

**PROPOSALS TO EXTEND
MCERTS
TO CONTINUOUS
AMBIENT AIR-QUALITY MONITORS**



The Environment Agency's Monitoring Certification Scheme

A report prepared by the National Physical Laboratory and AEA Technology (National Environmental Technology Centre) on behalf of the Environment Agency's National Compliance Assessment Service.

ENVIRONMENT AGENCY



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National Centre for Environmental
Data and Surveillance

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For the Attention of: _____

FOREWORD

The Environment Agency has specific responsibilities for regulating major industries under environmental protection legislation, and a duty to report on the state of the environment. Our strategy focuses on the need to address the state of the environment at any time, identify the pressures that are affecting it, consider options and, where required, ensure regulated industries implement appropriate controls.

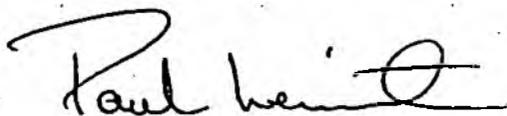
The Agency is interested in the monitoring of ambient air quality as a measure of the environmental impact of the industries it regulates. We can then ensure actions are taken to prevent or minimise the impacts and prevent potential harm from occurring. Clearly, if we are to make informed quality decisions, these have to be based on reliable monitoring data that industry, regulators and the public can have confidence in.

In addition to the ambient monitoring carried out by the Agency and industry, the Department of the Environment, Transport and the Regions' (DETR) Air Quality Division monitors air quality in the UK through its extensive Automatic Urban and Rural Air Quality Networks. A number of Local Authorities also carry out air quality monitoring as part of their statutory responsibilities.

Requirements for ambient air quality monitoring are likely to increase over the next few years both from an Agency perspective and as the various EC Ambient Air Quality Directives are implemented. The Directives require member states to operate continuous ambient monitoring systems, with the systems undergoing product certification prior to acceptance for use.

Proposals for the establishment of the Agency's Monitoring Certification Scheme MCERTS were first issued for public consultation in 1996. These focused initially on the certification of continuous stack-emission monitoring systems (CEMs). Considerable interest was shown in these proposals and the responses received were overwhelmingly supportive. Following this positive response we proceeded with the development of the Scheme. Sira Certification Service (SCS) was appointed to manage the Certification Service and MCERTS for CEMs was successfully launched in April 1998.

The Agency, with support from the DETR's Air Quality Division, now proposes to extend MCERTS to cover certain categories of ambient air-quality monitoring systems (CAMs). This document describes the proposed performance characteristics and Performance Standards for CAMs and also provides an outline of the test procedures that would be used to assess instrument performance.



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1. INTRODUCTION

- 1.1 The Environment Agency has established its Monitoring Certification Scheme (MCERTS) to promote quality monitoring based on international standards. The Scheme focused initially on the product certification of certain categories of continuous emission-monitoring systems (CEMs) used for monitoring industrial stack and flue gas emissions. Performance Standards for certain types of CEMs have already been published [1], and the associated Performance Standards for testing, have been drafted [2] for publication.
- 1.2 This document describes the Agency's proposals to extend MCERTS to cover the product certification of certain categories of continuous ambient air-quality monitoring systems (which will be referred to subsequently in this document as CAMs).
- 1.3 For the purpose of this document CAMs are instrumental systems which either:
- continuously monitor ambient pollutant concentrations in-situ and automatically produce results;
 - sample ambient air over an extended period (eg days or weeks) onto a filter, or a similar device, which is subsequently analysed in the laboratory to determine, for example, the amount of particulates, metals, or PAHs present. Such samplers may be used to obtain a continuous, or a discontinuous, longer-term, average value of the pollutant concentration, by carrying out sequential sampling over time. In these cases the instrumental characteristic which would be tested would be the valid sampling of the particulate matter containing the substances to be monitored, although recommendations are also provided in this document on the subsequent analytical procedure.

These proposals do not cover open-path instruments.

- 1.4 MCERTS Performance Standards for the following air pollutants are proposed: nitrogen monoxide (NO), nitrogen dioxide (NO₂), sulphur dioxide (SO₂), carbon monoxide (CO), ozone (O₃), particulate matter (PM₁₀ and PM_{2.5}), lead, other metals (cadmium, arsenic, nickel and mercury), benzene, and poly-aromatic-hydrocarbons (PAHs).
- 1.5 The following is a complete list of all the performance characteristics for CAMs, which would be assessed using a combination of laboratory and field tests. Some of the tests are for specific types of analysers and would only be performed where applicable (see below).

Laboratory tests

- response time, consisting of lag rise time, rise time, lag fall time and fall time (where applicable);
- laboratory repeatability standard deviation;
- zero and span drift;

- accuracy of measurement of the pollutant concentration (or accuracy of sample collection in the case of certain particulate CAMs, and in the case of all CAMs which monitor metals and polyaromatic hydrocarbons (PAHs));
- detection limit and quantification limit ;
- averaging of short-term fluctuations in determinand concentration (where applicable);
- linear fit;
- cross sensitivity to interfering substances;
- NOx converter efficiency test (where applicable);
- carry over (where applicable);
- flow accuracy and stability (where applicable);
- influence of atmospheric sample pressure and temperature;
- susceptibility to physical disturbances;

Field Tests

- field repeatability (comparison of the CAM against a reference method where this is available, and/or against another CAM);
- long-term zero and span drift;
- availability and maintenance interval.

The definitions of the performance characteristics and brief explanations of the tests are given in Appendix 1.

- 1.6 The general requirements and the Performance Standards to be met by CAMs are presented in this document in Sections 2, 3 and 4 respectively. Detailed definitions of the instrument performance characteristics on which these are based, and brief summaries of the procedures that would be used to test conformity with the Standards, are described in Appendix 1. The main published and draft international and national standards on which these Performance Standards are based are presented in Appendix 2. The range of standard environmental operating conditions for CAMs are described in Appendix 3.
- 1.7 The Performance Standards have been defined so that MCERTS-certified CAMs would, in principle, be capable of meeting the requirements of both the EC Framework Directive 96/62 (EC "Ambient Air Quality Assessment and Management" [3]), and its associated Air Quality Daughter Directives, and also the requirements implicit in the UK National Air Quality Strategy. In the case of EC Directives, the total allowable uncertainties at the specified limit values for CAMs monitoring sulphur dioxide, oxides of nitrogen and PM₁₀ particulates are now published in a new EC Air Quality Daughter Directive [4]. In addition, a draft Daughter Directive has been prepared to cover carbon monoxide and benzene [5] and this also specifies the total allowable uncertainties at the proposed limit values for these pollutants. These Daughter Directives are to be enacted in more detail in appropriate CEN Standards, which are now being drafted for certain of the air quality pollutants covered in this document. (A list of the relevant CEN Technical Committees, and their associated Working Groups, is provided in Appendix 2.2). The central objective, therefore, in defining the Performance Standards specified in this MCERTS document, is that they should be compatible with these up-coming CEN standards, when they are

subsequently published. (Close liaisons are maintained with the appropriate CEN Committees and their Working Groups to ensure that this compatibility is maintained).

- 1.8 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 MONITOR CERTIFICATION

- 2.1 The EC Ambient Air Quality Directives require that certain CAMs that are used to report air-quality results undergo a product-certification or type-approval process prior to acceptance for use. The proposed extension of MCERTS is designed to meet these requirements.

2.2 AIR QUALITY LIMIT VALUES

- 2.2.1 The Performance Standards proposed in Section 4 of this document are generally expressed as maximum allowable deviations in the performance characteristics of a CAM, expressed in absolute concentration units eg ppb, $\mu\text{g.m}^{-3}$. The Standards are independent of the absolute concentration of the gas sample at which the test is performed.

- 2.2.2 Tables 2.1a and 2.1b give the European Union air-quality limit values, and the UK's National Air Quality Standards (NAQS), for the pollutants in this document. The EU limit values are, in general, very similar to the concentrations given in the UK's NAQS. The limit values used in deriving the Performance Standards are given in Table 2.2. EU limit values have been chosen where these are available. Where these have not been defined UK NAQS limit values have been adopted.

- 2.2.3 For completeness, the Performance Standards in Section 4 have also been expressed as 'percentages of the limit values' given in Table 2.2. Where no limit value is specified 80% of the certification range (as defined in Section 3.4) would be used as the value at which the CAM's performance characteristics are determined.

- 2.2.4 Currently the UK requires fifteen-minute average values for SO_2 ambient air-quality concentrations to be reported, whereas the EU Directive specifies hourly average values, formed from ten-minute averages collected as an indicator of short-term variability. It is possible that the UK will propose a procedure which shows equivalence with the EU requirements but continue to report fifteen-minute SO_2 average concentrations. This would be taken into account by the relevant MCERTS Certification Committee when this is an issue.

Table 2.1a: UK National Air Quality Standard

Pollutant	UK NAQS Averaging Time	UK NAQS Standard ¹	Existing Objective	Proposed NAQ Issued in Janu
SO ₂	15 min. mean	100 ppb	99.9th percentile to be achieved by 2005	100 ppb to be
	1 hour	131 ppb	-	max. 24 exceed
	24 hour	48.6 ppb	-	max. 3 exceeda
	calendar year & winter	7 ppb	-	rural areas - by
NO ₂	1 hour mean annual mean	150 ppb 21 ppb	hourly mean annual mean	104.6 ppb - by 21 ppb retained new national of
NO _x	-	-	-	-
PM ₁₀	running 24 hour mean	50 µg.m ⁻³	99th percentile	New annual ob of 50 µg.m ⁻³ (n 50 µg.m ⁻³ to be parameter - by New indicative level of 50 µg.l
	-	-	-	-
	-	-	-	-
Pb	annual mean	0.5 µg.m ⁻³	0.5 µg.m ⁻³	0.5 µg.m ⁻³ by e
Benzene	running annual mean	5ppb	5ppb by 2005	5ppb - by end 2 2005
CO	running 8-hour mean	10 ppm	10 ppm by 2005	10 ppm by end
1,3, butadiene	running annual mean	1 ppb	1ppb by 2005	1 ppb by end 20
O ₃	running 8-hour mean	50 ppb	97th percentile	50 ppb retained

¹ Based on the UK NAQS Report issued March 1997 (Rep

Table 2.1b: European Union Air Quality Lim

Pollutant	Period	Limit	Exceedance standard
SO ₂	1 hour ¹	131 ppb	Not to be exceeded > 2-
	24 hours	48.6 ppb	Not to be exceeded > 3 x p
	calendar year & winter	7 ppb	Rural areas
NO ₂	1 hour	104.6 ppb	Not to be exceeded > 18 tim
	calendar year	21 ppb	year
NO _x	calendar year	15.7 ppb	Rural areas
PM ₁₀	STAGE 1: 24 hours	50 µg.m ⁻³	Not to be exceeded > .
	STAGE 1: calendar year	40 µg.m ⁻³	year
	STAGE 2: 24 hours	50 µg.m ⁻³	Not to be exceeded > .
	STAGE 2: calendar year	20 µg.m ⁻³	year
Pb	calendar year	0.5 µg.m ⁻³	
Benzene	calendar year	1.66 ppb *	-
CO	rolling 8 hour mean	8.5 ppm *	-
O ₃	-	-	-

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

* currently proposed values

* A decreasing Margin of Tolerance is applicable until this date

** or 2010 at industrial sites contaminated with lead.

¹ formed from 10 minute averages

Table 2.2 Limit Values Used For The Proposed MCERTS Performance Standards

Pollutant	Limit value
Sulphur Dioxide	131 ppb
Nitrogen Dioxide	104.6 ppb
Ozone	50 ppb
Carbon Monoxide	8.5 ppb
Particulate Matter (PM ₁₀)	50 µg.m ⁻³
Lead	0.5 µg.m ⁻³
Benzene	1.66 ppb

2.3 COMBINED PERFORMANCE CHARACTERISTIC

2.3.1 The EC directives require that the overall uncertainty in a result produced by a CAM meets stated requirements [4,5]. It is therefore proposed that a measure of the overall performance of a CAM be determined by combining together statistically all the relevant performance characteristics of the instrument. Only those performance characteristics which influence directly the uncertainty of the measurements should be used to derive the combined performance, which shall be expressed as an expanded uncertainty at 95% confidence interval. The methodology that should be used is based on that described in the ISO Guide to the Expression of Uncertainty in Measurement (GUM) and in ISO Draft Standard 14956. The combined standard uncertainty u_c would be calculated by summing, in quadrature, the individual standard uncertainties u_i , determined for each relevant performance characteristic.

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

The combined expanded uncertainty U_c , expressed at the 95% confidence interval, shall then be derived from the combined standard uncertainty u_c by multiplying by a coverage factor determined from the total number of degrees of freedom according to GUM and, where appropriate, the Welch-Satterthwaite[6] equation.

2.3.2 The expanded uncertainty calculated using the above procedure is referred to in this document as the **combined performance characteristic** of a CAM.

2.3.3 The combined performance characteristic of a CaM would have to meet the relevant Performance Standard proposed in this document. The CAM would have to satisfy this requirement, **in addition** to meeting the Performance Standards specified for all individual performance characteristics. It should be noted that this combined performance characteristic requirement will not be met if **all** the individual performance characteristics contributing to the combined standard uncertainty are at their maximum allowed limit values. The individual Performance Standards allow a given CAM to have relatively worse performance for certain characteristics, as long as the combined performance characteristic meets the relevant Performance Standard. (As a guide, on average a CAM should have individual performance characteristics

that are half the required individual Performance Standards, in order to meet the Performance Standard for the combined performance characteristic).

2.4 OPERATIONAL CATEGORIES

2.4.1 It is proposed that CAM systems will be assessed against Performance Standards that relate to particular applications. Two broad operational categories have been identified. These are:

- Category 1 - Rural and Remote Sites;
- Category 2 - Urban Centre/Background, Suburban, Kerbside, Roadside and Industrial Sites.

2.4.2 In rural and remote sites, very low concentration levels may be encountered, and CAMs should have low detection limits and minimal zero and span drift characteristics. In urban locations, including kerbside sites, CAMs would be expected to monitor rapidly-varying concentrations, over a wide dynamic range. Also at these locations the level of cross-interferent species is likely to be higher, and could have a greater effect on the CAM. Where CAMs would be expected to measure in both the above categories they would in general be tested under Category 2 conditions.

2.4.3 The intended application category of a CAM would have implications on its required performance characteristics, particularly regarding potential interferents, the likely temporal variability of the pollutant concentration, the certification range and the detection limit.

2.4.4 Typical levels of pollutant concentrations measured in the UK are given in Table 2.3 for guidance.

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
Carbon Monoxide	200 ppb hourly average	100 ppb annual average	4 ppm hourly average	2 ppm annual average
Lead	N/A	0.01 $\mu\text{g.m}^{-3}$ annual average	N/A	0.15 $\mu\text{g.m}^{-3}$ 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
Particulates (PM ₁₀)	35 $\mu\text{g.m}^{-3}$ hourly average	25 $\mu\text{g.m}^{-3}$ annual average	35 $\mu\text{g.m}^{-3}$ annual average	25 $\mu\text{g.m}^{-3}$ annual average
Sulphur dioxide	10 ppb hourly average	5 ppb annual average	30 ppb hourly average	15 ppb annual average

3. GENERAL REQUIREMENTS

3.1 CAMS SUBMITTED FOR CERTIFICATION

3.1.1 Manufacturers are required to submit the following:

- two identical, complete air quality monitoring systems (CAMs);
- calibration artifacts (where appropriate);
- for gaseous CAMs, all components required for the connection to a sampling manifold (but not the sampling manifold itself);
- all necessary components for operation under field conditions;
- for particulate monitors, all sampling components including the sampling head;
- for systems (eg metals, PAHs) which require subsequent laboratory analyses, all sample collection, sample conditioning and sample handling systems.

3.1.2 The CAM submitted for testing shall have output indicator(s) (including, for example, analogue and/or digital indicators) that allow the provision of negative readings with respect to the zero reading of at least 15% of the certification range (see paragraph 3.4), so as to ensure that the instrument performance tests carried out around this zero reading are valid (eg tests on zero drift, detection limit and cross interferences), and not truncated at the CAM's zero reading.

3.1.3 The determinand concentrations indicated by a CAM 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, whilst the second of these (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 CAM manufacturers or suppliers shall confirm which concentration units are being used, so that the test house can take these conversion calculations and any uncertainties into account when carrying out relevant tests (eg the accuracy test). The test house shall, where required, provide comments to the MCERTS Certification Committee on the validity of any such algorithm employed by the CAM supplier or manufacturer, to ensure its proper subsequent use. It is therefore essential that the measurement units used by the CAM and any conversions to reference conditions applied (eg of gas pressure and temperature) be 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 293K, pressure of 101.3 kPa) as required by the EC Air-quality Daughter Directives.

3.1.4 The manufacturer shall agree with the MCERTS Certification Committee the range of environmental conditions that are to be applied to the CAM to demonstrate it is fit for purpose for its intended application. This range will be recorded on the Certificate.

3.1.5 For CAMs with output readings that are sensitive to ambient air temperature and/or pressure, corrections may be made by:

- using in-built or external pressure and temperature sensors. The manufacturer or supplier shall inform the test house if any in-built temperature and pressure corrections are being applied;
- or where no internal corrections are applied, the manufacturer or supplier providing the test house with any algorithms that are required for the conversion of the CAM's readings to different ambient temperatures and pressures.

3.1.6 The CAM shall be in conformity with all applicable EC Directives. This includes the Electro-magnetic Compatibility Directive 89/336/EEC and its amendments 92/31/EEC and 93/68/EEC. It also includes the Directive 72/23/EEC covering electrical equipment designed for use within certain voltage limits, and its amendment 93/68/EEC. (Equipment within the scope of the Hazardous Atmospheres Directives falls outside the scope of this document). CAM manufacturers or suppliers shall supply declarations of conformity to all relevant Directives applicable to the equipment.

3.2 RESPONSE TIMES

3.2.1 It is proposed that all the various response times defined in Appendix A1 will be determined as a part of the performance tests. A minimum performance requirement in this document is that the CAM should have response times which are less than 25% of the required averaging period (ISO Draft Standard 14956). Table 3.1 lists examples of the averaging times required by the UK's National Air Quality Strategy (NAQS) in reporting ambient air quality information. In the proposed Performance Standards the response times have been reduced (where appropriate) to take account of residence times observed in a typical manifold, as it is proposed not to test these. In addition, in order to average correctly the small time-scale variations seen in real situations, particularly in Category 2 applications, more stringent requirements on the response times have, in general, been specified in such applications. (It should be noted, however, that minimum performance requirements for manifolds and/or sampling lines etc are given in Appendix 5).

3.2.2 CAMs should have response times to positive and negative changes in concentration which are the same within a specified criterion (Table 4.2) to ensure fast fluctuations of air-quality concentrations are averaged correctly, and this criterion would be assessed during the tests - as prescribed in Appendix A1. A further test would therefore be performed on CAMs intended for Category 2 applications in order to determine the effect of rapid changes in the concentration of the pollutant concentration being measured (paragraphs A1.1.33-A1.1.38).

3.3 AVERAGING TIMES

3.3.1 Most of the performance requirements given in this document apply to results produced by CAMs that are averaged values of the pollutant concentration over a period which is defined in this document as T_a . In cases where the CAM internally produces averaged results and where the averaging period T_a is selectable, then it

would be selected by the CAM manufacturer, or supplier, in conjunction with the MCERTS Certification Committee and the test house(s). Under normal operation the averaging period is usually selected to allow the averages required for reporting the results to be readily calculated, and also, where requested, to allow short-term variations of the pollutant concentration to be observed. In most cases the averaging times given in Table 3.1 should be used. The settings actually used will be stated on the MCERTS Certificate when certification is granted.

Table 3.1: Examples of Reported Averaging Times and Averaging Times used in the UK

Pollutant	Reported Averaging Time (T _{av} [*])	Typical Averaging Time (T _{av} [*]) (also sampling time for metals, benzene and PAH CAMs)
Benzene	Running annual mean	1 hour
Carbon Monoxide	Running 8-hour mean	15 min
Lead	Annual mean	24 hour
Nitrogen Dioxide	1 hour mean	15 min
	Annual mean	
Ozone	Running 8-hour mean	15 min
Particulates (PM ₁₀)	Running 24-hour mean	15 min
Sulphur Dioxide	15 minute mean	15 min

*defined in Appendix A1.

