to a normalised scale, then an output must be available to flag which internal range setting applies to the output data signal.

5.4.6 The certificate will list all the ranges certified and the OPAM settings used, and will state explicitly the performance characteristics tested and the application category for which each range is certified, together with any relevant limit value (where applicable).

5.5 Zero and span drift

5.5.1 During the field tests, the measurement of both the short-term and the long-term drift will be made by supplying certified zero and calibration gases externally to the calibration cell of the OPAM. Short-term drift tests will be performed every 23 hours for the first 14 days of the field tests, and the results obtained will be compared with the performance standards.

5.5.2 In addition, the OPAM will have associated with it, where possible, a methodology using either an automated or a manual method to measure the zero drift and span drift of the complete system. The OPAM supplier or manufacturer shall provide a description of the methodology used to determine these drifts. This will be assessed during the field tests. In cases where it is not possible for the zero and span system to determine the total drift that arises from all the components of the OPAM, the Certification Committee will include a statement to this effect on the MCERTS certificate.

5.6 Cross-sensitivity to interfering substances

5.6.1 The OPAM's response to interferent gases shall be tested. The interferent gas concentrations shall be set at levels appropriate for different measurement category locations.

5.6.2 Cross-sensitivity tests shall be performed using binary mixtures of each interferent gas with the determinand gas at the limit value given in Table 2.2 and using a mixture of all interferent gases with the determinand gas at the limit value. This tests the assumption of additivity of the OPAM's cross-sensitivity response. The ambient concentration values of a range of interferent gases used for cross-sensitivity testing are given in Table 5.3.

5.6.3 Samples containing the determinand gas alone at the limit concentration shall be introduced to the OPAM between the interference tests to provide a reference response.

5.7 Test of linear fit

5.7.1 This performance criterion is the only one to be specified as the percentage of the measured value. Linearity shall be assessed at six points approximately equally spaced across the measurement range, with one point at zero concentration. The differences between the best-fit line and an average at each point expressed as percentages of the measured value will be compared with the performance standard. The linear fit at zero point shall be assessed using the lowest non-zero measurement point. The uncertainty contribution due to linear fit shall be expressed at the limit value and calculated from the difference between the limit value and the best-fit line.

Table 5.3 Concentrations of interferent gases to be used for cross-sensitivity testing

Interferent Gas	Chemical formula	Concentration (1)
Methane	CH_4	3000 ppm
Ethane	C_2H_4	400 ppb
Benzene	C_6H_6	35 ppb

Sulphur dioxide	SO_2	300 ppb
Carbon monoxide	CO	3000 ppb
Carbon dioxide	CO_2	3000 ppm
Hydrogen sulphide	H_2S	330 ppb
Ozone	O_3	200 ppb
Nitrogen monoxide	NO	350 ppb
Acetone	C_3H_6O	400 ppb
Dinitrogen monoxide	N_2O	330 ppb
Ammonia	NH_3	330 ppb
Formaldehyde	HCHO	1500 ppb

(1) Concentration in the calibration cell should be calculated to correspond to the indicated value using constant path length concentration product.

5.8 Assessment of maximum path length for equivalence with point analyser

5.8.1 Maximum path length for equivalence with a point analyser depends on the zone in which the equipment has been installed. As a general rule better agreement can be expected in well-mixed air pockets such as those encountered in background and rural areas. Presence of local sources of pollution and complicated urban topography may lead to shorter distances than those found in well mixed rural environments. More reliable comparison can be produced reducing the volume of ambient test zone by use of multiple-reflection systems with mirror spacing not greater than 50m. The equivalence with point analysers should be calculated and expressed in terms of field repeatability. The repeatability calculated in the course of such field studies should not be treated as a performance parameter but rather as a guideline allowing for the interpretation of the measurement results in terms of air quality standards designed for point analysers.

5.9 Effect of calibration cell length on path length-pollutant concentration product

5.9.1 During the process of calibration the concentration of calibration gas used depends on the length of the calibration cell and the selected open path length assuming that the product of concentration and the path length remain constant. There is a wide selection of calibration cell types available for the calibration of DOAS instruments ranging from 10m down to about 10mm in length. As a general rule, the longer the cell the more closely the calibration process reproduces the real operational conditions. When using very short calibration cells it is necessary to verify that their performance is checked against a suitable long calibration cell and that the resulting error is within acceptable limits. The performance standards for the calibration cells are given in Table 5.4.