3.4 CERTIFICATION RANGE

- 3.4.1 The CAM manufacturer, or supplier, shall specify and agree with the relevant MCERTS Certification Committee, for each pollutant concentration to be measured, a "certification range" of concentrations over which the CAM is to be tested for each determinand.
- 3.4.2 Each certification range would comprise a range which is 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.
- 3.4.3 Typical values of the certification range are given in Table 3.2, for each application category specified in paragraph 2.4.1. These ranges are recommended unless the CAM manufacturer, or supplier, and the Certification Committee agree that there is a strong justification for selecting different ranges. If a manufacturer, or supplier, wishes to demonstrate performance over different ranges from the agreed certification range, additional testing would be required for each range. CAMs measuring CO, O₃ and particulates should generally be tested only in Category 2 situations. This is because for O₃ and particulate CAMs Category 2 testing is also appropriate for Category 1 applications, and because for CO no low concentration (non urban) limit values have currently been defined or proposed.

- 3.4.4 If testing is required in situations where no limit value is defined, the testing range should be as specified in Table 3.2, and the performance standards should be defined with respect to 80% of the maximum testing range.
- 3.4.5 Where the CAM has user-selectable settings (for example range) these would be chosen by the CAM manufacturer, or supplier, and agreed with the Certification Committee in conjunction with the test house(s), to be appropriate to the certification range. It is likely that, in practice the CAM range selected would be similar to the certification range, although this is not essential. However, the CAM would be tested only over the certification range. The CAM settings, once chosen, will not be altered during the tests. If certification is granted the settings used will be stated on the MCERTS Certificate.
- 3.4.6 Auto-ranging CAMs would not have their ranges adjusted in any way by the test house(s) during the tests. The MCERTS 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 CAM may have switched during the tests. If the CAM manufacturer, or supplier, wishes to certify the CAM at specific internal range settings, separate tests shall be performed, using agreed certification ranges. Where the output of an auto-ranging CAM 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.

Table 3.2: Typical Certification Ranges for Different Applications

	Category 1		Category 2	
	Scale min.	Scale max.	Scale min.	Scale max.
NO	0.0 ppb	200 ppb	0.0 ppb	2000 ppb
NO _x	0.0 ppb	200 ppb	0.0 ppb	2000 ppb
SO _x	0.0 ppb	200 ppb	0.0 ppb	2000 ppb
CO	0.0 ppm	10 ppm	0.0 ppm	50 ppm
O ₃	0.0 ppb	500 ppb	0.0 ppb	500 ppb
PM ₁₀	0.0 µg.m ⁻³	250 µg.m ⁻³	0.0 µg.m ⁻³	1000 µg.m ⁻³
PM _{2.5}	0.0 µg.m ⁻³	250 µg.m ⁻³	0.0 µg.m ⁻³	1000 µg.m ⁻³

Category 1 - Rural and Remote Sites

Category 2 - Urban Background/Centre, Suburban, Kerbside, Roadside and Industrial Sites

- 3.4.7 The MCERTS Certificate will list all the ranges certified, the CAM settings used, and will state explicitly the performance characteristics tested and the application category for which each range is certified for, together with any relevant limit value (where applicable).
- 3.5 ZERO AND SPAN DRIFT**
- 3.5.1 During field tests, the measurement of both the twenty-four hour and the long-term drift will be made by supplying certified zero and calibration gases externally to the sampling port of the CAM.

3.5.2 In addition, it is recommended that the CAM should, where possible, have associated with it a methodology, using either an automated or a manual method, whereby the zero drift and span drift of the complete system can be measured as far as practical. A description of the methodology used by the CAM to determine these drifts shall be provided by the CAM supplier or manufacturer. This will be assessed during the field tests. In cases where it is not possible for the internal zero and span system to determine the total drift which arises from all the components of the CAM, the Certification Committee will include a statement to this effect on the Certificate.

3.6 NO_x ANALYSERS

3.6.1 NO₂ is not directly measured by most current nitrogen-oxide CAMs, but instead is obtained by subtracting the measured NO concentration from the measured NO_x concentration. The performance characteristics for NO₂ will generally be derived from the measured NO and NO_x performance characteristics. To measure the performance characteristics for the NO and NO_x channels, NO test gas would be used for all tests except the accuracy test for which both NO and NO₂ calibration gases will be used.

3.6.2 During the averaging tests, the NO_x and NO channels will be monitored to check if the CAM is reporting negative NO₂ concentrations (paragraphs A1.1.33-A1.1.38).

3.6.3 Under typical atmospheric conditions where the NO₂ concentration approaches the limit value concentration, the concentration of NO is typically 5 to 6 times the NO₂ concentration. Therefore, when testing the CAM's performance characteristics with NO test gas, this will be done at a NO concentration of about 600 ppb. This applies to the following tests: the averaging effect, the cross sensitivity and the NO accuracy. The NO₂ accuracy test will be performed at the limit value concentration.

3.7 SAMPLING LINE, SAMPLING MANIFOLD, AND PARTICULATE FILTER

(i) Sampling line and manifold

3.7.1 Sampling manifolds will not be tested. Appendix 5, however, provides minimum requirements for the design of manifolds and sample lines.

(ii) Particulate filter.

3.7.2 A particulate filter is generally required to precondition the sample before it enters the analytical unit of the CAM. This particulate filter should retain all particulate matter likely to alter the performance of the CAM analytical unit. The filter housing should be constructed so that it does not retain or convert the determinand(s) of interest. Tests of the CAM will be carried out with this particulate filter included, where it is required.

3.8 CROSS-SENSITIVITY TO INTERFERING SUBSTANCES

3.8.1 The CAMs response to gases which may be present in the atmosphere other than the determinand gas will be tested. Possible interferent gases and their test concentrations

are given in Appendix 9. These concentrations have been set at levels that might be expected to be found at the different measurement category locations.

- 3.8.2 Cross-sensitivity tests would be performed using both binary mixtures of each interferent 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 is to test the assumption of additivity of the CAM's cross-sensitivity response.
- 3.8.3 Samples containing just the determinand gas at the limit concentration would be introduced to the CAM to provide a reference response.

4. THE INSTRUMENT PERFORMANCE STANDARDS

4.1 INTRODUCTION

- 4.1.1 This Section presents the proposed MCERTS Performance Standards for CAMs. These have been chosen such that a CAM meeting the MCERTS Standards, if calibrated and operated correctly, would be able to satisfy the measurement uncertainty requirements given in the Air Quality Daughter Directives of the EC Framework Directive 92/96. These requirements are expressed as the maximum allowable percentage expanded uncertainty at the EU limit values for the pollutant concentrations concerned.
- 4.1.2 As noted in Section 2.2, the Performance Standards are based on the limit values given in Table 2.2, which are based on information from CEN standardisation work where this is available. If different limit values are subsequently defined, the Performance Standards would be reviewed and amended as appropriate. The Performance Standards are expressed as expanded measurement uncertainties at a 95% confidence interval, in keeping with international procedures.
- 4.1.3 The Performance Standards are expressed in absolute concentration units, and for completeness, are also provided as percentages of the limit values given in Table 2.2.
- 4.1.4 Detailed descriptions of the performance characteristics covered in this document are given in Appendix 1 to enable the reader to have a clear concise view of all of the individual Performance Standards. In each of the Performance Standards tables, the second column refers the reader to the appropriate descriptions in Appendix 1. Appendix 1 also includes outlines of the proposed test procedures.

4.2 PERFORMANCE STANDARDS FOR CONTINUOUS AMBIENT AIR QUALITY MONITORING INSTRUMENTS MEASURING SO₂, NO_x, O₃ & CO

(i) Background

- 4.2.1 CAMs that are used for monitoring SO₂, NO_x, O₃ and CO, draw in a sample of ambient air usually from a manifold, into an analytical system where the concentration of the relevant pollutant is measured. For NO_x monitoring systems, however, a catalytic converter is used to reduce NO₂ to NO, and two measurements of NO are made, with and without the converter, to allow the NO₂ concentration to be

determined by difference. It is recognised that most NO_x monitors will be sensitive to certain nitrogen oxide species other than NO and NO₂. However, these other species will be at much lower concentrations in nearly all of the scenarios in which these Performance Standards are applicable.

(ii) Performance Characteristics Determined by Laboratory Tests

4.2.2 The performance characteristics and related Performance Standards that would be determined under laboratory conditions are given in Tables 4.1a, 4.1b and 4.2. Tables 4.1a and 4.1b list the Performance Standards common to both operational categories (see paragraph 2.4.1). Table 4.2 lists the Performance Standards that are dependent on operational category.

4.2.3 The Performance Standards given in Tables 4.1a, 4.1b and 4.2 are the maximum allowable for any CAM for individual performance criteria. The final row in Tables 4.1a and 4.1b show the additional overarching combined Performance Standard, which shall be derived by combining each of the relevant individual measured performance characteristics for any given CAM (see paragraphs 2.3.1-2.3.2 and Appendix 1).

**Table 4.1a part 1: Performance Standards for CAMs Measuring SO₂, NO_x, O₃, and CO
(Laboratory Tests):
Expressed in Absolute Concentration Units**

Performance characteristic	Cross reference to test description in Appendix A1.1	Expanded Uncertainty (at 95% confidence interval)	Performance Standard (Expressed at 95% confidence interval)			
			SO ₂	NO _x , NO ⁽¹⁾	O ₃	CO
drift (12 hours) zero and span	iv, ii		<= ±4 ppb	<= ±2 ppb	<= ±2ppb	<= ±0.3 ppm
repeatability	ii	U _{sp}	<= ±13 ppb	<= ±7 ppb	<= ±5 ppb	<= ±0.9 ppm
accuracy	iii	U _A	<= ±13 ppb	<= ±7 ppb	<= ±5 ppb	<= ±0.9 ppm
averaging effect	v	U _{AV}	<= ±13 ppb	<= ±7 ppb	<= ±5 ppb	<= ±0.9 ppm
linearity	vi	U _L	<= ±13 ppb	<= ±7 ppb	<= ±5 ppb	<= ±0.9 ppm
cross sensitivity	vii	U _C	<= ±13 ppb	<= ±7 ppb	<= ±5 ppb	<= ±0.9 ppm
converter efficiency	viii	U _{CI}	N/A	<= 98%	N/A	N/A
effect of sample pressure change (Δ _p = +3%)	ix	U _{SP}	<= ±13 ppb	<= ±7 ppb	<= ±5 ppb	<= ±0.9 ppm
effect of sample temperature (ΔT = 10°C)	ix	U _{ST}	<= ±13 ppb	<= ±7 ppb	<= ±5 ppb	<= ±0.9 ppm
zero shift due to ambient temperature change of 10°C (ΔT = 10°C)	ix	U _{TZ}	<= ±13 ppb	<= ±7 ppb	<= ±5 ppb	<= ±0.9 ppm
span shift due to ambient temperature change of 10°C (ΔT = 10°C)	ix	U _{TS}	<= ±13 ppb	<= ±7 ppb	<= ±5 ppb	<= ±0.9 ppm
Combined Performance Characteristic ⁽²⁾	xii	U _c , U _e	<= ± 20 ppb	<= ± 11 ppb	<= ± 7.5 ppb	<= ± 1.3 ppm

Table 4.1a part 2: Other Minimum Operational Requirements

Instrument settings and requirements	Cross reference to test description in Appendix A1.1	Operating Range			
		SO ₂	NO _x , NO ⁽¹⁾	O ₃	CO
operational temperature range (°C)	x	5 to 40	5 to 40	5 to 40	5 to 40
operational humidity range (%RH)	x	20 to 80	20 to 80	20 to 80	20 to 80
NO ₂ converter temperature	viii	N/A	< 400°C	N/A	N/A

⁽¹⁾ NO_x CAMs would normally be tested over the complete range of laboratory tests using NO. However, both NO_x and NO channels would be recorded and performance standards would apply to both channels. For the accuracy test, tests will be carried out using both NO and NO₂ calibration gases, and both results will be reported. (See section 3.6.)

⁽²⁾ Expressed as an expanded uncertainty, having a 95% confidence interval.

**Table 4.1b part 1: Performance Standards for CAMs Measuring SO₂, NO_x, O₃, and CO
(Laboratory Tests):
Expressed as a Percentage of the Limit Value (Table 2.2)**

Performance characteristic	Cross reference to test description in Appendix A1.1	Expanded Uncertainty (at 95% Confidence interval)	Performance Standard (Expressed at 95% confidence interval)			
			SO ₂	NO _x , NO ⁽¹⁾	O ₃	CO
drift (12 hours) zero and span	ii, iv		≤3.3%	≤2.3%	≤3.3%	3.3%
repeatability	ii	U _{rn}	≤10%	≤7%	≤10%	≤10%
accuracy	iii	U _A	≤10%	≤7%	≤10%	≤10%
averaging effect	v	U _{AV}	≤10%	≤7%	≤10%	≤10%
linearity	vi	U _L	≤10%	≤7%	≤10%	≤10%
cross sensitivity	vii	U _C	≤10%	≤7%	≤10%	≤10%
effect of sample pressure change (Δp = +3%)	ix	U _{SP}	≤10%	≤7%	≤10%	≤10%
effect of sample temperature (ΔT = 10°C)	ix	U _{ST}	≤10%	≤7%	≤10%	≤10%
zero shift due to ambient temperature change of 10°C (ΔT = 10°C)	ix	U _{TZ}	≤10%	≤7%	≤10%	≤10%
span shift due to ambient temperature change of 10°C (ΔT = 10°C)	ix	U _{TS}	≤10%	≤7%	≤10%	≤10%
Combined Performance Characteristic ⁽²⁾	xii	U _c , U _{c'}	≤±15%	≤±15%	≤±15%	≤±15%

Table 4.1b part 2: Other Minimum Operational Requirements

Instrument settings and requirements	Cross reference to test description in Appendix A1.1	Operating Range			
		SO ₂	NO _x , NO ⁽¹⁾	O ₃	CO
operational temperature range (°C)	x	5 to 40	5 to 40	5 to 40	5 to 40
operational humidity range (%RH)	x	20 to 80	20 to 80	20 to 80	20 to 80
NO ₂ converter temperature	viii	N/A	< 400°C	N/A	N/A

⁽¹⁾ NO_x CAMs would normally be tested over the complete range of laboratory tests using NO. However, both NO₂ and NO channels would be recorded and performance standards would apply to both channels. For the accuracy characteristic, the test would be carried out using both NO and NO₂, and both results reported.

⁽²⁾ Expressed as an expanded uncertainty, with a 95% confidence interval.

Table 4.2 Performance Standards which are Dependent on Operational Category⁽¹⁾

Performance characteristic	Cross reference to test description in Appendix A1.1	Expanded Uncertainty (95% confidence interval)	Pollutant Species	Operational Category 1 ⁽¹⁾	Operational Category 2 ⁽¹⁾ (at 95% confidence interval)
Response Times ⁽²⁾ RT _{rise} and RT _{fall}	i		SO ₂ , NO _x , NO, O ₃ , CO	< 220 seconds	< =120 seconds
Detection limit	iv iv		SO ₂	0.5 ppb	1 ppb
			NO	0.5 ppb	1 ppb
			NO _x	0.5 ppb	1 ppb
			O ₃	0.5 ppb	1 ppb
			CO	0.1 ppm	0.1 ppm
Quantification limit	iv iv		SO ₂	1 ppb	2 ppb
			NO	1 ppb	2 ppb
			NO _x	1 ppb	2 ppb
			O ₃	1 ppb	2 ppb
			CO	0.2 ppm	0.2 ppm
Averaging effect	v	U _{AV}	SO ₂ , NO _x , NO, O ₃ , CO	none specified	<= 5%

¹ Operational categories are defined in paragraph 2.2.1

² The following additional condition shall also apply with respect to response times:

$$\frac{RT_{rise} - RT_{fall}}{RT_{rise}} < 10\% \quad \text{eq 4.1}$$

(iii) Performance Characteristics Determined by Field Tests

4.2.5 The performance characteristics and related Performance Standards for CAM systems that would be determined under field conditions are given in Tables 4.3a and 4.3b.

**Table 4.3a part 1: Performance Standards for CAMs Measuring SO₂, NO_x, O₃ and CO
(Field Tests):
Expressed in Absolute Concentration Units**

Performance characteristic	Cross reference to test description in Appendix A1.2	Expanded Uncertainty at 95% confidence interval	Performance Standards (Expressed at 95% confidence interval)				
			NO	NO _x	SO ₂	CO	O ₃
zero drift (24 hours)	iv		±5 ppb	±5 ppb	±9 ppb	±0.6 ppb	±3.5 ppb
span drift (24 hours)	vii		±5 ppb	±5 ppb	±9 ppb	±0.6 ppb	±3.5 ppb
zero drift (over maintenance interval) ¹	v	U _{ZM}	±7 ppb	±7 ppb	±13 ppb	±0.6 ppb	±5 ppb
span drift (over maintenance interval) ¹	viii	U _{SM}	±7 ppb	±7 ppb	±13 ppb	±0.9 ppb	±5 ppb

¹ These zero and span drifts will be determined as the drift measured over the maintenance period. The maintenance period will be determined as defined in A1.2 ii (see table 4.3a part 2 below).

Table 4.3a part 2: Other Minimum Operational Requirements

Instrument requirements	Cross reference to test description in Appendix A1.2	Expanded Uncertainty (95% confidence interval)	Performance Standards				
			NO	NO _x	SO ₂	CO	O ₃
field repeatability	i	U _R	±7 ppb	±7 ppb	±13 ppb	±0.9ppm	±5 ppb
maintenance interval	ii		≥14 days*	≥14 days*	≥14 days*	≥14 days*	≥14 days*
converter efficiency	x		N/A	≥ 95%	N/A	N/A	N/A
cross sensitivity to 1ppm m-xylene	x		N/A	N/A	≤ 5ppb	N/A	N/A
availability (data capture)	ix		90%	90%	90%	90%	90%

*Actual maintenance interval will be reported on the MCERTS Certificate.

**Table 4.3b part 1: Performance Standards for CAMs Measuring SO₂, NO_x, O₃ and CO
(Field Tests):
Expressed as Percentage of the Limit Value (Table 2.2)**

Performance characteristic	Cross reference to test description in Appendix A1.2	Expanded Uncertainty (95% confidence)	Performance Standard Expressed at 95% confidence interval				
			NO	NO _x	SO ₂	CO	O ₃
zero drift (24 hours)	iv		≤±5%	≤±5%	≤±7%	≤±7%	≤±7%
span drift (24 hours)	vii		≤±5%	≤±5%	≤±7%	≤±7%	≤±7%
zero drift (over maintenance interval) ¹	v	U _{ZM}	≤±7%	≤±7	≤±10%	≤±10%	≤±10%
span drift (over maintenance interval) ¹	viii	U _{SM}	≤±7%	≤±7%	≤±10%	≤±10%	≤±10%

¹ These zero and span drifts will be determined as the drift measured over the maintenance period. The maintenance period will be determined as defined in A1.2 ii (see table 4.3b part 2 below).

Table 4.3b part 2: Other Minimum Operational Requirements

Instrument requirements	Cross reference to test description in Appendix A1.2	Expanded Uncertainty (95% confidence)	Performance Standards				
			NO	NO _x	SO ₂	CO	O ₃
field repeatability	i	U _r	< 7%	< 7%	< 10%	< 10%	< 10%
maintenance interval	ii		≥14 days*	≥14 days*	≥14 days*	≥14 days*	≥14 days*
converter efficiency	x		N/A	≥ 95%	N/A	N/A	N/A
cross sensitivity to 1ppm m-xylene	x		N/A	N/A	≤ 5ppb	N/A	N/A
availability (data capture)	ix		90%	90%	90%	90%	90%

* Actual maintenance interval will be reported on the MCERTS Certificate.

4.3 PERFORMANCE STANDARDS FOR PARTICULATE MATTER (PM₁₀ & PM_{2.5})

(i) Background

4.3.1 Particulate monitoring CAMs collect particulate material over a defined averaging period (T_a) and either:

- dynamically determine the incremental mass increase; by direct mass measurement, or by a surrogate technique - eg by using a Tapered Element Oscillating Microbalance (TEOM) or a β-attenuation gauge;

- or retain the collected material for subsequent analysis (weighing);

4.3.2 The sampling system is inherent to gravimetric particulate monitors as they require size-selective sampling heads to collect preferentially particulate material according to its aerodynamic size. Two categories of particulate material are currently monitored, PM₁₀ and PM_{2.5}. These refer to the aerodynamic size of ambient particulates collected with sampling heads for which a 50% cut-off is achieved.

(ii) Performance Characteristics Determined by Laboratory Tests

4.3.3 The performance characteristics and related Performance Standards for particulate monitors that would be determined under laboratory conditions are given in Tables 4.4a and 4.4b.

4.3.4 The laboratory testing would be carried out using a Laboratory Particulate Generator (LPG) which can provide well-characterised and reproducible particulate size distributions with a mass concentration variable from 0 µg.m⁻³ to 500 µg.m⁻³ at a gas flow velocity of between 1.0 m.s⁻¹ and 10 m.s⁻¹.

4.3.5 No span drift test is specified in the laboratory particulate tests, due to the difficulty of running a LPG continuously with the required particle loading for a period of twelve hours (the period used in the tests on gaseous CAMs).