5.10 Effect of light level change due to lamp intensity on measurement result

5.10.1 The illumination intensities at the receiver obtained during the field measurements depend on the lamp age and on the environmental conditions leading to light obscuration such a fog or snowfall. To ensure that the system performs satisfactorily it is necessary to check the effect of the reduction of the level of light reaching the receiver on the measurement result. This effect is expressed as the percentage change of the measured value corresponding to the reduction of lamp intensity by a fixed value. The performance standards related to light intensity are given in Table 5.4.

5.11 Effect of light level change due to transmitter-receiver misalignment on the measurement result

5.11.1 OPAM instruments require very good mechanical alignment between the transmitter and receiver units for optimum performance. A very slight sideways movement of the transmitter may result in substantial reduction of the light level at the receiver with the potential effect on the measurement results. This effect is assessed by introducing a degree of misalignment between the transmitter and the receiver units and measuring the change observed in the measurement result. The performance criteria related to unit misalignment are given in Table 5.4.

Table 5.4 Optical performance criteria

Parameter	Degree of change	Effect on the measurement result
Effect of calibration cell length	Relative to 10m cell	≤ 2%
Effect of lamp light intensity	15%	≤ 2%
Effect of transmitter-receiver misalignment	Reduction of light level to 5%	≤ 2%

6. Determinand specific requirements

6.1 Introduction

6.1.1 This section defines the determinand specific requirements for OPAMs.

6.1.2 The performance standards are expressed in terms of measurement ranges from which standard uncertainties can be derived, in keeping with international procedures.

6.2 Performance standards for OPAMs

6.2.1 OPAMs used for monitoring SO_2, NO_2, O_3, ammonia, formaldehyde, benzene toluene, xylene and methane based on DOAS measure these pollutants typically over the open path length up to 1000m and can be used for simultaneous determination of all species. Calibration of the system is carried out with the help of a cell with quartz glass windows inserted into the optical path between the light source and the receiver assuming constant value of the product of concentration and distance. In addition to the cell method calibration of FTIR systems can also be realized by complete spectral monitoring. This method is based on the approximation of the measured spectrum by a spectrum represented by a model. The model consists of two sub-models: a radiative transfer model and an instrument line shape function. The radiative transfer calculation is performed using reference spectra of the specific absorption coefficient. The reference spectra are calculated based on molecular line data contained in the relevant data-bases. Various methods for the determination of the best fit parameters are applied in different implementations of a FTIR system.

6.2.2 The MCERTS performance standards are given in Table 6.1 for laboratory tests and in Table 6.2 for field tests. Default values for the calculation of combined uncertainty values are given in Table 6.3.

Table 6.1 Performance standards for different channels of OPAMs (laboratory tests)