**Table 4.4a part 1: Performance standards for CAMs Measuring PM₁₀ and PM_{2.5}
(Laboratory Tests):
Expressed in Absolute Concentration Units**

Performance characteristic	Cross reference to test description in Appendix A1.3	Expanded Uncertainty (at 95% confidence interval)	Performance Standard (Expressed at 95% confidence interval)
response time (when reported)	i		≤ 220 seconds
detection limit	ii		$\leq 0.1 \mu\text{g.m}^{-3}$
quantification limit	ii		$\leq 0.2 \mu\text{g.m}^{-3}$
zero drift (12 hours)	iii		$\leq \pm 1.7 \mu\text{g.m}^{-3}$
repeatability	iv	U_{sp}	$\leq \pm 5 \mu\text{g.m}^{-3}$
accuracy	v	U_A	$\leq \pm 5 \mu\text{g.m}^{-3}$
linearity	vi	U_L	$\leq \pm 5 \mu\text{g.m}^{-3}$
cross sensitivity to composition of dust	vii	U_I	$\leq \pm 8 \mu\text{g.m}^{-3}$
zero shift due to ambient temperature change of 1°C ($\Delta T = 10^\circ\text{C}$)	viii	U_{tz}	$\leq \pm 5 \mu\text{g.m}^{-3}$
flow	ix	U_p	$\leq \pm 1 \mu\text{g.m}^{-3}$
Combined Performance Characteristic ⁽¹⁾	x	U_c, U_e	$\leq \pm 12.5 \mu\text{g.m}^{-3}$

⁽¹⁾ Expressed as an expanded uncertainty, with a 95% confidence interval.

Table 4.4a part 2: Other Minimum Operational Requirements

Instrument settings and requirements	Cross reference to test description in Appendix A1.3	Expanded Uncertainty at 95% confidence interval	Operating Range
operational temperature range (°C)	viii	n/a	5 to 40
operational humidity range (%RH)	viii	n/a	20 to 80

**Table 4.4b part 1: Performance Standards for CAMs Measuring PM₁₀ and PM_{2.5}
(Laboratory Tests):
Expressed as Percentage of Limit Value (Table 2.2)**

Performance characteristic	Cross reference to test description in Appendix A1.3	Expanded Uncertainty (95% confidence)	Performance Standard (95% confidence interval)
response time (when reported)	i		≤ 220 seconds
detection limit	ii		$\leq 0.2\%$
quantification limit	ii		$\leq 0.4\%$
zero drift (12 hours)	iii		$\leq \pm 3.3\%$
repeatability	iv	U_{SD}	$\leq \pm 10\%$
accuracy	v	U_A	$\leq \pm 10\%$
linearity	vi	U_L	$\leq \pm 10\%$
cross sensitivity to composition of dust	vii	U_I	$\leq \pm 16\%$
zero shift due to ambient temperature change of 1°C ($\Delta T = 10^\circ C$)	viii	U_{TZ}	$\leq \pm 10\%$
flow	ix	U_F	$\leq \pm 2\%$
Combined Performance Characteristic ⁽¹⁾	x	U_c U_c	$\leq \pm 25\%$

⁽¹⁾ Expressed as an expanded uncertainty, with a 95% confidence interval.

Table 4.4b part 2: Other Minimum Operational Requirements

Instrument settings and requirements	Cross reference to test description in Appendix A1.3	Expanded Uncertainty at 95% confidence interval	Operating Range
operational temperature range (°C)	viii	n/a	5 to 40
operational humidity range (%RH)	viii	n/a	20 to 80

(iii) **Performance Characteristics Determined by Field Tests**

4.3.8 The performance characteristics and related Performance Standards for particulate monitors that would be determined under field conditions are given in Table 4.5.

Table 4.5: Performance Standards for CAMs Measuring PM₁₀ and PM_{2.5} (Field Tests)

Performance characteristic	Cross reference to test description in Appendix A1.4	Expanded Uncertainty (95% confidence interval)	Performance Standard Expressed at (95% confidence interval)
Repeatability in the field	i	U _{3D}	<5 µg.m ⁻³ for mean concentrations <100 µg.m ⁻³ <5 % for mean concentrations >100 µg.m ⁻³
maintenance interval	v		>= 14 days
zero drift (24 hours)	ii		<= ±7% C _{limit}
span drift (24 hours)	iii		<= ±7% C _{limit}
zero drift (over maintenance interval) ¹	ii	U _{2M}	<= ±10% C _{limit}
span drift (over maintenance interval) ¹	iii	U _{3M}	<= ±10% C _{limit}
Accuracy with respect to CEN reference method EN12341	iv	U _{PA}	<10 µg.m ⁻³ for mean concentrations <100 µg.m ⁻³ <10 % relative for mean concentrations >100 µg.m ⁻³
availability (data capture)	vi		90%

C_{limit} = Concentration at Limit Value

1 These zero and span drifts will be determined as the drift measured over the maintenance period. The maintenance period will be determined as defined in A1.2 ii (see table 4.3a part 2 below).

4.4 PERFORMANCE STANDARDS FOR METALS-MEASURING CAMS

(i) Background

4.4.1 Airborne particles containing heavy metals (lead, cadmium, arsenic, nickel and mercury) are collected by drawing a measured volume of air through a filter mounted in a sampler designed to collect the PM₁₀ (or PM_{2.5}) fraction of the total suspended particulate matter in ambient air. The proposed Performance Standards refer only to the collection of the particulate matter, and do not cover its subsequent analysis (as this is not a part of the MCERTS product-certification). It is also judged that the valid collection of particulate matter with the required measurement uncertainty should serve as a satisfactory analogue for the collection of the metals content. If the particulate matter is collected satisfactorily the metals content would be sampled equivalently.

(ii) Performance Characteristics Determined by Laboratory Tests

4.4.2 CAMs monitoring metals should comply with all the performance requirements detailed in section 4.3 relating to the collection of particulate matter. However, it should be noted that the combined performance characteristic for heavy-metal

samplers would be determined slightly differently to those for PM₁₀ and PM_{2.5} (see paragraph 4.4.6 and Appendix A1.3.20).

- 4.4.3 In the case of metals-measuring CAMs the choice of filter medium is particularly important. The following requirements on the background content of metals within the filters used are therefore provided as guidance.
- 4.4.4 Only those filter media that retain $\geq 0.3 \mu\text{m}$ diameter particulates with an efficiency of $>99\%$ should be employed. All filter materials should have a low metal background content, as defined in Table 4.6. In addition, the handling and conditioning of filters must be carried out according to rigorous conditions.

Table 4.6: Maximum Blank Levels of Selected Heavy Metals on PTFE Filters

Metal	Blank levels of metal on filter (ng.cm ⁻²)	Background level ⁽¹⁾ on 47mm filter (ng)
Pb	2.0	35
As	0.8	14
Ni	0.3	6
Cd	0.7	10
Hg	0.4	7

(1) Background levels derived from one week samples and a sample flow of 16.7 l.min⁻¹.

- 4.4.5 Filters made from other media, (eg cellulose nitrate, quartz fibre or glass) are not recommended due to their relatively-high heavy-metal content.
- 4.4.6 The required total uncertainty for the measurement of metals content is $\pm 25\%$, and this is comprised of the combined uncertainty both of the sample collection and the subsequent laboratory analysis. Therefore, the MCERTS Standard for the combined performance characteristic for metals-measuring CAMs is more stringent than that required for particulate monitors, because in the latter there is no analysis stage contributing to the overall uncertainty. Uncertainties in laboratory analysis of particulate metals collected on filters should be better than $\pm 10\%$ (95% confidence interval).

(iii) Performance Characteristics Determined by Field Tests

- 4.4.7 Table 4.7 lists the performance characteristics and the related Performance Standards for the metal monitoring systems that would be determined under field conditions.

**Table 4.7: Performance Standards for CAMs Used to Measure Metals
(Field tests)**

Performance characteristic	Cross reference of test description in Appendix A1.6	Expanded Uncertainty (at 95% confidence interval)	Performance Standard Expressed at 95% confidence interval
field repeatability	i	U_R	$< 10\% LV^*$
flow stability	iii	U_{FS}	$\leq \pm 2\% LV^*$
flow accuracy	iv	U_{FA}	$\leq \pm 2\% LV^*$
combined performance characteristic ¹	i (A1.5)	$U_c U_c'$	$\leq \pm 25\% LV^*$

* LV = Limit Value

¹ including uncertainty of laboratory analysis

4.4.8 As noted above the performance of the analysis of sampled material for metals content is not within the scope of MCERTS product-certification, but recommendations are given in Appendix 6 for analysis of heavy-metals content.

4.5 PERFORMANCE STANDARDS FOR CAMS MEASURING POLY-AROMATIC HYDROCARBONS

(i) Background

4.5.1 The effects of exposure to PAHs are apparent only over the long term and are cumulative in effect. As a result, PAH ambient air-quality standards are set in terms of annual mean concentrations. This means that PAH measurements need to provide an estimate of the annual mean concentration without any requirement to provide measures of the short-term variability. This requirement can be satisfied using one of three different sampling strategies:

- the concentration is measured over a twenty-four hour sampling period on every sixth day to provide an estimate of the annual mean (at limited expense);
- the concentration is measured over consecutive twenty-four hour sampling periods over the year to give the annual mean directly (at greater expense);
- the concentration is measured over either seven or fourteen-day consecutive sampling periods over a year to give the annual mean.

4.5.2 There are a large number of PAHs present in the atmosphere and the epidemiological effects of all these PAHs are not yet known. Measurement and regulation of all of them is considered impractical at present. In consequence, air quality standards have generally been written in terms of benzo[a]pyrene, one of the less volatile but more carcinogenic of the PAHs. As a result, the only PAH of interest for routine air quality monitoring may be benzo[a]pyrene. The greatest problems are, however, with collecting and retaining the more volatile PAHs, eg particularly naphthalene. There may be requirements in future for the measurements of other PAHs.

- 4.5.3 The manufacturer, or supplier, of the CAM which measures PAHs will agree with the MCERTS Certification Committee the specific PAH species and the concentration range over which product-certification is sought, and species and range over which MCERTS Certification is granted will be reported in the Certificate.
- 4.5.4 PAH identification and quantification are not part of the scope of this document. However, it does affect the requirements for sampler design. This is because where isotope dilution with mass spectrometry is used, (normally gas chromatography-mass spectrometry (GC-MS)) corrections may be made for losses during sampling. However, correction for sample losses are not possible if analysis is carried out using high-performance liquid chromatography (HPLC).
- 4.5.5 The sampler designs and operating conditions for these approaches vary and the proposed MCERTS Performance Standards have been written to reflect this.
- 4.5.6 PAHs are collected by drawing a measured volume of air through a sampling medium. The sampling media used are designed to collect both the particle and volatile fraction of the PAHs in the ambient sample. The techniques used are normally a combination of a filter and an adsorbent layer - eg XAD-2 resin and polyurethane foam respectively. The inlet to the sampler will be size selective in its particle collection behavior. However, PAHs are predominantly associated with fine particles of typically 1-10 μm aerodynamic-diameter which most samplers are efficient at collecting.

(ii) Performance Characteristics Determined by Laboratory Tests

- 4.5.7 No EU Limit Value is currently specified for PAHs, and there is also no UK NAQS for these species. Therefore, the manufacturer, or supplier of a CAM for measurements of PAHs shall agree with the relevant MCERTS Steering Committee the measurement range for which certification is required. This will be reported on the Certificate.
- 4.5.8 There are currently no specified overall measurement uncertainty requirements in Europe for the reporting of PAH concentrations. Therefore, the combined performance characteristic does not include any requirement on the uncertainty of the laboratory analysis, and this overall performance characteristic applies to the sampling alone.
- 4.5.9 The performance characteristics and related MCERTS Performance Standards for PAH monitors that would be determined under laboratory conditions are given in Table 4.8. It should be noted that additional tests would be made in the laboratory on the efficiency of filter materials for the collection and retention of PAHs, and recommended tests to address this question are outlined in Appendix 1.7.
- 4.5.10 As sampling is carried out over at least a twenty-four hour period, measurements of response time and short-term drift (12 hour) are not required.

Table 4.8: Performance Standards for PAHs (Laboratory tests)

Performance characteristic	Cross reference of test description in Appendix A1.7	Expanded Uncertainty (at 95% confidence interval)	Performance Standard Expressed at 95% confidence interval
Sampling efficiency	i	U_{SE}	$\leq \pm 25\% LV^*$
Retention efficiency	i	U_{RE}	$\leq \pm 25\% LV^*$
Detection limit for 24 hr sample time	ii	U_D	18 ng (equivalent to 0.05 ng/m ³ drawn at 15m ³ per hour for 24 hrs)
Combined performance ¹	iii	U_c U_c'	$\leq \pm 25\%/LV^*$

* Expressed as percentage of LV = Limit Value (not yet defined in a European Directive) or as a percentage of an other agreed measurement range

¹ The uncertainty of the laboratory analysis of PAHs is not included.

(iii) Performance Characteristics Determined by Field Tests

4.5.11 Table 4.9 specifies the performance characteristics and related Performance Standards for PAH monitors that would be determined under field conditions.

Table 4.9: Performance Standards for PAHs (Field tests)

Performance characteristic	Cross reference of test description in Appendix A1.8	Expanded Uncertainty (at 95% confidence interval)	Performance Standard Expressed at 95% confidence interval
field repeatability	i	U_R	$< 10\% LV^*$
Sample retention capacity ¹	ii	U_{RC}	40 - 140 % LV [*]
flow accuracy	iv	U_{FA}	$\leq 10\% LV^*$
flow stability	v	U_{FS}	$\leq 10\% LV^*$

* LV = Limit Value (not yet defined in a European Directive)

¹ See Appendix A1.8.4-A1.8.6 for full specification of this Performance Standard

4.5.12 The performance of the analysis of sampled material for PAH content is not within the scope of the MCERTS product-certification Scheme. Recommendations for the analysis of collected PAH samples are, however, given in Appendix 7.

4.6 PERFORMANCE STANDARDS FOR BENZENE MONITORING SYSTEMS

(i) Background

4.6.1 These tests apply to cyclic automated CAMs that draw in a known volume of air through an adsorbant tube for a defined time, and then analyse the amount of benzene trapped on the adsorbant. The sampling period T_s would not be exactly the same as the time of absorption on the adsorbant tube. The effect on the CAM of rapidly varying atmospheric concentrations would therefore be tested as described in Appendix 1 in order to assess that there is correct averaging of varying concentrations.

Tests for long-term sampling CAMs, which do not analyse samples on-line, are not covered in this document.

- 4.6.2 The time coverage factor of the CAM and the fraction of time that ambient air is sampled would be calculated and stated on the Certificate.
- 4.6.3 As these CAMs use an absorbent to collect the sample before analysis, the effect of desorption inefficiencies would be assessed by measuring the amount of benzene carried over into a subsequent blank run.
- (ii) **Performance Characteristics Determined by Laboratory Tests**
- 4.6.4 The instrument performance standards for benzene monitoring CAMs are given in Table 4.10a and b.

**Table 4.10a part 1: Performance Standards for Benzene
(Laboratory Tests),
Expressed in Absolute Concentration Units**

Performance characteristic	Cross reference to test description in Appendix A1.9	Expanded Uncertainty (at 95% confidence interval)	Performance Standard expressed at 95% confidence interval
drift (12hours)			$\leq \pm 0.07$ ppb
detection limit	i		≤ 0.005 ppb
quantification limit	i		≤ 0.01 ppb
carry over	ii	U_c	$\leq \pm 0.07$ ppb
repeatability	ii	U_{rn}	$\leq \pm 0.33$ ppb
accuracy	iii	U_A	$\leq \pm 0.33$ ppb
averaging effect	iv	U_{Av}	$\leq \pm 0.33$ ppb
linearity	v	U_L	$\leq \pm 0.2$ ppb
cross sensitivity	vi	U_s	$\leq \pm 0.33$ ppb
effect of sample pressure (+3%)	vii	U_{sp}	$\leq \pm 0.33$ ppb
effect of sample temperature ($\Delta T = 10^\circ C$)	vii	U_{st}	$\leq \pm 0.33$ ppb
Combined Performance Characteristic ⁽¹⁾	viii	U_c, U_e	$\leq \pm 0.4$ ppb

⁽¹⁾ Expressed as an expanded uncertainty of the limit value concentration, with a 95% confidence interval.

Table 4.10a part 2: Other Minimum Operational Requirements

Instrument settings and requirements	Cross reference to test description in Appendix A1.9	Expanded Uncertainty (at 95% confidence interval)	Operational Range
operational temperature range ($^\circ C$)	vii	n/a	5 to 40
operational humidity range (%RH)	vii	n/a	20 to 80

**Table 4.10b part 1: Performance Standards for Benzene
(Laboratory Tests),
Expressed as Percentage of the Limit Value (Table 2.2).**

Performance characteristic	Cross reference of test description in Appendix A1.9	Expanded Uncertainty U (at 95% confidence interval)	Performance Standard expressed at 95% confidence interval
drift (12hours)			$\leq \pm 4\%$
detection limit / carry over	i		$\leq 0.3\%$
quantification limit	i		$\leq 0.6\%$
carry over	ii	U_c	$\leq \pm 4\%$
repeatability	ii	U_{rn}	$\leq \pm 20\%$
accuracy	iii	U_A	$\leq \pm 20\%$
averaging effect	iv	U_{AV}	$\leq \pm 20\%$
linearity	v	U_l	$\leq \pm 12\%$
cross sensitivity	vi	U_i	$\leq \pm 20\%$
effect of sample pressure (+3%)	vii	U_{sp}	$\leq \pm 20\%$
effect of sample temperature ($\Delta T = 10^\circ C$)	vii	U_{st}	$\leq \pm 20\%$
Combined Performance Characteristic ⁽¹⁾	viii	U_c	$\leq \pm 25\%$ of limit value

⁽¹⁾ Expressed as an expanded uncertainty, with a 95% confidence interval.

Table 4.10b part 2: Other Minimum Operational Requirements

Instrument settings and requirements	Cross reference to test description in Appendix A1.9	Expanded Uncertainty (at 95% confidence interval)	Operating Range
operational temperature range ($^\circ C$)	vii		5 to 40
operational humidity range (%RH)	vii		20 to 80

(iii) Performance Characteristics Determined by Field Tests

4.6.5 Table 4.11a and b specify the performance characteristics and related Performance Standards of benzene monitors that would be determined under field conditions.

**Table 4.11a part 1: Performance Standards for Benzene (Field Tests)
Expressed in Absolute Concentrations Units**

Performance characteristic	Cross reference of test description in Appendix A1.10	Expanded Uncertainty U (at 95% confidence interval)	Performance Standard
zero drift (24 hour)	iv		$\leq \pm 0.033$ ppb
zero drift (over maintenance interval) ¹	v	U_{2M}	$\leq \pm 0.066$ ppb
span drift (24 hours)	vii		$\leq \pm 0.033$ ppb
span drift (over maintenance interval) ¹	viii	U_{5M}	$\leq \pm 0.066$ ppb
zero signal	ix		$\leq \pm 0.033$ ppb

¹ These zero and span drifts will be determined as the drift measured over the maintenance period. The maintenance period will be determined as defined in A1.10 ii (see table 4.11a part 2 below).

Table 4.11a part 2: Other Minimum Operational Requirements

Instrument requirements	Cross reference to test description in Appendix A1.10	Expanded Uncertainty at 95% confidence interval	Performance Standards
field repeatability	i	U_r	< 0.33 ppb
maintenance interval	ii		≥ 14 days
availability (data capture)	x		90%

**Table 4.11b part 1: Performance Standards for Benzene (Field Tests)
Expressed as Percentage of the Limit Value (Table 2.2)**

Performance characteristic	Cross reference of test description in Appendix A1.10	Expanded Uncertainty U (at 95% confidence interval)	Performance Standard
zero drift (24 hour)	iv		$\leq \pm 2\%$
zero drift (over maintenance interval) ¹	v	U_{2M}	$\leq \pm 4\%$
span drift (24 hours)	vii		$\leq \pm 2\%$
span drift (over maintenance interval) ¹	viii	U_{5M}	$\leq \pm 4\%$
zero signal	ix		$\leq \pm 2\%$

¹ These zero and span drifts will be determined as the drift measured over the maintenance period. The maintenance period will be determined as defined in A1.10 ii (see table 4.11b part 2 below).

Table 4.11b part 2: Other Minimum Operational Requirements

Instrument requirements	Cross reference to test description in Appendix A1.10	Expanded Uncertainty at 95% confidence interval	Performance Standards
field repeatability	i	U_r	< 20%
maintenance interval	x		≥ 14 days
availability (data capture)	vii		90%

5. CONSULTATION ARRANGEMENTS

- 5.1 Comments are sought on the proposals. A period of 10 weeks has been set aside for consultation.
- 5.2 Comments should be submitted in writing by 18 February 2000 to the Environment Agency at the following address:

Environment Agency
 National Compliance Assessment Service
 Cameron House
 White Cross Industrial Estate
 South Road
 Lancaster
 LA1 4XQ

and marked for the attention of Nigel Jeal. Alternatively you may e-mail your comments to Nigel at nigel.jeal@environment-agency.gov.uk

REFERENCES

- 1 Performance Standards for Continuous Emission Monitoring Systems. Performance standards for SO₂, NO_x, CO, HCl, VOC's, O₂, H₂O, particulates, temperature, pressure and flow rate, Environment Agency, November 1988.
- 2 Performance Standards for the Testing of Continuous Emission Monitoring Systems under the MCERTS Scheme. Performance standards for test facilities measuring gas and particulate concentrations and stack gas flow, temperature and pressure, Environment Agency, May 1999 (draft).
- 3 European Air Quality Framework, Framework Directive, 96/62 EC, OJ L296, 21/11/1996
- 4 European Air Quality Framework and First Daughter Directives, Framework Directive, 96/62 EC, Daughter Directive for SO₂, NO₂, PM₁₀ and Lead, OJ C9/5, 1998.
- 5 Proposal for a Council Directive relating to limit values for benzene and carbon monoxide in ambient air, COM(1998) 591 final, Brussels, 1/12/1998.
- 6 Guide to the Expression of Uncertainty in Measurement, ISBN 92-67-10188-9, 1st Ed., Geneva, Switzerland, ISO 1993.

APPENDIX 1: DEFINITIONS OF PERFORMANCE CHARACTERISTICS

Sections A1.1 and 1.2 cover tests on SO₂, NO₂, O₃, CO CAMs

Sections A1.3 and 1.4 cover tests on particulates PM₁₀ and PM_{2.5} CAMs

Sections A1.5 and 1.6 cover tests on metals CAMs

Sections A1.7 and 1.8 cover tests on Poly-Aromatic Hydrocarbons CAMs

Sections A1.9 and 1.10 cover tests on benzene CAMs

A1.1 DEFINITIONS OF PERFORMANCE CHARACTERISTICS FOR CONTINUOUS GAS MEASURING INSTRUMENTS (LABORATORY TESTS)

A1.1.1 The instrument performance characteristics discussed in this document for gas monitoring CAMs are defined in this Appendix.

A1.1.2 The performance characteristics which would be determined in the laboratory are :

- Response Times (where applicable);
- Repeatability Standard Deviation;
- Short-term Span Drift;
- Accuracy;
- Detection Limit and Quantification Limit;
- Short-term Zero Drift;
- Averaging Effect (where applicable);
- Linear Fit;
- Cross Sensitivity to Interfering Substances;
- Effect of Sample Gas Temperature and Pressure;
- Environmental Conditions;
- NO_x Converter Efficiency (where applicable);
- Gas flow accuracy and stability (where applicable);
- Susceptibility to physical disturbances;
- Combined Performance;

These are defined below.

A1.1.3 The tests would be performed with respect to the agreed Certification Range, the assigned pollutant concentration limit value, and the defined averaging period, which should all be agreed between the manufacturer, the MCERTS Certification Committee and, where appropriate, the test house before testing commences. For NO₂ CAMs the averaging effect, cross sensitivity and NO accuracy tests should be performed using nationally-traceable calibration gases at NO concentrations close to 600 ppb, whilst the NO₂ accuracy test will be performed using nationally-traceable calibration gases close to the limit value concentration. For SO₂, CO and O₃ CAMs the averaging effect, cross sensitivity, and accuracy tests will be performed close to the limit value concentration.

A1.1.4 The following parameters defined below are used throughout the document to define performance characteristics:

- C_{max} Maximum of certification range, in pollutant concentration units;
- C_{min} Minimum of certification range, in pollutant concentration units, (for most ambient air-quality monitoring CAMs this will be zero concentration);
- C_{limit} Limit value for the specified pollutant concentration;
- T_n Required data averaging period. If data are reported over different averaging periods, T_n will be equal to the shortest period (see Table 3.1);
- T_s Averaging period used by the CAM (see Table 3.1);

(i) **Response Time Test , RT_{rise} and RT_{fall}**

A1.1.5 The response time is a measure of the dynamic response of the CAM to a step change in the input. An associated performance measure is that the difference between the CAM's response to a positive step change and a negative step change should be less than a specified value:

$$|RT_{rise} - RT_{fall}| < 10\% \text{ of } RT_{nom} \quad \text{eq A1.1}$$

A1.1.6 Two response times would be determined :

- RT_{rise} Response Time to a positive step change in pollutant concentration
- RT_{fall} Response Time to a negative step change in pollutant concentration

defined as

$$RT_{rise} = T_{rise} + T_{rise\ lag}$$

$$RT_{fall} = T_{fall} + T_{fall\ lag}$$

where:

- T_{rise} is defined as $Tr_{90} - Tr_{10}$
- $T_{rise\ lag}$ is defined as $Tr_{10} - T_{on}$
- T_{fall} is defined as $Tf_{10} - Tf_{90}$
- $T_{fall\ lag}$ is defined as $Tf_{90} - T_{off}$

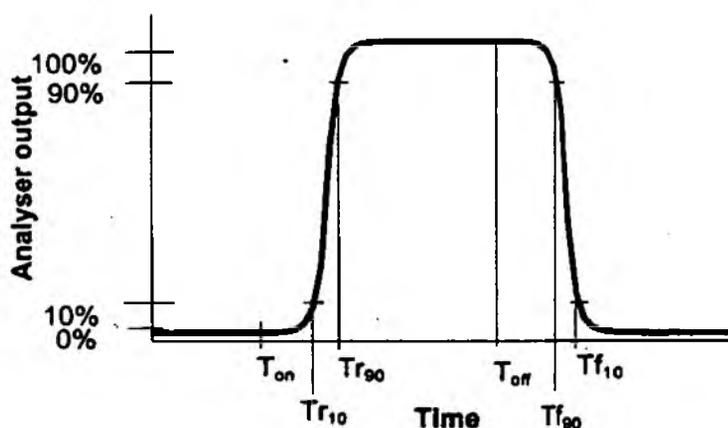
A1.1.7 Figure A1.1 shows the definition of these times. T_{on} is the time at which the positive step change in pollutant concentration is applied, T_{off} is the time at which a negative step change is applied. Tr_{10} and Tr_{90} are defined as the points at which the output reaches 10 percent and 90 percent of the maximum respectively during the rising edge, and Tf_{90} and Tf_{10} are defined as the points at which the output reaches 90 percent and 10 percent respectively of the maximum concentration value before the falling edge.

A1.1.8 The lag time ($T_{rise\ lag}$) is defined as the time taken for the output of the CAM under test to rise to 10% of the expected response, after the introduction of a positive step change in test gas concentration. The response time is defined as the time taken for this reading to reach 90% of the expected response after the same step

change. The rise time (T_{rise}) is defined as ($T_{90} - T_{10}$). The fall times (T_{fall} and $T_{fall\ lag}$) would be measured by performing a test using a negative step change in concentration.

- A1.1.9 The above test would be carried out by introducing a square step change in the concentration of the pollutant concentration at the input to the CAM system. The size of the step change would be nominally from zero to 80% C_{max} . If, as is expected to be the case with most gas analysers, the manifold is not integral to the system, an inlet line of nominal length three metres would be used to introduce the sample, to simulate a typical connection between the manifold and the CAM. (Note: this is in addition to any sample line, which is not tested under the MCERTS Scheme for ambient air-quality monitoring systems). The output from the CAM would be recorded and the response times determined as shown in Figure A1.1. Where the CAM produces an output in discrete time intervals eg single channel NOx analyser, the response times would be determined from the start of the relevant intervals. The response time test will be repeated four times and the maximum values reported.

Fig A1.1 Schematic of Response Time Test



- A1.1.10 The response time (both rise and fall) determined from this test should be less than 25% of the required averaging time T_a . If this is not the case a new value of T_a would be calculated, as four times the response time (rise or fall time whichever is the greater). This new value of T_a would be used in all subsequent tests. T_a should be less than T_n . If this is not the case the CAM is not fit for purpose for reporting averages over the period T_n .
- A1.1.11 The response time does not directly impact on the uncertainty of the results produced by the CAM. (They do, however, affect the length of time required between individual tests in order to obtain independent results.) However, the potential effect that response time effects may have on average value produced by the CAM are addressed by the separate performance characteristics on averaging effects, described in Paragraphs A1.1.33-A1.1.38.

(ii) **Repeatability Standard-deviation Test, and Short-term Span Drift**

- A1.1.12 Repeatability standard deviation is a measure of the variation between successive measurements made while maintaining the input span gas and all influence quantities as constant as practical.
- A1.1.13 The short-term span drift is a measure of the drift in the output signal over a time period which is representative of approximately the maximum time over which other performance characteristics would be determined. Short-term span drift is determined in order to check that drift is not a significant source of uncertainty in determining the other performance characteristics.
- A1.1.14 The repeatability standard deviation and short-term span drift would be determined during a single test run.
- A1.1.15 The CAM would be allowed to stabilise at laboratory temperatures for at least 24 hours or any other time scale which the manufacturer specifies.
- A1.1.16 A gas of known, stable, concentration, nominally at 80% of C_{max} , would be supplied continuously to the CAM for twelve hours, and generally for a period which is at least equal to the period of the longest continuous laboratory test (this would normally be the linearity test). A series of measurements would be made, each measurement being the average CAM reading over the sampling period T_s . The testing period should be sufficiently long so that at least three sets of ten such measurements can be taken. The first set would be used to calculate u_{sd} in the following Equation A1.2a.
- A1.1.17 Repeatability standard deviation is defined from the measured statistical variations of the CAM reading during the above test and is defined as a standard uncertainty:

$$u_{sd} = S_r \quad \text{eq A1.2a}$$

where:

S_r is the standard deviation of the measurements

The expanded uncertainty can be calculated from the standard uncertainty using the following formula:

$$U_{SD} = t_f(0.95)u_{sd} \quad \text{eq A1.2b}$$

where:

U_{SD} is the repeatability expressed in concentration units of the determinand.

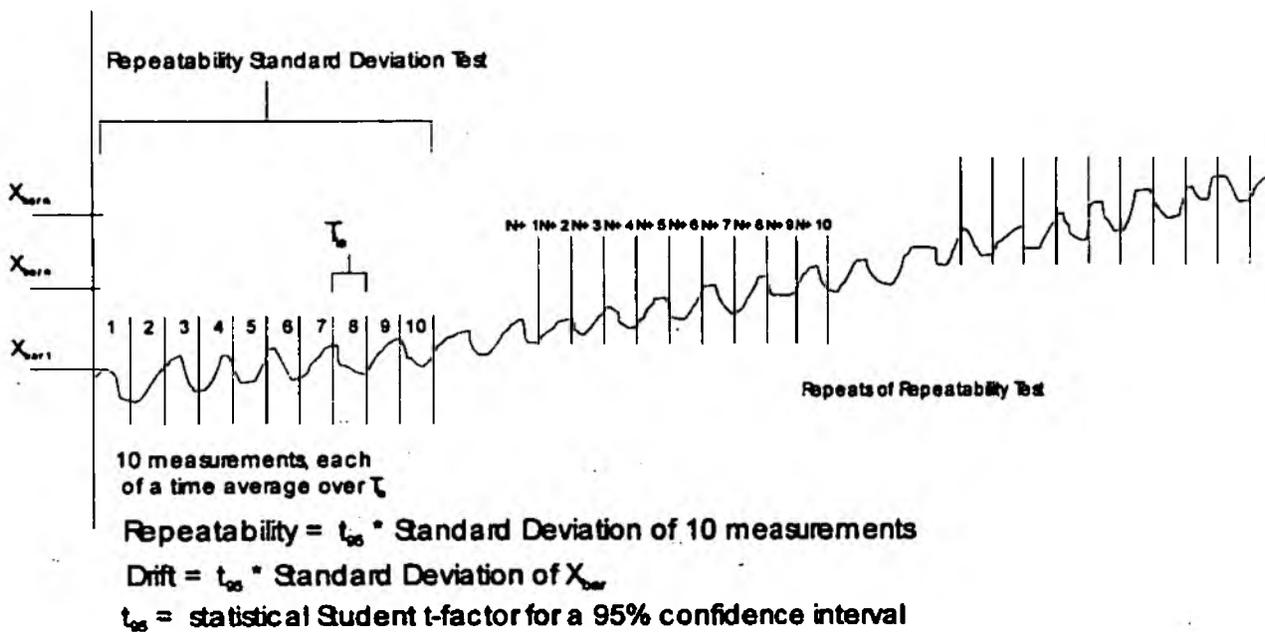
$(f + 1)$ is the number of measured values obtained.

$t_f(0.95)$ is the statistical Student t-factor for a 95% confidence interval with f degrees of freedom.

Repeatability standard deviation will be included as a contribution to the calculation of overall uncertainty of the CAM, required for the Combined Performance Characteristic (paragraphs 2.3.1-2.3.2).

A1.1.18 The repeatability would be calculated, according to equation A1.2b above, for each of the consecutive sets of ten measurements taken over the full test period. In addition, the mean of each set of ten measurements would be calculated. In addition an ANOVA (analysis of variance) test would be performed to show whether the drift is significant with respect to the variation seen within each set of ten measurements. A measure of the short term drift, U_{short} , would be calculated, derived from the standard deviation of the means of each set of ten measurements taken during this period, again using Equation A1.2b. U_{short} would be compared with the performance characteristics for short term span drift.

A1.1.19 Short-term span drift should not be included as a contribution to the calculation of overall uncertainty of the CAM required for the Combined Performance Characteristic (paragraphs 2.3.1-2.3.2), as the effects are included within other performance characteristics.



(iii) Accuracy

A1.1.20 The accuracy performance criterion is used to test the calibration of the CAM at a single point using a sample traceable to national standards. The aim of the test is to determine whether the calibration of the CAM carried out by the CAM manufacturer, or supplier, conforms to requirements, without the need for more accurate calibration.

A1.1.21 The CAM would be calibrated by the manufacturer either in the factory or at the start of the laboratory tests. The calibration must use the standard operating procedures defined for the CAM, and must use any artifacts which are normally recommended by the manufacturer for this purpose. It is recommended that any calibration gases used by the manufacturer should be traceable to national gas concentration standards. The gas concentrations and the accuracy of these values should be stated. The test house may comment on the calibration technique where this is appropriate.

A1.1.22 A test sample at the limit value concentration, and traceable to national standards, would be supplied to the CAM under test and the accuracy X_A determined from the difference between the measured and the true value. The measured value would be the average of at least 10 measurements, each measurement being the average output from the CAM over the sampling period T_s . The repeatability will also be calculated from the standard deviation, using equation eq A1.2b and compared with the value obtained from measurements at 80% C_{max} .

A1.1.23 Where failure of the test CAM in meeting the Performance Standard is directly attributable to poorly specified or incorrectly chosen calibration artifacts, or where incorrect conversion algorithms are employed, the CAM would be re-tested with calibration artifacts which meet the requirements. If the CAM then passes the re-test it would not fail the accuracy test, but the MCERTS Certificate will carry a warning alerting users to the need for satisfactory calibration.

A1.1.24 The standard uncertainty u_A due to the accuracy, X_A , will be derived as follows:

$$u_A = \frac{X_A}{\sqrt{3}} \quad \text{eq A1.3a}$$

The expanded uncertainty can then be calculated from the standard uncertainty using the following formula:

$$U_A = u_A \cdot k \quad \text{eq A1.3b}$$

The coverage factor $k = 1.65$ should be used to obtain a 95% confidence interval when the distribution is rectangular [ISO Guide to Measurement Uncertainty Annex G p59]. This component of the measurement uncertainty of the CAM would be included into the determination of the combined performance characteristic (paragraphs 2.3.2 and 2.3.3). If the uncertainty due to accuracy is a significant contribution and causes the CAM to fail with respect to the combined performance criteria, the CAM will not fail MCERTS. However, the Certificate will recommend the use of improved calibration artifacts.

(iv) **Detection Limit, Quantification Limit, and Short-Term Zero Drift.**

A1.1.25 The detection limit is a measure of the uncertainty, expressed as a 95% confidence interval, of the output signal from the CAM when a sample is applied which is free of the determinand. This is interpreted as the lowest output value which is statistically distinguishable from a zero value. The quantification limit is a further performance measure which is based on the detection limit. This is defined as the lowest CAM reading which, with a 95% confidence interval, could not have been produced from an input gas free of the determinand.

A1.1.26 Short-term zero drift is a measure of the drift in the output signal over a time period which is representative of the time over which other performance characteristics would be determined. Short-term zero drift is determined in order

to check that drift is not a significant source of uncertainty in determining other performance characteristics.

- A1.1.27 The detection limit, quantification limit and the short-term drift would be determined during a single test run.
- A1.1.28 The CAM would be allowed to stabilise at laboratory temperatures for at least 24 hours or any other time scale which the manufacturer specifies.
- A1.1.29 A gas certified to be free of the measured pollutant and interferences would be supplied to the test CAM and the standard deviation of its response would be determined. A series of measurements would be made, each measurement being the average CAM reading over the sampling period T_s . The testing would be sufficiently long so that at least three sets of ten such measurements can be taken. The first set of ten readings would be used to calculate X_D in the following Equation A1.4.

The detection limit is defined as:

$$X_D = t_f(0.95)S_0 \quad \text{eq A1.4}$$

where:

- X_D is the detection limit expressed in concentration units of the determinand gas
- S_0 is the standard deviation of the measurements
- $(f+1)$ is the number of measurement values obtained
- $t_f(0.95)$ is the statistical Student t-factor for a 95% confidence interval with f degrees of freedom.

- A1.1.30 The quantification limit is defined as twice the detection limit provided both these performance characteristics are quoted with identical confidence limits.

Therefore for a confidence limit of 95%:

$$X_Q = 2X_D \quad \text{eq A1.5}$$

where:

- X_Q is the quantification limit expressed in concentration units of the determinand gas

- A1.1.31 The repeatability X_D would be calculated, according to equation A1.4 above, for each of the consecutive sets of ten measurements taken over the full test period. In addition the mean of each set of ten measurements would be calculated. An ANOVA (analysis of variance) test would be performed to test whether the drift between consecutive sets of measurements is significant compared to the repeatability within each set.
- A1.1.32 A measure of the short term zero drift, U_{min} would also be calculated. This will be derived from the standard deviation of the means of each set of ten measurements

taken during this period, again using Equation A1.4 . U_{tot} would be compared with the performance characteristics for short term zero drift.

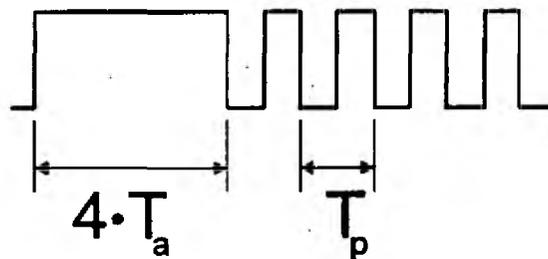
(v) **Averaging Effect**

A1.1.33 The averaging effect performance criterion provides a measure of the uncertainty in CAM results which are caused by short-term fluctuations in the input sample concentration that occur at time scales shorter than the CAM's averaging period of T_a .

A1.1.34 This test would only be applied to continuous reading CAMs, including single cell NOx analysers. Both the NO_x and NO channels will be recorded during the averaging test and checks will be made to determine whether the CAM is reporting negative NO₂ concentrations. If this is the case it will be reported on the certificate. The test procedure shown schematically in Figure A1.3 would be used.

A1.1.35 The CAM under test would be supplied with a fixed concentration of span gas at twice that of C_{limit} for a time period equal to at least four times the averaging period T_a . This would be followed by a period of at least four times T_a during which the CAM is supplied with step changes between zero and the fixed concentration, with an average concentration of one half of the fixed concentration. The period of the square wave (T_p), would comprise one minute of zero gas followed by one minute of span gas. These periods may be altered by the Certification Committee to suit individual CAM test requirements.

Figure A1.3 Schematic of the Averaging Test



A1.1.36 The averaging error X_w would be calculated according to :

$$X_w = \overline{C_{\text{const}}} - (2 \cdot \overline{C_{\text{var}}}) \quad \text{eq A1.6}$$

where:

C_{const} is the average measured concentration during the constant concentration period

C_{var} is the average measured concentration during the variable concentration period

The averaging error would be compared with the requirements given in Table 4.2 to determine whether the relevant performance standard is satisfied.