Performance characteristic	**Performance standard**						
Pollutant	**SO_2**	**NO, NO_2, CO, Nitrous oxide**	**O_3**	**Ammonia Ethane, Ethene Propene**	**Formaldehyde**	**Benzene Toluene Xylenes**	**Methane 1,3 butadiene Isobutene**
Response time in single gas operation mode	≤ 60 seconds	≤60 seconds	≤60 seconds	≤60 seconds	≤60 seconds	≤60 seconds	≤60 seconds
Repeatability at zero level (detection limit) at path length specified by the manufacturer[(2)]	≤ 2% of LV	≤ 1% of LV	≤ 1% of LV	≤ 5% of LV	≤ 5% of LV	≤ 5% of LV	≤ 5% of LV
Repeatability at span level at path length specified by the manufacturer	≤2% of LV	≤2% of LV	≤2% of LV	≤ 2% of LV	≤ 2% of LV	≤ 2% of LV	≤ 2% of LV
Linearity	≤2% of measured value	≤2% of measured value	≤5% of measured value	≤ 2% of measured value	≤ 2% of measured value	≤ 2% of measured value	≤ 2% of measured value
Short term drift at zero level (24 hrs)	≤ 2% of LV	≤ 2% of LV	≤ 2% of LV	≤ 2% of LV	≤ 2% of LV	≤ 2% of LV	≤ 2% of LV
Short term drift at span level (24 hrs)	≤ 2% of LV	≤ 2% of LV	≤ 2% of LV	≤ 2% of LV	≤ 2% of LV	≤ 2% of LV	≤ 2% of LV
Dependence of zero reading on surrounding air temperature change	≤ 2% of LV	≤ 2% of LV	≤ 2% of LV	≤ 2% of LV	≤ 2% of LV	≤ 2% of LV	≤ 2% of LV
Dependence of span reading on surrounding air temperature change	≤ 2% of LV	≤ 2% of LV	≤ 2% of LV	≤ 2% of LV	≤ 2% of LV	≤ 2% of LV	≤ 2% of LV
Dependence on supply voltage	≤ 2% of LV	≤ 2% of LV	≤ 2% of LV	≤ 2% of LV	≤ 2% of LV	≤ 2% of LV	≤ 2% of LV
Single gas interference	≤ 2% of LV	≤ 2% of LV	≤ 2% of LV	≤ 2% of LV	≤ 2% of LV	≤ 2% of LV	≤ 2% of LV
Cross-sensitivity to all interferents	≤ 5 % of LV	≤ 5 % of LV	≤ 5 % of LV	≤ 5% of LV	≤ 5% of LV	≤ 5% of LV	≤ 5% of LV
Combined performance	≤ 15% of limit value	≤ 15% of limit value	≤ 15% of limit value	≤ 20% of limit value	≤ 20% of limit value	≤ 20% of limit value	≤ 20% of limit value

1 Expressed as pass-fail value to be converted into standard uncertainty when calculating the uncertainty budget

2 Expressed as expanded uncertainty with a level of confidence of 95%

Table 6.2 Performance standards for different channels of OPAMs (field tests)

Performance characteristic	Performance standard						
Pollutant	**SO_2**	**NO, NO_2, CO, Nitrous oxide**	**O_3**	**Ammonia, Ethane, Ethene, Propene**	**Formaldehyde**	**Benzene Toluene Xylenes**	**Methane 1,3 Butadiene Isobutene**
Maintenance interval	30 days	30 days	30 days	30 days	30 days	30 days	30 days
Zero drift (over maintenance interval)	≤ 5% of limit value	≤ 5% of limit value	≤ 5% of limit value	≤ 5% of limit value	≤ 5% of limit value	≤ 5% of limit value	≤ 5% of limit value
Span drift (over maintenance interval)	≤ 5% of limit value	≤ 5% of limit value	≤ 5% of limit value	≤ 5% of limit value	≤ 5% of limit value	≤ 5% of limit value	≤ 5% of limit value
Field repeatability	≤ 8% of the average of three months period	≤ 8% of the average of three months period	≤ 8% of the average of three months period	≤ 8% of the average of three months period	≤ 8% of the average of three months period	≤ 8% of the average of three months period	≤ 8% of the average of three months period
Availability (data capture)	90%	90%	90%	90%	90%	90%	90%
Maximum path length for consistence with point analyser	300 m or shorter path with multiple reflection	300 m or shorter path with multiple reflection	300 m or shorter path with multiple reflection	300 m or shorter path with multiple reflection	300 m or shorter path with multiple reflection	300 m or shorter path with multiple reflection	300 m or shorter path with multiple reflection

Actual maintenance interval to be reported on the certificate.