- A1.1.37 The averaging error also contributes to the combined uncertainty in the CAM output. This contribution would depend on the real level of variability of the concentrations of the pollutant concentration present in the field. In this context, the test sample used above may reasonably be taken as a worst case. The measurement uncertainty shall then be assumed to be a rectangular distribution from 0 to X_{AV} . This distribution is not symmetrical about the 'true' value. Therefore, if no correction is applied to the data then the standard uncertainty based on this distribution is calculated according to :

$$u_{AV} = \frac{X_{AV}}{\sqrt{3}} \quad \text{eq A1.7a}$$

The expanded uncertainty can be calculated from the standard uncertainty using the following formula:

$$U_{AV} = u_{AV} \cdot k \quad \text{eq A1.7b}$$

The coverage factor $k = 1.65$ should be used to obtain a 95% confidence interval when the distribution is rectangular [ISO Guide to Measurement Uncertainty Annex G p59]

- A1.1.38 This component of the measurement uncertainty of the CAM would be included into the determination of the combined performance characteristic (paragraphs 2.3.2 and 2.3.3).

(vi) Test of Linear Fit

- A1.1.39 The CAM is assumed to have a linear response between the final output signals and the input pollutant concentrations. If this is not the case the CAM is not fit for purpose. This requirement places no restrictions on non-linear stages within the CAM, as long as these are compensated for when providing the final result of the pollutant concentration.

- A1.1.40 The linearity of the CAM would be tested over the range 0% to 90% of the agreed certification range, using at least five equally-distributed concentrations plus a zero concentration sample . All test gas concentrations would be accurate with respect to each other to better than $\pm 0.5\%$ of value. The number of measurements made at each calibration point shall be high enough to ensure that the uncertainty of the mean of the measurements at that concentration is less than $\pm 10\%$ of the required uncertainty of the linear fit.

- A1.1.41 A linear fit would be performed on the mean of the measured values at each calibration point. The largest residual from the linear fit would be taken as the lack of fit X_L . The residuals would also be plotted and the graph examined to check for trends.

- A1.1.42 The uncertainty on the CAM output due to this performance characteristic may be estimated by assuming that across the CAM's range (and hence at the limit value)

the maximum error due to non-linear fit is $\pm X_L$. Assuming this is a rectangular distribution the standard uncertainty is given by :

$$u_L = \frac{X_L}{\sqrt{3}} \quad \text{eq A1.8a}$$

The expanded uncertainty can be calculated from the standard uncertainty using the following formula:

$$U_L = u_L \cdot k \quad \text{eq A1.8b}$$

The coverage factor $k = 1.65$ should be used to obtain a 95% confidence interval when the distribution is rectangular [ISO Guide to Measurement Uncertainty Annex G p59]. This component of the measurement uncertainty of the CAM would be included into the determination of the combined performance characteristic (paragraphs 2.3.2 and 2.3.3).

(vii) **Cross-sensitivity to Interfering Substances**

A1.1.43 The sensitivity of the CAM would be established towards gases that are not its determinand gas, but which are expected to be present in its chosen measurement environment. These test gases should include water vapour where this is considered necessary. The concentrations of these test gases are listed in Appendix 9. The interferent gases would be delivered to the CAM in mixtures containing a known concentration of the determinand, nominally at the limit value. Samples containing just the determinand at this concentration would be introduced to provide a reference response R_r .

A1.1.44 Test gases would be introduced individually at the agreed concentrations into the CAM for a period at least four times the CAM averaging period, T_a , and its responses recorded R_k . Additional tests may be carried out where appropriate on other species where required by the Certification Committee. The response to the interferent would be calculated from the difference between the recorded responses and the reference response.

A1.1.45 The CAM's combined response, S_c , to all of the interfering substances would then be calculated using:

$$S_c = \sum_{i=1}^n R_i \quad \text{eq A1.9a}$$

where:

$R_i = R_k - R_r$ is the response to the specified concentration of interferent, inclusive of the sign of that response;

A1.1.46 The purpose of the S_c factor is to give an indication of the combined effect of the likely interferents.

A1.1.47 In addition to the individual application of interferent gases a mixture of all of the gases (except water), at the same concentrations used in the individual interferent tests, plus the determinand gas at the limit concentration would be injected into

the CAM for a period at least four times the CAM averaging period, T_a , and the output reading R_m would be recorded.

$$S_c = R_c - R_m \quad \text{eq A1.9b}$$

This would test the assumption of additivity made in equation A1.9a.

A1.1.48 The combined effect of all the interferent gases (represented by the S_c factor) should not exceed the cross sensitivity performance characteristic given in Section 3. Similarly the effect of the interferent mixture should not exceed this limit (the effect of water vapour as an interferent will be added by calculation from its individual response derived in paragraph A1.1.43 where water vapour has been shown to have a significant interferent effect).

A1.1.49 The uncertainty due to the interference effects would be estimated by assuming that in the worst case all interferents would be correlated (the approach used within Draft ISO standard 14956). The standard uncertainty due to interference effects u_i would be estimated by

$$u_i = \frac{S}{\sqrt{3}} \quad \text{eq A1.10a}$$

where:

S = The maximum of $|S_c|$ or $|S_m|$;

The expanded uncertainty should then be calculated from the standard uncertainty using the following formula:

$$U_i = u_i \cdot k \quad \text{eq A1.10b}$$

The coverage factor $k = 1.65$ should be used to obtain a 95% confidence interval when the distribution is rectangular [ISO Guide to Measurement Uncertainty Annex G p59]. This component of the measurement uncertainty of the CAM would be included into the determination of the combined performance characteristic (paragraphs 2.3.2 and 2.3.3).

(viii) NO_x Converter-efficiency Test

A1.1.50 A known concentration of NO, nominally at 80% of C_{max} , would be supplied to the CAM and the output left to stabilise for at least a time T_a . A first reading averaged over the period T_a would then be taken from both the NO and NO_x channels. The NO would then be reacted with O₃ to produce a concentration of NO₂. At least 80% of the NO will be converted to NO₂. This mixture would be supplied to the test CAM. By this means, a constant NO_x concentration would be supplied to the CAM and its output left to stabilise for at least T_a . A result averaged over a period T_a would then be taken from both the NO and NO_x channels. The O₃ supply would then be switched off and the CAM supplied again with only NO. The output would then be left to stabilise for at least a time T_a . A measurement averaged over the period T_a is then taken of the NO and NO_x channels to check that the values

return to their original levels. This procedure should be repeated three times and the results averaged. The NO_x converter efficiency would then be calculated using:

$$X_{CI} = \left[1 - \left(\frac{\Delta NO_x}{\Delta NO} \right) \right] \cdot 100 \quad \text{eq A1.11}$$

where:

- X_{CI} is the converter efficiency expressed as a percentage (eg 98%);
- ΔNO_x is the averaged measured change in NO_x output, corrected for the zero reading;
- ΔNO is the averaged measured change in NO output, corrected for the zero reading;

A1.1.51 Converter efficiency generally leads to a systematic effect in the measured NO₂ concentration at a given concentration. In field operations it is normally corrected for, or kept within certain limits. The uncertainty contribution which arises from the converter efficiency measurement would, therefore, be estimated by assuming a rectangular distribution, giving rise to a standard uncertainty contribution *u_{CI}* of :

$$u_{CI} = \frac{C_{lim} \cdot \left(1 - \frac{X_{CI}}{100}\right)}{\sqrt{3}} \quad \text{eq A1.12a}$$

The expanded uncertainty can then be calculated from the standard uncertainty using the following formula:

$$U_{CI} = u_{CI} \cdot k \quad \text{eq A1.12b}$$

The coverage factor *k* = 1.65 should be used to obtain a 95% confidence interval when the distribution is rectangular [ISO Guide to Measurement Uncertainty Annex G p59]. This component of the measurement uncertainty of the CAM would be included into the determination of the combined performance characteristic (paragraphs 2.3.2 and 2.3.3).

(ix) Effect of Sample Gas Pressure and Temperature

A1.1.52 The influence of variations of sample-gas pressure and temperature would be measured on the response of the CAM. To test this, a sample gas, in air or nitrogen as appropriate, containing the determinand gas at a nominal concentration of *C_{limit}*, would be injected into the sample input of the CAM, using the range of test conditions agreed between the manufacturer or supplier and the relevant MCERTS Certification Committee. Each test condition would be repeated four times and the maximum effect for each test condition reported.

A1.1.53 The influence of the sample-gas pressure on the output signal of the CAM would be measured with the sample gas injected into the CAM at a pressure close to ambient atmospheric pressure, and then with the same gas at a pressure approximately 3 kPa above this. The difference in the CAM output indicator

reading at the two pressures would be used to calculate the response factor per unit sample gas pressure (X_{SP}). The pressure measurements should be made with sufficient accuracy that they do not affect significantly the accuracy of the result X_{SP} .

A1.1.54 The influence of sample-gas temperature on the output signal of the CAM would be measured with the sample gas at a temperature that is injected into the sample inlet of the CAM successively at the bottom and top of the specified temperature range, and then at the middle of the range (the middle temperature would be omitted if the specified range is less than 30°C). The results would be used to calculate the CAM output indicator response change per unit temperature (X_{ST}). The temperature measurements should be made with sufficient accuracy that they do not affect significantly the accuracy of result X_{ST} .

A1.1.55 The standard uncertainty contributions caused by the influence of sample gas temperature and pressure over the range of gas temperatures and pressures which had been agreed by the Certification Committee and the CAM supplier would be derived as follows:

$$u_{SP} = X_{SP} \cdot \frac{(P_{max} - P_{min})}{\sqrt{3}} \quad \text{eq A1.13a}$$

$$u_{ST} = X_{ST} \cdot \frac{(T_{max} - T_{min})}{\sqrt{3}} \quad \text{eq A1.14a}$$

The expanded uncertainties can then be calculated from the standard uncertainties using the following formulas:

$$U_{SP} = u_{SP} \cdot k \quad \text{eq A1.13b}$$

$$U_{ST} = u_{ST} \cdot k \quad \text{eq A1.14b}$$

The coverage factor $k = 1.65$ should be used to obtain a 95% confidence interval when the distribution is rectangular [ISO Guide to Measurement Uncertainty Annex G p59]. This component of the measurement uncertainty of the CAM would be included into the determination of the combined performance characteristic (paragraphs 2.3.2 and 2.3.3).

x) **Environmental Conditions**

A1.1.56 The extent of the testing would be agreed between the CAM manufacturer, or supplier, and the Certification Committee, taking into account the environment likely to be encountered in the application category for which product certification is sought. The Certification Committee would consider whether different elements of multi-part CAMs should be subjected to different levels of environmental testing. During the tests, the CAM would be subjected to the specified range of environmental conditions and the changes in its output signal determined when tested with zero and span concentration values. The range of conditions tested will be recorded on the Certificate. The CAM may also be tested over a wider range of environmental conditions, where required by the manufacturer or the Certification Committee. This could include, for example, where relevant tests of the effects of ambient humidity and dust. These additional tests would not be used to quantify any effects on the CAM response, but will be reported on the Certificate.

A1.1.57 The CAM would be tested to determine whether it is influenced by changes in ambient temperature by determining its responses to zero and span values.

A1.1.58 The changes of the CAM's output readings due to changes in ambient temperature would be tested by supplying the CAM successively with zero gas and span gas while the temperature of its surroundings is held at different levels. Different temperatures would be used, which are situated at the top, middle and bottom of the CAM's agreed temperature test range provided that the specified temperature range is $\geq 30^{\circ}\text{C}$. The mean output of the CAM, as determined over 10 successive readings of its output indicator, would be recorded at each temperature. Each reading would be averaged over the period T_p . If the agreed range of the ambient temperature tests is less than 30°C , then only two temperatures will be tested, at the top and bottom of the range. During this time the temperature of the gas at the probe of the CAM would be maintained at $20^{\circ}\text{C} \pm 5^{\circ}\text{C}$, or another value agreed between the manufacturer and the Certification Committee. The response would be calculated for each 10°C interval, and should be less than the values shown in Tables 4.1a and 4.1b.

A1.1.59 The tests to establish the CAM's responses to variations in ambient temperature would be conducted with the CAM in an active condition at all times - ie the CAM would not be taken to an extreme value of ambient temperature and then switched on.

The standard uncertainty contributions caused by the influence of ambient temperature on the CAM's output would be derived from:

$$u_{AT} = X_{AT} \cdot \frac{(T_{\max} - T_{\min})}{\sqrt{3}} \quad \text{eq A1.15a}$$

where T_{\max} and T_{\min} are the maximum and minimum temperatures respectively over which the CAM will be tested, as agreed between the CAM manufacturer, or supplier, and the Certification Committee.

The expanded uncertainty can be calculated from the standard uncertainty using the following formula:

$$U_{AT} = u_{AT} \cdot k \quad \text{eq A1.15b}$$

The coverage factor $k = 1.65$ should be used to obtain a 95% confidence interval when the distribution is rectangular [ISO Guide to Measurement Uncertainty Annex G p59]. This component of the measurement uncertainty of the CAM would be included into the determination of the combined performance characteristic (paragraphs 2.3.2 and 2.3.3).

(xi) Physical Disturbance

A1.1.60 The extent of physical disturbance testing will be agreed between the CAM manufacturer or supplier and the Certification Committee. It shall be based on the tests described in IEC 68-1:1988 (BSEN 60068), taking into account the environment likely to be encountered in the application category for which product certification is sought. The following is a list of possible tests.

a) Vibration

A1.1.61 This test should be made with reference to IEC 68-2-6: 1995 which is equivalent to BS EN 60068-2-6: 1996 test Fc Vibration (sinusoidal). The CAM should be mounted by its normal fixings. The CAM should remain powered and would be subjected to swept sinusoidal vibration in each of three mutually perpendicular axes in turn. Multi-point vibrational control should be used. The vibration envelope would be:

10 to 60 Hz at a constant displacement of 0.15 mm (peak)
60 to 150 Hz at a constant acceleration of 19.6 m.s⁻² (peak)

The sweep rate should not exceed 1 octave per minute. At least 5 sweep cycles shall be applied to each axis.

A1.1.62 If any resonant frequencies are observed, then a vibration test should be carried out at each observed frequency for two minutes at an amplitude in accordance with the defined envelope. In the event that more than 5 resonant frequencies are found then only the 5 frequencies at which the amplitude magnification is greatest need to be tested. In the event that no resonant frequencies are observed the test should be carried out at 50 Hz. A functional test (see paragraph A1.1.71) shall be conducted before and after the test.

b) Mechanical Shock

A1.1.63 The CAM would be placed on a rigid surface in its normal operating orientation.

A1.1.64 The test should be carried out by raising each lower edge of the CAM in turn 25 mm above a steel plate which is at least 10 mm thick, wet-floated on concrete, (subject to a maximum inclination of 30° to this steel plate), and then allowing the

CAM to fall freely onto the surface. A functional test (see paragraph A1.1.71) shall be conducted before and after the test.

c) Magnetic Field

A1.1.65 The CAM should be placed in an alternating magnetic field of frequency 50 Hz and an intensity of 60 A.m^{-1} such as may be produced by a square coil of 50 turns, linear dimensions 1 m, carrying a current of 1 Amp. The use of a Helmholtz coil is recommended for this test. The field shall be applied during a functional test (see paragraph A1.1.71)..

d) Ageing Test

A1.1.66 The CAM should be operated in an environmental chamber for eight hours. The chamber should be maintained at a temperature of 40°C and a relative humidity of 90%.

A1.1.67 At the end of the period the power shall be turned off and the conditions in the chamber changed to 60°C and 30% RH over a period of not less than one hour. These conditions should then be maintained for a further period of one hour.

A1.1.68 The conditions shall be returned to ambient and the CAM allowed to stabilise. Once stabilised the CAM should be subjected to a further vibration test. The conditions for this vibration test are given in paragraph A1.1.64.

A1.1.69 The CAM shall be operated again in the chamber and subjected to rapid temperature cycling. Temperature cycling should be 0°C to 40°C for a period of sixteen hours, changing from one temperature to the other every hour, the change to take place in about 30 minutes in each direction. During this temperature cycling, condensation on the CAM shall be avoided. This would be achieved by reducing the relative humidity to 30%, as specified by the Organisation Internationale de Métrologie Legal (OIML)

A1.1.70 At the end of this ageing test the CAM shall be returned to room temperature and humidity, and a functional test (paragraph A1.1.71) will be performed:

e) Functional Test

A1.1.71 A functional test will consist of a check on the correct operation of the CAM by injecting a known test gas at a concentration greater than zero (generally 70%-80% of the maximum of the Certification Range) for a period of at least one averaging period, T_a , before and after the individual physical disturbance tests, and recording the CAM's output. The CAM's output indicator should not vary in concentration value by greater than $\pm 10\%$ before and after each of the physical disturbance tests.

xi) **Combined Performance Characteristic**

A1.1.72 The standard combined uncertainty discussed in Section 2 of this document would be calculated by summing the results of the relevant performance tests according to the equation:

$$u_c = \sqrt{\sum_{i=1}^n u_i^2} \quad \text{eq A1.16}$$

A1.1.73 The individual standard uncertainties u_i should be derived as described in sections i) to x) above, and the long term drift determined in the field tests described in A1.2. Only those performance characteristics which contribute to the overall uncertainty would be combined as follows :

$$u_c = \sqrt{u_{SD}^2 + u_{ZM}^2 + u_{SM}^2 + u_A^2 + u_{AV}^2 + u_L^2 + u_I^2 + u_{CI}^2 + u_{SP}^2 + u_{ST}^2 + u_{AT}^2} \quad \text{eq A1.17}$$

Note, u_{CI} is only applicable to NO_x systems.

A1.1.74 In addition a separate estimate of u_c would be determined using the uncertainty determined from the field repeatability tests performed during the Field Tests, described in A1.2. This gives a separate estimate of u_c because field repeatability may directly measure a number of uncertainty sources, namely all those influence variables which vary during the field tests. It does not, however, test these over controlled ranges, neither does it give any indication of the relative effects of these influences. It does nevertheless demonstrate the performance of the CAM under real conditions with representative correlation's between influence variables. u_c would then be calculated by applying the above equation to the following uncertainty sources :

$$u_c' = \sqrt{u_R^2 + u_{ZM}^2 + u_{SM}^2 + u_A^2 + u_{AV}^2 + u_L^2 + u_I^2 + u_{CI}^2 + u_{SP}^2 + u_{ST}^2 + u_{AT}^2} \quad \text{eq 1.18}$$

Note, u_{CI} is only applicable to NO_x systems.

The expanded combined uncertainties U_c and $U_{c'}$, when expressed at the 95% confidence interval, will be derived from the combined standard uncertainties u_c and $u_{c'}$ by multiplying by coverage factors determined from the total number of degrees of freedom according to GUM and the Welch-Satterthwaite[6] equation. Conformance with the Performance Standards in this document would require the conformance of both U_c and $U_{c'}$ with the combined performance characteristic (Table 4.1a part 1).

A1.2 DEFINITIONS OF PERFORMANCE CHARACTERISTICS FOR CONTINUOUS GAS MEASURING INSTRUMENTS (FIELD TESTS)

A1.2.1 The candidate CAMs would be operated in the field for a period of three months with an appropriate quality-assured sample line. The CAMs would be located at a site appropriate to the requirement for certification, urban rural etc, which shall be selected in accordance with recognised siting criteria.

A1.2.2 The CAMs would be installed and initially calibrated by the manufacturer. The CAMs would be operated continuously for the test period during which the following parameters would be tested.

- Repeatability in the Field
- Maintenance interval
- Zero Drift
- Span Drift
- Availability (data capture)

These are discussed below.

(i) Repeatability in the Field

A1.2.3 Two identical analysers would be co-located at a site specific to the application category (paragraph 2.4.1) as agreed between the CAM manufacturer, or supplier, the Certification Committee and the test house, and both would be set to sample the same atmospheric air. The field repeatability would be determined from the standard deviation of the difference, X_{sd} , between the two measurements made at the same time over the test period. Each measurement will be an average over the period T_s . The mean of the differences, X_{bias} , will also be calculated to show the bias between the two CAMs.

The field repeatability is defined from the measured statistical variations of the CAM readings during the above test and can be defined as a standard uncertainty:

$$u_R = X_{sd} \quad \text{eq A1.19a}$$

The expanded uncertainty can be calculated from the standard uncertainty using the following formula:

$$U_R = (t_f(0.95)u_R) + \left(\frac{X_{bias}}{\sqrt{3}} \cdot k \right) \quad \text{eq A1.19b}$$

where:

- (f + 1) is the number of measured values obtained;
- $t_f(0.95)$ is the statistical Student t-factor for a 95% confidence interval with f degrees of freedom;

The coverage factor $k = 1.65$ should be used to obtain a 95% confidence interval when the distribution is rectangular [ISO Guide to Measurement Uncertainty Annex G p59].