Table 6.3 Default values for calculation of overall combined-uncertainty

Pollutant	SO_2	NO_2	CO	O_3	Ammonia	Formaldehyde	Benzene Toluene Xylene	Methane
Surrounding air temperature variation	± 15 K	± 15 K	± 15 K	± 15 K	± 15 K	± 15 K	± 15 K	± 15 K
Voltage variations	± 20 V ± 10% (whichever is smallest)	± 20V ± 10% (whichever is smallest)	± 20V ± 10% (whichever is smallest)	± 20 V ± 10% (whichever is smallest)	± 20V ± 10% (whichever is smallest)	± 20 V ± 10% (whichever is smallest)	± 20V ± 10% (whichever is smallest)	± 20V ± 10% (whichever is smallest)
Uncertainty of the calibration gases	3% of certification range	3% of certification range	3% of certification range	3% of certification range	3% of certification range	3% of certification range	3% of certification range	3% of certification range
Calibration frequency	3 months	3 months	3 months	3 months	3 months	3 months	3 months	3 months
Limit value	131 ppb	104 ppb	8.6 ppm	120 ppb	350 ppb	150 ppb	1.66 ppb 500 ppb 1000 ppb	TBA
Certification range	380 ppb	262 ppb	86 ppm	250 ppb	350 ppb	150 ppb	50 ppb 500 ppb 1000 ppb	TBA
Average over 3 month period	131ppb	104 ppb	8.6 ppm	120 ppb	350 ppb	150 ppb	50 ppb 500 ppb 1000 ppb	TBA
Measured value	131 ppb	104 ppb	8.6 ppm	120 ppb	350 ppb	150 ppb	50 ppb 500 ppb 1000 ppb	TBA
Span level (≅ 80% CR)	300 ppb	210 ppb	69 ppm	200 ppb	280 ppb	120 ppb	40 ppb 400 ppb 800 ppb	TBA

Table 6.3 Default values for calculation of overall combined-uncertainty (continued)

Pollutant	**Ethane**	**Ethene**	**1,3 butadiene**	**Propene**	**Nitrous oxide**	**Isobutene**
Surrounding air temperature variation	± 15 K	± 15 K	± 15 K	± 15 K	± 15 K	± 15 K
Voltage variations	± 20 V ± 10% (whichever is smallest)	± 20V ± 10% (whichever is smallest)	± 20V ± 10% (whichever is smallest)	± 20 V ± 10% (whichever is smallest)	± 20V ± 10% (whichever is smallest)	± 20 V ± 10% (whichever is smallest)
Uncertainty of the calibration gases	3% of certification range	3% of certification range	3% of certification range	3% of certification range	3% of certification range	3% of certification range
Calibration frequency	3 months	3 months	3 months	3 months	3 months	3 months
Limit value	N/A	N/A	N/A	N/A	N/A	N/A
Certification range	500 ppb	250 ppb	10 ppb	50 ppb	350 ppb	10 ppb
Average over 3 month period	100 ppb	50 ppb	2 ppb	10 ppb	100 ppb	2 ppb
Measured value	150 ppb	100 ppb	5 ppb	5 ppb	200 ppb	1 ppb
Span level (≅ 80% CR)	400 ppb	200 ppb	8 ppb	40 ppb	280 ppb	8 ppb

Appendix 1: Main standards underpinning the MCERTS performance standards

Determinand	International standard used as basis for performance standards
General	BS EN ISO 9169: Air Quality - Definition and determination of performance characteristics of an automatic measuring system. Guide to the demonstration of equivalence of ambient air monitoring methods-Report by an EC Working Group on Guidance for the Demonstration of Equivalence, January 2010.
SO_2	BS EN 14212: Ambient air quality - Standard method for the measurement of the concentration of sulphur dioxide by ultraviolet fluorescence
CO	BS EN 1626: Ambient air quality - Standard method for the measurement of carbon monoxide concentrations in ambient air by non-dispersive infrared spectroscopy.
NO_x	BS EN 14211: Ambient air quality - Standard method for the measurement of the concentration of nitrogen dioxide and nitrogen monoxide by chemiluminescence.
O_3	BS EN 14625: Ambient air quality - Standard method for the measurement of the concentrations of ozone by ultraviolet photometry.
Benzene	BS EN 14662-3: Ambient air quality - Standard method for the measurement of benzene concentrations: Automated pumped sampling with in situ gas chromatography.
Air quality integrated over long path	BS EN 15483: Ambient air quality - Atmospheric measurements near ground with FTIR spectroscopy.
Air quality integrated over long path	BS EN 16253: Air quality - Atmospheric measurements near ground with active Differential Optical Absorption Spectroscopy (DOAS) - Ambient air and diffuse emission measurements.