(ii) Maintenance Interval

A1.2.4 The maintenance interval is defined as the time in the operating environment in the field over which the CAM's zero and span drifts remain within the limits specified in this document. This would serve as an indication of the level of maintenance which would be required operationally. It may be necessary to replace consumables (eg desiccants or sample inlet filters) within the maintenance interval, as specified by the manufacturer, to ensure proper CAM performance. In this case a maintenance period will also be defined which will be the maximum period between the replacement of consumables. During the tests on the maintenance interval, the CAM's calibration and maintenance will be carried out using documented procedures, and no adjustments will be made which will alter the response of the CAM. The minimum allowable maintenance period will be as defined in Table 4.3a.

A1.2.5 The test CAM would be operated according to the manufacturer's instructions over a three-month period. The maintenance period would be determined by repeated injections of span and zero gas at two weekly intervals, as described under the long term drift tests in Section A1.2 v and viii below.

(iii) Zero-drift Tests

A1.2.6 Zero drift is defined as the change which takes place in the CAM's response to a certified zero gas over a specified period of time. The different times over which zero drift should be tested are given below.

(iv) Twenty-four Hour Zero Drift

A1.2.7 A gas certified to be free of the measured pollutant and interferences would be supplied to the CAMs under test for the recommended averaging period of the CAM, T_r . The twenty-four hour zero drift would be calculated as the difference between the average of two stable zero values made on two consecutive days, averaged over the period.

$$X_{24hr} = \frac{1}{2} \cdot (Z_{1a} + Z_{2a}) - \frac{1}{2} \cdot (Z_{1b} + Z_{2b}) \quad \text{eq A1.20}$$

Where:-

- Z_{1a} = 1st Zero reading on Day 1;
- Z_{2a} = 2nd Zero reading on Day 1;
- Z_{1b} = 1st Zero reading on Day 2;
- Z_{2b} = 2nd Zero reading on Day 2;

(v) **Long-term Zero Drift**

A1.2.8 A gas certified to be free of the measured pollutant and interferents would be supplied to the CAM and two stable measurements taken over consecutive periods equal to the recommended averaging period, T_s , would be made. This would be repeated every two weeks. Long-term zero drift X_{ZM} would be calculated from the difference between the average of two stable zero readings made at the beginning and end of the maintenance interval, where the maintenance interval would be determined as defined in Section A1.2 ii above.

$$X_{ZM} = \frac{1}{2} \cdot (Z_{1a} + Z_{2a}) - \frac{1}{2} \cdot (Z_{1b} + Z_{2b}) \quad \text{eq A1.21}$$

Where :-

- Z_{1a} = 1st Zero reading at start of maintenance interval;
- Z_{2a} = 2nd Zero reading at start of maintenance interval;
- Z_{1b} = 1st Zero reading at end of maintenance interval;
- Z_{2b} = 2nd Zero reading at end of maintenance interval;

The standard uncertainty due to zero drift u_{ZM} would be calculated from :

$$u_{ZM} = \frac{X_{ZM}}{\sqrt{3}} \quad \text{eq A1.22a}$$

The expanded uncertainty can be calculated from the standard uncertainty using the following formula:

$$U_{ZM} = u_{ZM} \cdot k \quad \text{eq A1.22b}$$

The coverage factor $k = 1.65$ should be used to obtain a 95% confidence interval when the distribution is rectangular [ISO Guide to Measurement Uncertainty Annex G p59]. This component of the measurement uncertainty of the CAM would be included into the determination of the combined performance characteristic (paragraphs 2.3.2 and 2.3.3).

(vi) **Span-drift Tests**

A1.2.9 Span drift is defined as the change which takes place in the CAM's response to span gas over a specified period of time. The different times over which span drift should be tested are given below.

(vii) **Twenty-four Hour Span Drift**

A1.2.10 A test gas with a known concentration value, which is nominally 80% of C_{max} , would be supplied to the CAM and readings would be averaged over the period T_s . The twenty-four hour span drift (X_{S24}) would then be calculated as the difference

between the averaged values of the stable output indicator readings obtained on two consecutive days expressed as a percentage of the limit value:

$$X_{\text{st}} = \frac{S_n - S_{n-1}}{C_{\text{test}}} \times C_{\text{limit}} \quad \text{eq A1.23}$$

Where:

S_n = Average of two stable span readings on Day 2 - average of two stable zero readings on Day 2;

S_{n-1} = Average of two stable span readings on Day 1 - average of two stable zero readings on Day 1;

C_{test} = Test gas concentration

(viii) Long-term Span Drift

A1.2.11 A test gas with a known value, nominally 80% of C_{max} , would be supplied to the CAM and two stable measurements taken over consecutive periods equal to the recommended averaging period, T_a , would be made. This would be repeated every two weeks. Long-term span drift X_{SM} , would be calculated from the difference between the average of two stable span readings made at the beginning and end of the maintenance interval, where the maintenance interval would be determined as defined in Section A1.2 ii above.

$$X_{SM} = \frac{S_n - S_{n-1}}{C_{\text{test}}} \cdot C_{\text{limit}} \quad \text{eq A1.24}$$

Where:

S_{n-1} = Average of two stable span readings at start of maintenance interval - average of two stable zero readings at start of maintenance period;

S_n = Average of two stable span readings at end of maintenance interval - average of two stable zero readings at end of maintenance period;

C_{test} = Test gas concentration;

The standard uncertainty due to the span drift, u_{SM} , would be calculated from :

$$u_{SM} = \frac{X_{SM}}{\sqrt{3}} \quad \text{eq A1.25a}$$

The expanded uncertainty can be calculated from the standard uncertainty using the following formula:

$$U_{SM} = u_{SM} \cdot k \quad \text{eq A1.25b}$$

The coverage factor $k = 1.65$ should be used to obtain a 95% confidence interval when the distribution is rectangular [ISO Guide to Measurement Uncertainty Annex G p59]. This component of the measurement uncertainty of the CAM would be included into the determination of the combined performance characteristic (paragraphs 2.3.2 and 2.3.3).

(ix) **Availability (Data capture)**

A1.2.12 The CAM's availability is defined as the fraction of the total time for which data of acceptable quality which would be suitable for inclusion into national networks, and for reporting to the EU within its Air Quality Directive, is available. Data from the CAM would be collected automatically and total data capture will be determined for the operating period of the field test.

(x) **Additional tests for NO_x and SO₂ CAMs**

A1.2.13 At the beginning and end of the field test programme, a NO_x converter efficiency test will be carried out on both CAMs as described in A1.1.50. If the initial converter efficiency is less than 95% then the field tests will be suspended until a repair is carried out, and this will be reported in the test report. If the converter efficiency at the end of the tests is less than 95%, the field test will be deemed invalid.

A1.2.14 At the beginning and end of the field test, the cross sensitivity of the SO₂ CAMs to hydrocarbons will be tested by injecting 1 ppm meta-xylene (traceable to national gas standards) into both CAMs. This test is to determine the efficiency of the 'scrubber' which measures hydrocarbons that may interfere with the CAMs response to SO₂. If the CAM's response is greater than 5ppb for the first cross-sensitivity test, the field tests will be suspended until a repair of the hydrocarbon scrubber is carried out. This will be reported on the test certificate. If the field test is carried out and CAM's response at the end of the field test is greater than 5ppb, this will also be reported.

A1.3 DEFINITIONS OF PERFORMANCE CHARACTERISTICS FOR PARTICULATE-MEASURING INSTRUMENTS (LABORATORY TESTS)

A1.3.1 The laboratory testing of particulate monitors would be carried out using a test facility Laboratory Particulate Generator (LPG) which can provide a well-characterised and reproducible particulate size distribution with a mass concentration which may be varied from 0 µg.m⁻³ to 500 µg.m⁻³ at a gas flow velocity of between 1.0 m.s⁻¹ to 10 m.s⁻¹ in a filtered particulate-free background. These tests provide a known test sample which would be used to test certain parameters of the CAMs operation under repeatable laboratory conditions.

The performance characteristics to be determined in the laboratory are :

- Response Time⁽¹⁾
- Repeatability Standard Deviation⁽¹⁾
- Accuracy
- Detection Limit / Quantification Limit
- Short Term Zero Drift⁽¹⁾
- Linear Fit
- Cross-sensitivity to Other Parameters⁽¹⁾

- Environmental Conditions
- Physical Disturbance
- Sample Flow
- Combined Performance

(1) These tests will only be performed on continuous measuring CAMs, in cases where the Certification Committee decide they are applicable. It is recommended that instruments which provide continuous readings of particulate levels, eg TEOM and Beta Gauge instruments should be subjected to these tests.

These performance characteristics are discussed in more detail below.

(i) Response Time

A1.3.2 The response time performance characteristics outlined in A1.1 (i) for gaseous CAMs will also apply to certain particulate monitors tested using an LPG test facility.

(ii) Detection Limit and Quantification Limit

A1.3.3 The detection limit of the CAM would be measured by injecting standard particulate material into the LPG at a typical velocity (~2 m.s⁻¹) and reducing the particulate concentration until the CAM ceases to respond to changes in particulate concentration. If the CAM remains sensitive to the lowest particulate concentration achievable, a gas certified free of significant particulate concentration (zero gas) would be used to monitor the instrumental noise at the detection limit. Five sequential measurements, each taken over the CAM's averaging period, T_a, would be recorded at the lowest particulate level, and used to calculate the detection limit according to equation A1.26 .

The detection limit is defined as:

$$X_D = t_f(0.95)S_0 \quad \text{eq A1.26}$$

where:

- X_D is the detection limit expressed in concentration units of the determinand gas;
- S₀ is the standard deviation of five measurements;
- (f + 1) is the number of measurement values obtained;
- t_f(0.95) is the statistical Student t-factor for a 95% confidence interval with f degrees of freedom;

A1.3.4 The quantification limit is defined as twice the detection limit when both these performance characteristics are quoted with identical confidence limits.

Therefore for a confidence limit of 95%:

$$X_Q = 2X_D \quad \text{eq A1.27}$$

where:

X_Q is the quantification limit expressed in concentration units of the determinand gas;

(iii) **Short-term Zero drift**

A1.3.5 The performance characteristics described in A1.1(iv) for gaseous CAMs would also apply to certain particulate monitors tested in an LPG test facility using the performance standards specified in Section 4.3.

(iv) **Repeatability Standard Deviation**

A1.3.6 The performance characteristics described in A1.1(ii) for gaseous CAMs would also apply to particulate monitors tested in an LPG test facility using the performance characteristics specified in Section 4.3.

A1.3.7 Repeatability standard deviation is defined from the measured statistical variations of the CAM determined during the above test, and is defined as a standard uncertainty:

$$u_{sd} = S_r \quad \text{eq A1.28a}$$

where:

S_r is the standard deviation of the measurements

The expanded uncertainty can be calculated from the standard uncertainty using the following formula:

$$U_{SD} = t_f(0.95)u_{sd} \quad \text{eq A1.28b}$$

where:

U_{SD} is the repeatability expressed in concentration units of the determinand;

$(f + 1)$ is the number of measured values obtained;

$t_f(0.95)$ is the statistical Student t-factor for a 95% confidence interval with f degrees of freedom;

(v) **Accuracy**

A1.3.8 The CAM would be calibrated by the manufacturer, or supplier, in the factory, or at the start of the laboratory tests. The calibration should use the standard operating procedures defined for calibrating the CAM, and should use any calibration (if applicable) artifacts which are normally recommended by the manufacturer, or supplier, for this purpose. The artifacts used to calibrate the CAM should be traceable to national standards of particulate concentration, where possible, and the measurement uncertainty and traceability of these values should be stated.

A1.3.9 A test sample with a known value, at the limit value concentration, would be supplied to the CAM under test and in parallel to an isokinetically-sampling reference sampler, using nationally-traceable weighing procedures. The measured value is the average of at least ten measurements, each measurement being the average output from the CAM over a sampling period T_s . The CAM under test should have been calibrated according to manufacturers' instructions using any artifacts supplied or specified by them for this purpose. The accuracy would be determined by calculating the difference between the measured value and the collected mass of the particulate from the reference sampler. The repeatability will also be calculated from the measured standard deviation, using equation A1.31b, and this will be compared with the value obtained from measurements at about 80% of C_{max} .

A1.3.10 Where failure of the CAM to meet the Performance Standard is directly attributable to poorly-specified calibration artifacts provided by the CAM manufacturer or supplier, or to incorrect algorithms which are employed for the use of these artifacts, the CAM would be re-tested with calibration artifacts which meet requirements. If the CAM passes the re-test, it would not fail the accuracy test, but the MCERTS Certificate will carry a warning alerting users to the need for correct calibration.

A1.3.11 The accuracy is a measure of the uncertainty due to calibration. The correct treatment of this source of measurement uncertainty on the air-quality results requires a knowledge of the operational procedures under which the CAM would be operated in the field. For example, it will depend on how many calibrations are performed within the reporting period, and whether the uncertainty is due to random or systematic causes (ISO Standard 11222 gives a full treatment of this issue). An estimate of the uncertainty contribution of the accuracy may be made, if it is assumed that for a given calibration there is an equal probability of the true value lying between $-X_A$ and $+X_A$. The standard uncertainty due to the accuracy of the CAM, defined as u_A , would then be determined from X_A as follows:

$$u_A = \frac{X_A}{\sqrt{3}} \quad \text{eq A1.29a}$$

The expanded uncertainty can be calculated from the standard uncertainty using the following formula:

$$U_A = u_A \cdot k \quad \text{eq A1.29b}$$

The coverage factor $k = 1.65$ should be used to obtain a 95% confidence interval when the distribution is rectangular [ISO Guide to Measurement Uncertainty Annex G p59]. This component of the measurement uncertainty of the CAM would be included into the determination of the combined performance characteristic (paragraphs 2.3.2 and 2.3.3).

(vi) Test of Linear Fit

A1.3.12 The linearity of the CAM under test would be tested over the range 0 to 90% of the agreed certification range, using at least five concentrations plus a zero point,

at a typical air flow velocity of 7 m.s⁻¹. The number of measurements made at each calibration point shall be large enough to ensure that the uncertainty of the mean of the measurements at that concentration is less than ±10% of the required uncertainty of fit. A linear fit would be performed on these mean values. The largest residual from the linear fit would be used to define the lack of fit. The residual departures from least square fitting values would also be plotted and this graph would be examined to check for systematics or trends.

- A1.3.13 The uncertainty on the CAM output due to this performance characteristic may be estimated by assuming that across the CAM's range (and hence at the limit value) the maximum error due to non linear fit is ± X_L. This document assumes that this is a rectangular distribution with a standard uncertainty is which given by :

$$u_L = \frac{X_L}{\sqrt{3}} \quad \text{eq A1.30a}$$

The expanded uncertainty can then be calculated from the standard uncertainty using the following formula:

$$U_L = u_L \cdot k \quad \text{eq A1.30b}$$

The coverage factor k = 1.65 should be used to obtain a 95% confidence interval when the distribution is rectangular [ISO Guide to Measurement Uncertainty Annex G p59]. This component of the measurement uncertainty of the CAM would be included into the determination of the combined performance characteristic (paragraphs 2.3.2 and 2.3.3).

(vii) Cross Sensitivity of the Particulate CAM to Wind Velocity and the Fractional Composition of Particulate Matter

- A1.3.14 The sensitivity of the particulate CAM to the following potential types of interferent would be tested, using the LPG test facility, where required by the Certification Committee,:

a) An LPG test facility would be used to monitor the effect of velocity changes at a fixed particulate concentration at the limit value, using up to ten different velocities at equal steps between 1.0 m.s⁻¹ and 10.0 m.s⁻¹.

b) The effect of changing the size of the particulate employed in the LPG would be monitored and reported on the Certificate.

- A1.3.15 The Certification Committee would define which of the above interferent tests should be conducted on each CAM, in consultation with the manufacturer, or supplier, and the test house. This decision would be based on an expert understanding of the measurement methodology employed by the CAM.

- A1.3.16 The tests for each interfering condition would be repeated four times and the maximum effect observed under each condition would be reported. The measurement uncertainty due to the interference effects would be determined by

assuming that in the worst case all interferences would be correlated (the approach used within ISO 14956). The standard uncertainty due to interference effects u_i would be estimated from :

$$u_i = \frac{S}{\sqrt{3}} \quad \text{eq A1.31a}$$

where:

S = The maximum of $|S_c|$ or $|S_m|$

and where:

S_c is the cross sensitivity due to changes in wind velocity;
 S_m is the cross sensitivity due to fractional compositional changes of the particulate matter;

The expanded uncertainty can be calculated from the standard uncertainty using the following formula:

$$U_i = u_i \cdot k \quad \text{eq A1.31b}$$

The coverage factor $k = 1.65$ should be used to obtain a 95% confidence interval when the distribution is rectangular [ISO Guide to Measurement Uncertainty Annex G p59]. This component of the measurement uncertainty of the CAM would be included into the determination of the combined performance characteristic (paragraphs 2.3.2 and 2.3.3).

(viii) Environmental Conditions and Physical Disturbance

A1.3.17 The performance characteristics described in A1.1 for gases also apply to particulate monitors, except that the zero particulate value only would be tested.

A1.3.18 The standard uncertainty contributions caused by the influence of ambient temperature on the CAM's output would be derived from:

$$u_{AT} = X_{AT} \cdot \frac{(T_{\max} - T_{\min})}{\sqrt{3}} \quad \text{eq A1.32a}$$

Where T_{\max} and T_{\min} are the maximum and minimum temperatures respectively which have been agreed between the Certification Committee and the CAM manufacturer, or supplier, as the range of environmental temperature conditions which would be encountered operationally.

The expanded uncertainty can then be calculated from the standard uncertainty using the following formula:

$$U_{AT} = u_{AT} \cdot k \quad \text{eq A1.32b}$$

The coverage factor $k = 1.65$ should be used to obtain a 95% confidence interval when the distribution is rectangular [ISO Guide to Measurement Uncertainty

Annex G p59]. This component of the measurement uncertainty of the CAM would be included into the determination of the combined performance characteristic (paragraphs 2.3.2 and 2.3.3).

(ix) Sample-gas Flow

A1.3.19 The sample-gas flow of the sampler Q_{av} , would be measured, using a mass flow meter directly traceable to national flow standards. Ten repeat measurements of flow would be carried out during the sampling period and the average difference between the indicated flow and the mass flow meter readings, X_F , would be compared with the performance characteristic. The standard uncertainty contribution due to X_F would then be calculated from:

$$u_F = \frac{X_F \cdot C_{limit}}{Q_{av} \sqrt{3}} \quad \text{eq A1.33a}$$

The expanded uncertainty should then be calculated from the standard uncertainty using the following formula:

$$U_F = u_F \cdot k \quad \text{eq A1.33b}$$

The coverage factor $k = 1.65$ should be used to obtain a 95% confidence interval when the distribution is rectangular [ISO Guide to Measurement Uncertainty Annex G p59]. This component of the measurement uncertainty of the CAM would be included into the determination of the combined performance characteristic (paragraphs 2.3.2 and 2.3.3).

(x) Combined Performance Characteristic

A1.3.20 The standard combined measurement uncertainty would be calculated by summing the results of the relevant performance tests according to the equation given in Section 2.3 (which is repeated below for completeness):

$$u_c = \sqrt{\sum_{i=1}^n u_i^2} \quad \text{eq A1.34}$$

A1.3.21 The individual standard uncertainties u_i should be derived as described in the Sections above, and the long term drift determined in the field tests described in A1.4. Only those performance characteristics which contribute to the overall uncertainty would be combined as follows :

$$u_c = \sqrt{u_{SD}^2 + u_A^2 + u_{ZM}^2 + u_{SM}^2 + u_L^2 + u_I^2 + u_{AT}^2 + u_F^2} \quad \text{eq A1.35}$$

A1.3.22 In addition, a separate estimate of u_c would be obtained using the overall measurement uncertainty determined from the Field Tests, described in A1.4

below. This gives a separate estimate of u_c because field repeatability will measure directly a number of uncertainty sources, namely all those influence variables which vary during the field tests. It does not, however, test these over controlled ranges, and neither does it give any indication of the effects of these influences. It does nevertheless provide data on the performance of the CAM under real conditions with representative correlations between all the influence variables.

This overall uncertainty defined as u_c would in this case be determined by applying equation A1.34 to the following uncertainty sources:

$$u_c = \sqrt{u_R^2 + u_{AF}^2 + u_{ZM}^2 + u_{SM}^2 + u_L^2 + u_I^2 + u_{AT}^2 + u_F^2} \quad \text{eq A1.36}$$

A1.3.23 The expanded combined uncertainties, U_c and $U_{c'}$, when expressed at the 95% confidence interval will be derived from the combined standard uncertainties u_c and $u_{c'}$ by multiplying them by coverage factors which are determined from the total number of degrees of freedom according both to the GUM and to the Welch-Satterthwaite[6] equation. Conformance with the Performance Standards in this document would require the conformance of both U_c and $U_{c'}$ with the combined performance characteristic (Table 4.4a part 1).

A1.4 DEFINITIONS OF PERFORMANCE CHARACTERISTICS FOR CONTINUOUS (PM₁₀ AND PM_{2.5}) PARTICULATE-MEASURING INSTRUMENTS (FIELD TESTS)

A1.4.1 The candidate CAMs would be operated in the field for a period of three months. The samplers would be located at a site appropriate to the operational category (paragraph 2.4.1) required for product certification, (urban, rural etc), which will also be selected in accordance with the siting criteria described in CEN Reference Method EN12341.

A1.4.2 The samplers would be installed and initially calibrated by the manufacturer. The samplers would be operated continuously for the test period during which the following parameters would be tested.

- Repeatability in the Field
- Zero drift⁽¹⁾
- Span Drift⁽¹⁾
- Accuracy
- Maintenance interval
- Availability (data capture)

⁽¹⁾ These tests will only be performed for continuous measuring CAMs, where these are applicable.

(i) **Repeatability in the Field**

A1.4.3 Two identical samplers would be co-located at a site specific to the application category (paragraph 2.4.1) as agreed between the CAM manufacturer, or supplier, the Certification Committee and the test house, and both would be set to sample the same atmospheric air for a period sufficient to obtain at least forty valid daily average values. For manual CAMs, filter samples would be weighed and conditioned using standard procedures as detailed in Appendix 8. The repeatability in the field would be determined from the standard deviation of the difference, X_{sd} , between the two measurements made at the same time over the test period. The mean of the differences, X_{bar} , will also be calculated to determine any bias between the results obtained from the two CAMs involved in the field tests.

The repeatability in the field is determined from the measured statistical variations of the CAMs during the above test, and can be defined as a standard uncertainty:

$$u_R = X_{sd} \quad \text{eq A1.37a}$$

The expanded uncertainty will be calculated from the standard uncertainty using the following formula:

$$U_R = [t_f (0.95) u_R] + \left(\frac{X_{bar}}{\sqrt{3}} \cdot k \right) \quad \text{eq A1.37b}$$

where:

(f + 1) is the number of measured values obtained;
 $t_f(0.95)$ is the statistical Student t-factor for a 95% confidence interval with f degrees of freedom;

The coverage factor $k = 1.65$ should be used to obtain a 95% confidence interval when the distribution is rectangular [ISO Guide to Measurement Uncertainty Annex G p59].

(ii) **Zero-drift Tests**

A1.4.4 **Zero-drift tests** will only be possible if the sampler is able to accommodate a system - such an air filter to introduce particulate free air. If this is the case then the zero drift will be determined as specified for gaseous CAMs described in A1.2 Section (iii).

The standard uncertainty due to zero drift u_{ZM} would be calculated from :

$$u_{ZM} = \frac{X_{ZM}}{\sqrt{3}} \quad \text{eq A1.38a}$$

The expanded uncertainty can be calculated from the standard uncertainty using the following formula:

$$U_{ZM} = u_{ZM} \cdot k \quad \text{eq A1.38b}$$

The coverage factor $k = 1.65$ should be used to obtain a 95% confidence interval when the distribution is rectangular [ISO Guide to Measurement Uncertainty Annex G p59]. This component of the measurement uncertainty of the CAM would be included into the determination of the combined performance characteristic (paragraphs 2.3.2 and 2.3.3).

(iii) Span-drift Tests

A1.4.5 Span-drift tests will only be possible if the sampler is fitted with a device, to trigger span checks, (eg the absorption filter disk fitted to beta-ray attenuation particulate-monitoring systems). If this is the case the span drift would be determined as specified for gaseous CAMs described in section A1.2. section vi.

The standard uncertainty due to span drift u_{SM} would be calculated from :

$$u_{SM} = \frac{X_{SM}}{\sqrt{3}} \quad \text{eq A1.39a}$$

The expanded uncertainty can be calculated from the standard uncertainty using the following formula:

$$U_{SM} = u_{SM} \cdot k \quad \text{eq A1.39b}$$

The coverage factor $k = 1.65$ should be used to obtain a 95% confidence interval when the distribution is rectangular [ISO Guide to Measurement Uncertainty Annex G p59]. This component of the measurement uncertainty of the CAM would be included into the determination of the combined performance characteristic (paragraphs 2.3.2 and 2.3.3).

(iv) Accuracy With Respect To CEN Reference Method EN12341

A1.4.6 The CAM may be corrected for bias with regard to the Reference Method specified in EN12341 before commencement of the test. The details of any correction applied should be supplied to the test house, and will be reported. The candidate CAMs would then be co-located with a Reference Method, as given in EN12341, and all the samplers would be operated in parallel for a period sufficient to obtain at least twenty valid daily average values. The correlation between daily average concentrations would be calculated using an appropriate regression function.

The following specifications, which are derived from EN12341, would then apply as MCERTS Performance Standards:

The relationship $Y = f(X)$ calculated from the regression function for the particulate concentrations obtained by the candidate samplers should conform to the acceptance band stated below:

$Y = X \pm 10 \mu\text{g.m}^{-3}$ for concentrations $< 100 \mu\text{g.m}^{-3}$

$Y = 0.9X$ to $1.1X$ for concentrations $> 100 \mu\text{g.m}^{-3}$

Where:

X = the measured value of concentration obtained by the Reference Method.

Y = the measured value of concentration obtained from the CAM

These criteria are equivalent to a requirement that:

- the measured value Y is within $\pm 10\%$ of the reference value X for values of X greater than $100 \mu\text{g.m}^{-3}$;
- for values of X below $100 \mu\text{g.m}^{-3}$ Y should be within $\pm 10 \mu\text{g.m}^{-3}$ of X.

The variance coefficient R^2 must be > 0.95 over the complete concentration range

The standard uncertainty due to the accuracy, with respect to the CEN reference method, of the CAM, defined as u_{AF} , would then be determined from Y as follows:

$$u_{AF} = \frac{|C_{limit} - Y|}{\sqrt{3}} \quad \text{eq A1.40a}$$

Equation A1.40a is only valid in cases where both X and C_{limit} are less than $100 \mu\text{g.m}^{-3}$, even if X is not equal to C_{limit} . This is due to the assumption of constant variance made in EN 12341 for values of X below $100 \mu\text{g.m}^{-3}$. In other cases a more rigorous statistical analysis would be required.

The expanded uncertainty can be calculated from the standard uncertainty using the following formula:

$$U_{AF} = u_A \cdot k \quad \text{eq A1.40b}$$

The coverage factor $k = 1.65$ should be used to obtain a 95% confidence interval when the distribution is rectangular [ISO Guide to Measurement Uncertainty Annex G p59]. This component of the measurement uncertainty of the CAM would be included into the determination of the combined performance characteristic (paragraphs 2.3.2 and 2.3.3).

(v) **Maintenance interval**

A1.4.7 The maintenance interval is defined as the time in the operating environment in the field over which the CAM's zero and span drifts remain within the limits specified in this document. This would serve as an indication of the level of maintenance which would be required operationally. It may be necessary to replace consumables (sample filters) within the maintenance interval, as specified by the manufacturer, to ensure proper CAM performance. In this case a maintenance period will also be defined which will be the maximum period between the replacement of consumables. During the tests on the maintenance interval, the CAM's calibration and maintenance will be carried out using documented procedures, and no adjustments will be made which will alter the

response of the CAM. The minimum allowable maintenance period will be as defined in Table 4.5a.

The test CAM would be operated according the manufacturer's instructions over a three-month period. Where appropriate the maintenance period would be determined by repeated measurements of span and zero at two weekly intervals, as described under the long term drift tests in Section A1.4 ii and iii above.

(vi) Availability (Data capture)

A1.4.8 The CAM's availability is defined as the fraction of the total time for which data of acceptable quality which would be suitable for inclusion into national networks, and for reporting to the EU within its Air Quality Directive, is available. Data from the CAM would be collected automatically and total data capture will be determined for the operating period of the field test.

(vii) Filter weighing procedures

A1.4.9 Filter weighing procedures are not within the scope of a CAM product certification scheme. Recommendations for weighing procedures are described in Appendix 8.

A1.5 DEFINITIONS OF PERFORMANCE CHARACTERISTICS FOR METALS MEASURING CAMS (LABORATORY TESTS)

A1.5.1 The laboratory testing of metals monitoring systems would involve testing the sampling system to ensure that the system correctly samples particulate matter. The tests performed would include all the tests used for particulate systems since these are relevant to the CAMs used for metals monitoring. The performance characteristics to be determined are :

- Repeatability Standard Deviation;
- Accuracy;
- Linear Fit;
- Flow;
- Environmental Conditions;
- Combined Performance;

A1.5.2 These would be determined in the same manner as for particulate monitoring CAMs. It should be noted that metals monitoring CAMs collect the total particulate matter over a comparatively long period of time T_s , and hence performance characteristics such as response time and averaging effects are not applicable.

(i) **Combined Performance Characteristic**

A1.5.3 The standard combined uncertainty would be calculated by summing the results of the relevant performance tests according to the equation given in Section 2.3 (repeated below):

$$u_c = \sqrt{\sum_{i=1}^n u_i^2} \quad \text{eq A1.41}$$

A1.5.4 The individual standard uncertainties u_i should be derived as described above. Only those performance characteristics which contribute to the overall uncertainty would be combined as follows :

$$u_c = \sqrt{u_{SD}^2 + u_A^2 + u_L^2 + u_{AT}^2 + u_F^2 + u_{AN}^2} \quad \text{eq A1.42}$$

where:

u_{AN} = standard uncertainty due to analysis all;
all other terms are defined in Appendix A1.3;

A1.5.5 In addition, a separate estimate of u_c would be made using the uncertainty determined from the field repeatability tests performed during the Field Tests, described in A1.6. This gives a separate estimate of u_c because field repeatability may directly measure a number of uncertainty sources, namely all those influence variables which vary during the field tests. It does not test these over controlled ranges, neither does it give any indication of the relative effects of these influences. However it does show the performance of the CAM under real conditions with representative correlations between influence variables. u_c would be determined by applying the above equation to the following uncertainty sources:

$$u_{c'} = \sqrt{u_R^2 + u_{AF}^2 + u_L^2 + u_{AT}^2 + u_F^2 + u_{AN}^2} \quad \text{eq A1.43}$$

where:

u_{AN} = standard uncertainty due to analysis
all other terms are defined in Appendix A1.3.

A1.5.6 The expanded combined uncertainties U_c and $U_{c'}$ expressed at the 95% confidence interval, will be derived from the combined standard uncertainties u_c and $u_{c'}$ by multiplying them by coverage factors which are determined from the total number of degrees of freedom according to GUM and the Welch-Satterthwaite[6] equation. Conformance with the Performance Standards in this document would require the conformance of both U_c and $U_{c'}$ with the combined performance characteristic (Table 4.4.a part 1).

A1.6 DEFINITIONS OF PERFORMANCE CHARACTERISTICS FOR METALS MEASURING CAMS (FIELD TESTS)

A1.6.1 The candidate CAM would be operated in the field for a period of 3 months. The sampler would be located at a site appropriate to the requirement for certification, urban, rural etc, which be selected in accordance with recognised siting criteria.

A1.6.2 The sampler(s) would be installed and initially calibrated by the manufacturer. The sampler(s) would be operated continuously for the test period during which the following parameters would be tested.

- Repeatability in the field;
- Flow stability;
- Flow accuracy.

(i) Repeatability in the Field

A1.6.3 Two candidate samplers would be operated in parallel for a period sufficient to obtain at least forty valid daily average values. Filter samples would be weighed and conditioned using standard procedures as detailed in Appendix 8. The field repeatability would be determined from the standard deviation of the difference, X_{sd} , between the two measurements made at the same time over the test period. The mean of the differences, X_{bias} , will also be calculated to show the bias between the two CAMs.

The field repeatability is defined from the measured statistical variations of the CAM during the above test and can be defined as a standard uncertainty:

$$u_R = X_{sd} \quad \text{eq A1.44a}$$

The expanded uncertainty can be calculated from the standard uncertainty using the following formula:

$$U_R = [t_f(0.95)u_R] + \left(\frac{X_{bias}}{\sqrt{3}} \cdot k \right) \quad \text{eq A1.44b}$$

where:

- (f + 1) is the number of measured values obtained;
- $t_f(0.95)$ is the statistical Student t-factor for a 95% confidence interval with f degrees of freedom;

The coverage factor $k = 1.65$ should be used to obtain a 95% confidence interval when the distribution is rectangular [ISO Guide to Measurement Uncertainty Annex G p59]. This component of the measurement uncertainty of the CAM will be included into the determination of the combined performance characteristic (paragraphs 2.3.2 and 2.3.3).

(ii) **Flow-rate Measurement**

A1.6.4 The flow-rate at the sampler inlet would be measured using a volumetric flow meter, calibrated for the flow rate of the sampler, in a manner which is traceable to national flow standards. While a flow meter which provides a direct indication of volumetric flow rate is preferred for this test, an alternative certified flow measurement device may be used as long as appropriate volumetric flow rate corrections are made, based on measurements of actual ambient temperature and pressure conditions. Flow measurements would be recorded every thirty minutes over a six-hour test period. Ambient temperature and pressure would also be recorded during the test period and the measured flow rates would be adjusted to a standard temperature and pressure, where applicable.

(iii) **Flow-rate Stability**

A1.6.5 Flow-rate stability is assessed from the measured statistical variations of the flow during the test and is defined as a standard uncertainty:

$$u_{FS} = \frac{Q_{SD}}{Q_{av}} \cdot C_{limit} \quad \text{eq A1.45a}$$

where:

Q_{SD} is the standard deviation of the measured flow
 Q_{av} is the mean flow rate measured in section iv

The expanded uncertainty can be calculated from the standard uncertainty using the following formula:

$$U_{FS} = t_f(0.95)u_{FS} \quad \text{eq A1.45b}$$

The coverage factor $k = 1.65$ should be used to obtain a 95% confidence interval when the distribution is rectangular [ISO Guide to Measurement Uncertainty Annex G p59]. This component of the measurement uncertainty of the CAM would be included into the determination of the combined performance characteristic (paragraphs 2.3.2 and 2.3.3)

(iv) **Flow-rate Accuracy**

A1.6.6 The mean flow rate (Q_{av}) for the sample period would be calculated as

$$Q_{av} = \frac{\sum_{i=1}^n q_i}{n} \quad \text{eq A1.46}$$

Where:

n = the number of discrete certified flow rate measurements over the test period.

A1.6.7 The difference between the indicated flow and the mean flow rate, X_{FA} would be compared with the performance characteristic. The standard uncertainty contribution due to X_{FA} would be calculated from:

$$u_{FA} = \frac{(1 - \frac{X_{FA}}{Q_{sv}}) \times C_{limit}}{\sqrt{3}} \quad \text{eq A1.47a}$$

The expanded uncertainty can be calculated from the standard uncertainty using the following formula:

$$U_{FA} = u_{FA} \cdot k \quad \text{eq A1.47b}$$

The coverage factor $k = 1.65$ should be used to obtain a 95% confidence interval when the distribution is rectangular [ISO Guide to Measurement Uncertainty Annex G p59]. This component of the measurement uncertainty of the CAM would be included into the determination of the combined performance characteristic (paragraphs 2.3.2 and 2.3.3).

(v) Filter weighing procedures

A1.6.8 Filter weighing procedures are not within the scope of the MCERTS product certification scheme, but recommendations for weighing procedures are described in Appendix 8.

A1.7 DEFINITION OF PERFORMANCE CHARACTERISTICS FOR PAH MONITORING SYSTEMS (LABORATORY TESTS)

A1.7.1 The laboratory testing of PAH monitoring systems involves the testing of the sampling system to ensure that the system correctly retains PAHs collected over the sampling period. The performance characteristics to be determined are:

- Sampling efficiency
- Dynamic retention capacity
- Detection limit

(i) Sampling Efficiency and Dynamic-Retention Efficiency

A1.7.2 For both tests a spiking solution is necessary containing those compounds for which certification is required. The spiking solution should be dissolved in a volatile solvent such as hexane. Spiking levels should correspond to at least three times, but not more than ten times the anticipated concentrations of the target compounds in the air to be measured. Following spiking with the solution, the spiked filter or sorbent would be allowed to dry in a clean dark area, for at least one hour prior to the time when the CAM is used to sample the ambient air.

A1.7.3 The sampling rate and sampling period should correspond to that of the certification range. Ambient temperatures during the test should be similar to

those expected during ambient sampling, particularly if warm ambient temperatures are expected.

A1.7.4 Sampling efficiency is determined by adding the spiking solution onto a clean particle filter, backed up with the vapour collecting adsorbent cartridge. Then a volume of air equivalent to the maximum sample volume is pulled through the assembly. The spiking solution would be added dropwise to the filter, so as to uniformly load it and avoid over saturation. The sorbent and spiked filter must be analysed separately and any residue retained by the filter subtracted from the internal spike quantity for calculation of sampling efficiencies. This test would be repeated five times.

A1.7.5 The sampling efficiency, SE, is defined as:

$$SE = \frac{W}{W_0 - W_r} \quad \text{eq A1.48}$$

where :

W is the quantity of PAH extracted from the sorbent after air is drawn through it;

W_0 is the quantity of PAH initially applied to the filter;

W_r is the quantity of PAH remaining on the filter after the air is pulled through it.

The sampling efficiency would be determined for each repeated test and the average sampling efficiency SE_{av} would be calculated. The standard uncertainty for sampling efficiency is defined using the following formula:

$$u_{SE} = \frac{(1 - SE_{av}) \times C_{limit}}{\sqrt{3}} \quad \text{eq A1.49a}$$

The expanded uncertainty, for each PAH for which certification is required, can then be calculated from the standard uncertainty using the following formula:

$$U_{SE} = u_{SE} \cdot k \quad \text{eq A1.49b}$$

The coverage factor $k = 1.65$ should be used to obtain a 95% confidence interval when the distribution is rectangular [ISO Guide to Measurement Uncertainty Annex G p59]. This component of the measurement uncertainty of the CAM would be included into the determination of the combined performance characteristic (paragraphs 2.3.2 and 2.3.3)

A1.7.6 Retention efficiency is determined by spiking the sorbent directly, placing it behind a clean filter in the sampling module and pulling through the maximum sample volume. The spiking solution is carefully injected into the inlet face of the sorbent bed in a manner that would apply the solution uniformly across the face and to a depth of no more than 1 cm. For determination of retention efficiencies only the sorbent is analysed. This test would be repeated five times.

A1.7.7 The dynamic retention efficiency, RE, is defined as:

$$RE = \frac{W}{W_0} \quad \text{eq A1.50}$$

where:

W is the quantity of PAH extracted from the sorbent after air is pulled through it
W₀ is the quantity of PAH initially applied to the sorbent bed.

The retention efficiency would be determined for each of the tests and the average retention efficiency RE_{av} would be calculated. The standard uncertainty for retention efficiency is defined using the following formula:

$$U_{RE} = \frac{(1 - RE_{av}) \times C_{limit}}{\sqrt{3}} \quad \text{eq A1.51a}$$

The expanded uncertainty, for each PAH for which certification is required, can then be calculated from the standard uncertainty using the following formula:

$$U_{RE} = u_{RE} \cdot k \quad \text{eq A1.51b}$$

The coverage factor k = 1.65 should be used to obtain a 95% confidence interval when the distribution is rectangular [ISO Guide to Measurement Uncertainty Annex G p59]. This component of the measurement uncertainty of the CAM would be included into the determination of the combined performance characteristic (paragraphs 2.3.2 and 2.3.3).

(ii) Detection Limit

A1.7.8 The detection limit for analysis would be determined by the analytical laboratory from analysis of five analytical blanks and five field blanks. These blanks will be produced according to the procedures given in Appendix 7.

The detection limit is defined as:

$$U_D = t_f(0.95)S_0 \quad \text{eq A1.52}$$

where:

- U_D is the detection limit expressed in mass of the determinand
- S₀ is the standard deviation of the measurements
- (f+1) is the number of measurement values obtained
- t_f(0.95) is the statistical Student t-factor for a 95% confidence interval with f degrees of freedom.

In addition a statistical test (ANOVA) would be carried out to test whether there is any significant difference between the laboratory and field blank results. Any such difference would be reported.

(iii) **Combined Performance Characteristic**

A1.7.9 The standard combined uncertainty would be calculated by summing the results of the relevant performance tests according to the equation given in Section 2.3 (repeated below):

$$u_c = \sqrt{\sum_{i=1}^n u_i^2} \quad \text{eq A1.53}$$

A1.7.10 The individual standard uncertainties u_i should be derived as described in sections above, and the flow uncertainties calculated from the field tests. Only those performance characteristics which contribute to the overall uncertainty would be combined as follows :

$$u_c = \sqrt{u_{SE}^2 + u_{RE}^2 + u_{RC}^2 + u_{FS}^2 + u_{FA}^2} \quad \text{eq A1.54}$$

u_c should be calculated for each PAH for which certification is required.

A1.7.11 In addition a separate estimate of u_c would be made using the uncertainty determined from the field repeatability tests performed during the Field Tests, described in A1.8. This gives a separate estimate of u_c because field repeatability may directly measure a number of uncertainty sources, namely all those influence variables which vary during the field tests. It does not test these over controlled ranges, neither does it give any indication of the relative effects of these influences. However it does show the performance of the CAM under real conditions with representative correlations between influence variables. u_c would be determined by applying the above equation to the following uncertainty sources:

$$u_{c'} = \sqrt{u_R^2 + u_{SE}^2 + u_{RE}^2 + u_{RC}^2 + u_{FS}^2 + u_{FA}^2} \quad \text{eq A1.55}$$

$u_{c'}$ should be calculated for each PAH for which certification is required.

A1.7.12 The expanded combined uncertainties U_c and $U_{c'}$ expressed at the 95% confidence interval will be derived from the combined standard uncertainties u_c and $u_{c'}$ by multiplying it by a coverage factor determined from the total number of degrees of freedom according to GUM and the Welch-Satterthwaite[6] equation. Conformance with the Performance Standards in this document would require the conformance of both the U_c and $U_{c'}$ with the requirements given in Table 4.8.

A1.8 **DEFINITIONS OF PERFORMANCE CHARACTERISTICS FOR PAH MONITORING SYSTEMS (FIELD TESTS)**

A1.8.1 The candidate CAM would be operated in the field for a period of three months. The sampler would be located at a site appropriate to the requirement for

certification, which would be selected in accordance with recognised siting criteria.

A1.8.2 The sampler(s) would be installed and initially calibrated by the manufacturer. The sampler(s) would be operated continuously for the test period during which the following parameters would be tested:

- Field repeatability;
- Sample retention capacity;
- Flow accuracy;
- Flow stability.

(i) Repeatability in the Field

A1.8.3 Two candidate samplers would be operated in parallel for a period sufficient to obtain at least twenty valid paired values. The field repeatability would be determined from the standard deviation of the difference, X_{sd} , between the two measurements made at the same time over the test period. The mean of the differences, X_{bar} , will also be calculated to show the bias between the two CAMs. Field repeatability would be determined for each PAH for which certification is sought.

The field repeatability is defined from the measured statistical variations of the CAM during the above test and can be defined as a standard uncertainty:

$$u_R = X_{sd} \quad \text{eq A1.56a}$$

The expanded uncertainty can be calculated from the standard uncertainty using the following formula:

$$U_R = (t_f(0.95)u_R) + \left(\frac{X_{bar}}{\sqrt{3}} \cdot k \right) \quad \text{eq A1.56b}$$

where:

- (f + 1) is the number of measured values obtained;
- $t_f(0.95)$ is the statistical Student t-factor for a 95% confidence interval with f degrees of freedom;

The coverage factor $k = 1.65$ should be used to obtain a 95% confidence interval when the distribution is rectangular [ISO Guide to Measurement Uncertainty Annex G p59].

(ii) Sample Retention Capacity

A1.8.4 Before sampling, five of each sampling cartridge (either filter or filter and adsorbent) should be spiked with a known quantity of a mixture of isotope-labeled PAHs. The isotope-labeled PAH standards shall be either labelled with deuterated or carbon-13. The mixture shall contain known quantities of each PAH for which certification is required. The solvent used for the mixture shall be no higher in boiling point than nonane.

A1.8.5 The sampler shall be operated over the specified sampling time under the same conditions as used in the field repeatability test above. Care should be taken that these conditions represent the likely range of co-contaminants and concentrations to be encountered. The recovery of each of the individual isotope labeled standards should be measured and expressed as a percentage of the quantity added to that sample. Recoveries between 40% and 140% are accepted with this Performance Standard. In addition, the mean should be taken for each compound and the standard deviation calculated. The mean should be compared with the acceptance standard. A standard deviation greater than 50% of the mean value would be unacceptable for this Performance Standard.

A1.8.6 The mean isotope-labeled standard retention capacity requirement depends on the analytical approach taken. If the sampler is to be used with HPLC analysis then the criteria should be that the retention efficiency for each compound for which certification is given shall be between 80% and 140%. If sampling and analysis is carried out using sampling standards and isotope dilution then certification shall be given for results between 40% and 140%.

The standard uncertainty due to sample retention capacity for each compound of interest can be calculated from the following equation:

$$u_{rc} = \frac{(1 - \frac{RC}{100}) \times C_{limit}}{\sqrt{3}} \quad \text{eq A1.57a}$$

where

RC is the retention capacity of the PAH of interest

The expanded uncertainty needs to be calculated for every PAH for which certification is required, and is calculated from the following formula

$$U_{rc} = u_{rc} \cdot k \quad \text{eq A1.57b}$$

The coverage factor $k = 1.65$ should be used to obtain a 95% confidence interval when the distribution is rectangular [ISO Guide to Measurement Uncertainty Annex G p59]. This component of the measurement uncertainty of the CAM would be included into the determination of the combined performance characteristic (paragraphs 2.3.2 and 2.3.3).

(iii) **Flow-rate Measurement**

A1.8.7 The flow rate at the sampler inlet would be measured using a volumetric flow meter, calibrated for the flow rate of the sampler, which is traceable to national flow standards. While a flow meter which provides a direct indication of volumetric flow rate is desirable for this test, an alternative nationally-traceable flow measurement device may be used as long as appropriate volumetric flow rate corrections are made - which are based on measurements of actual ambient temperature and pressure conditions. Flow measurements would be recorded every thirty minutes over at least a six-hour test period (ie a minimum of 12

measurements). Ambient temperature and pressure would also be recorded during the test period and the measured flow rates would be adjusted to a standard temperature and pressure if applicable. All ambient temperature and pressure measurements should be made with an accuracy which does not significantly affect the accuracy of the volume flow measurement.

(iv) **Flow-rate Accuracy**

A1.8.8 The mean flow rate (Q_{av}) for the sample period would be calculated as:

$$Q_{av} = \frac{\sum_{i=1}^n Q_i}{n} \quad \text{eq A1.58}$$

where:

n = the number of discrete certified flow rate measurements over the test period (see A1.8.7).

The difference between the indicated flow and the mean flow rate, X_{FA} would be compared with the performance characteristic. The standard uncertainty contribution due to X_{FA} would be calculated from:

$$u_{FA} = \frac{\left(1 - \frac{X_{FA}}{Q_{av}}\right) \times C_{limit}}{\sqrt{3}} \quad \text{eq A1.59a}$$

The expanded uncertainty can be calculated from the standard uncertainty using the following formula:

$$U_{FA} = u_{FA} \cdot k \quad \text{eq A1.59b}$$

The coverage factor $k = 1.65$ should be used to obtain a 95% confidence interval when the distribution is rectangular [ISO Guide to Measurement Uncertainty Annex G p59]. This component of the measurement uncertainty of the CAM would be included into the determination of the combined performance characteristic (paragraphs 2.3.2 and 2.3.3).

(v) **Flow-rate Stability**

A1.8.9 Flow rate stability is defined as the measured statistical variations of the flow during the test and is defined as a standard uncertainty:

$$u_{FS} = \frac{Q_{SD}}{Q_{av}} \cdot C_{limit} \quad \text{eq A1.60a}$$

where:

Q_{SD} is the standard deviation of the measured flow

The expanded uncertainty can be calculated from the standard uncertainty using the following formula:

$$U_{FS} = t_f(0.95)u_{FS} \quad \text{eq A1.60b}$$

The coverage factor $k = 1.65$ should be used to obtain a 95% confidence interval when the distribution is rectangular [ISO Guide to Measurement Uncertainty Annex G p59]. This component of the measurement uncertainty of the CAM would be included into the determination of the combined performance characteristic (paragraphs 2.3.2 and 2.3.3).

A1.9 DEFINITIONS OF PERFORMANCE CHARACTERISTICS FOR BENZENE MONITORING SYSTEMS (LABORATORY TESTS)

A1.9.1 The instrument performance characteristics defined here for benzene monitoring systems are presented in the order in which they would be tested in the laboratory.

The performance characteristics to be determined are :

- Detection Limit / Quantification Limit;
- Repeatability Standard Deviation;
- Carry Over;
- Accuracy;
- Linear Fit;
- Cross Sensitivity to Interferent Substances;
- Environmental Conditions;
- Combined Performance.

(i) Detection limit

A1.9.2 The detection limit is a measure of the uncertainty, expressed as a 95% confidence interval, of the output signal from the CAM when a sample is applied which is free of the determinand. This is interpreted as the lowest output value which is statistically distinguishable from a zero value. The quantification limit is a performance measure based on the detection limit, which is defined as the lowest CAM reading which, with a 95% confidence interval, could not have been produced from an input gas free of the determinand.

A certified pure air sample with a concentration of ≤ 50 ppt (50 parts in 10^{12} by volume or mole fraction) of benzene would be supplied to the CAM, and the standard deviation of a minimum of five measurements would be calculated.

The detection limit is defined as:

$$X_D = t_f(0.95)S_0 \quad \text{eq A1.61}$$

where:

- X_D is the detection limit expressed in concentration units of the determinand gas
- S_0 is the standard deviation of the measurements
- $(f+1)$ is the number of measurement values obtained
- $t_f(0.95)$ is the statistical Student t-factor for a 95% confidence interval with f degrees of freedom.

A1.9.3 The quantification limit is defined as twice the detection limit when both these performance characteristics are quoted with identical confidence intervals.

Therefore for a confidence interval of 95%:

$$X_Q = 2X_D \quad \text{eq A1.62}$$

where:

- X_Q is the quantification limit expressed in concentration units of the determinand gas

(ii) Repeatability Standard Deviation and Carry Over

A1.9.4 Benzene monitoring CAMs would be tested for carry over of benzene from one sample to the next. The CAM would be supplied with calibration gas for one hour, at a nominal concentration of 80% of C_{max} , followed by an hour where zero gas is injected. This procedure would be repeated ten times and the results would be used to measure both repeatability and carry over.

A1.9.5 Repeatability standard deviations are calculated at both the span and zero concentrations and are defined as the measured statistical variations of the CAM during the above test. The standard uncertainties at span and zero are defined as follows :

$$\begin{aligned} u_z &= S_z \\ u_s &= S_s \end{aligned} \quad \text{eq A1.63a}$$

where:

- S_s is the standard deviation of the span measurements
- S_z is the standard deviation of the zero measurements

The expanded uncertainties will be calculated from the standard uncertainties using the following formulae:

$$\begin{aligned} U_c &= t(0.95)u_z \\ U_{SD} &= t_f(0.95)u_s \end{aligned} \quad \text{eq A1.63b}$$

where:

- U_{SD} is the expanded uncertainty of the measurements made at the span concentration;

- U_c is the expanded uncertainty of the measurements made at zero concentration;
- $(f + 1)$ is the number of measured values obtained.
- $t_{(0.95)}$ is the statistical Student t-factor for a 95% confidence interval with f degrees of freedom.

(iii) Accuracy

A1.9.6 The CAM should be calibrated according to manufacturer's instructions and using any artifacts supplied or specified for this purpose at the beginning of the test. A test gas sample with a known value, at the limit value concentration, traceable to national gas concentration standards, would be supplied to the CAM. The accuracy would be determined from the difference between the measured and the true value. The measured value would be the average of at least four measurements. The repeatability will be calculated as the standard deviation of these measurements, using equation eq A1.63b and this will be compared with the value obtained from measurements at 80% $^{\circ}C_{max}$.

A1.9.7 Where failure of the CAM to meet the Performance Standard is directly attributable to poorly specified or chosen calibration artifacts provided by the CAM manufacturer or supplier, or to incorrect conversion algorithms, the CAM would be re-tested with the calibration artifacts which meet requirements. If the CAM passes the re-test, it would not fail the accuracy test, but the MCERTS Certificate will carry a warning alerting users to the need for adequate calibration.

A1.9.8 The accuracy is a measure of the uncertainty due to calibration. The correct treatment of this source of measurement uncertainty on the air quality results requires a knowledge of the operational procedures under which the CAM would be operated in the field. For example, it will depend on how many calibrations are performed within the reporting period, and whether the uncertainty is due to random or systematic causes (ISO 11222 gives a full treatment of this issue). An estimate of the uncertainty contribution of the accuracy may be made, if it is assumed that for a given calibration there is an equal probability of the true value lying between $-X_A$ and $+X_A$. The standard uncertainty due to the accuracy of the CAM, defined as u_A , would then be determined from X_A as follows:

$$u_A = \frac{X_A}{\sqrt{3}} \quad \text{eq A1.64}$$

The expanded uncertainty can then be calculated from the standard uncertainty using the following formula:

$$U_A = u_A \cdot k \quad \text{eq A1.64b}$$

The coverage factor $k = 1.65$ should be used to obtain a 95% confidence interval when the distribution is rectangular [ISO Guide to Measurement Uncertainty Annex G p59]. This component of the measurement uncertainty of the CAM would be included into the determination of the combined performance characteristic (paragraphs 2.3.2 and 2.3.3). If the uncertainty due to accuracy is a

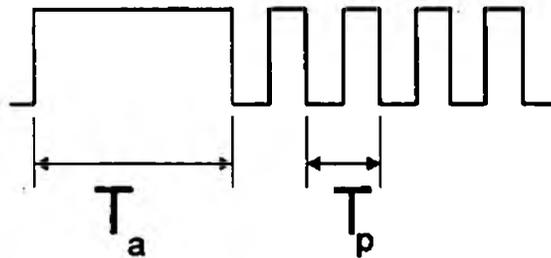
significant contribution and causes the CAM to fail the combined performance characteristic (paragraph 2.3.1) will not fail MCERTS. However the Certificate will contain recommendations for improved calibration artifacts.

(iv) **Averaging Effect**

A1.9.9 The averaging effect performance criterion provides a measure of the uncertainty in CAM results which are caused by short-term fluctuations in the input sample concentration that occur at time scales shorter than the CAM's averaging period of T_a .

A1.9.10 The CAM under test would be supplied with a concentration at twice the limit value for a time period equal to the sample collection period, T_a . During the next sample collection period the CAM would be supplied with step changes between zero and the fixed concentration, with an average concentration of one half of the fixed concentration. The period of the square wave (T_p), would comprise one minute of zero gas followed by one minute of span gas. These periods may be altered by the Certification Committee to suit individual CAM test requirements.

Figure A1.4 Schematic of the Averaging Test



A1.9.11 The averaging error X_{av} would be calculated according to :

$$X_{av} = \overline{C_{const}} - (2 \cdot \overline{C_{var}}) \quad \text{eq A1.65}$$

where:

C_{const} is the average measured concentration during the constant concentration period

C_{var} is the average measured concentration during the variable concentration period

The averaging error would be compared with the requirements given in Tables 4.10 a and b to determine whether this performance standard is satisfied.

A1.9.12 The averaging error also leads to a measurement uncertainty in the CAM output. This would depend on the real level of variability of the concentrations of the pollutant concentration present in the field. In this context, the test sample used above may reasonably be taken as a worst case. The measurement uncertainty shall then be assumed to be a rectangular distribution from 0 to X_{AV} . This distribution is not symmetrical about the 'true' value. If no correction is applied to

the data then the standard uncertainty based on this distribution is calculated according to :

$$u_{AV} = \frac{X_{AV}}{\sqrt{3}} \quad \text{eq A1.66a}$$

The expanded uncertainty can be calculated from the standard uncertainty using the following formula:

$$U_{AV} = u_{AV} \cdot k \quad \text{eq A1.66b}$$

The coverage factor $k = 1.65$ should be used to obtain a 95% confidence interval when the distribution is rectangular [ISO Guide to Measurement Uncertainty Annex G p59].

A1.9.13 This component of the measurement uncertainty of the CAM would be included in the determination of the combined performance characteristic (paragraphs 2.3.1 and 2.3.2).

(v) **Test of Linear Fit**

A1.9.14 The CAM is assumed to have a linear response between the input determinand concentrations and the final output signals (see paragraph A1.1.39). The linearity of the CAM under test would be tested over the range 0% to 90% of the agreed certification range, using at least five concentrations plus a zero point. All test gas concentrations would be accurate with respect to each other to better than $\pm 0.5\%$ of value. Measurements at each concentration would be made and a linear fit applied to the mean measurements. The number of measurements made at each calibration point shall be high enough to ensure that the uncertainty of the mean of the measurements at that concentration is less than $\pm 10\%$ of the required uncertainty of the linear fit. A linear fit would be performed on the mean of the measured values at each calibration point. The largest residual from the linear fit would be taken as the lack of fit X . The residuals would also be plotted and the graph examined to check for trends.

A1.9.15 The uncertainty on the CAM output due to this performance characteristic may be estimated by assuming that across the CAM's range (and hence at the limit value) the maximum error due to non linear fit is $\pm X_L$. Assuming this is a rectangular distribution the standard uncertainty is given by :

$$u_L = \frac{X_L}{\sqrt{3}} \quad \text{eq A1.67a}$$

The expanded uncertainty can be calculated from the standard uncertainty using the following formula:

$$U_L = u_L \cdot k \quad \text{eq A1.67b}$$

The coverage factor $k = 1.65$ should be used to obtain a 95% confidence interval when the distribution is rectangular [ISO Guide to Measurement Uncertainty Annex G p59]. This component of the measurement uncertainty of the CAM would be included into the determination of the combined performance characteristic (paragraphs 2.3.2 and 2.3.3).

(vi) **Cross-sensitivity to Interfering Substances**

A1.9.16 Cross sensitivity will be tested in the same manner as for continuous gaseous monitoring CAMs but with those gaseous species that are most likely to interfere with the measurement of benzene. Such gaseous species may be different for different techniques. The test procedure is described in appendix A1.1 section (vii).

A1.9.17 The uncertainty due to the interference effects would be estimated by assuming that in the worst case all interferents would be correlated (the approach used within ISO 14956). The standard uncertainty due to interference effects u_i would then be estimated by

$$u_i = \frac{S}{\sqrt{3}} \quad \text{eq A1.68a}$$

where:

S = The maximum of $|S_c|$ or $|S_m|$;

S_c = The response due to the summed effect of the individual interferent tests;

S_m = The response due to the combined effect of the mixture interferent test;

The expanded uncertainty can be calculated from the standard uncertainty using the following formula:

$$U_i = u_i \cdot k \quad \text{eq A1.68b}$$

The coverage factor $k = 1.65$ should be used to obtain a 95% confidence interval when the distribution is rectangular [ISO Guide to Measurement Uncertainty Annex G p59]. This component of the measurement uncertainty of the CAM would be included into the determination of the combined performance characteristic (paragraphs 2.3.2 and 2.3.3).

(vii) **Effects of Sample Gas Pressure and Temperature, Environmental Conditions, and Physical Disturbance**

A1.9.18 These tests would be carried out as detailed for continuous gas measurements CAMs in Appendix A1.1 Sections (ix) to (xi).

A1.9.19 The standard uncertainty contributions caused by the influence of sample gas temperature and pressure would be derived as follows

$$u_{SP} = X_{SP} \cdot \frac{(P_{\max} - P_{\min})}{\sqrt{3}} \quad \text{eq A1.69a}$$

$$u_{ST} = X_{ST} \cdot \frac{(T_{\max} - T_{\min})}{\sqrt{3}} \quad \text{eq A1.70b}$$

The expanded uncertainties can be calculated from the standard uncertainties using the following formulas:

$$U_{SP} = u_{SP} \cdot k \quad \text{eq A1.69b}$$

$$U_{ST} = u_{ST} \cdot k \quad \text{eq A1.70b}$$

The coverage factor $k = 1.65$ should be used to obtain a 95% confidence interval when the distribution is rectangular [ISO Guide to Measurement Uncertainty Annex G p59]. This component of the measurement uncertainty of the CAM would be included into the determination of the combined performance characteristic (paragraphs 2.2.2 and 2.2.3).

The standard uncertainty contributions caused by the influence of ambient temperature on the CAM's output would be derived from

$$u_{AT} = X_{AT} \cdot \frac{(T_{\max} - T_{\min})}{\sqrt{3}} \quad \text{eq A1.71a}$$

The expanded uncertainty can be calculated from the standard uncertainty using the following formula:

$$U_{AT} = u_{AT} \cdot k \quad \text{eq A1.71b}$$

The coverage factor $k = 1.65$ should be used to obtain a 95% confidence interval when the distribution is rectangular [ISO Guide to Measurement Uncertainty Annex G p59]. This component of the measurement uncertainty of the CAM would be included into the determination of the combined performance characteristic (paragraphs 2.3.2 and 2.3.3).

(viii) Combined Performance Characteristic

A1.9.20 Combined performance would be determined in the same way as for continuous monitoring CAMs described in appendix A1.1.

A1.9.21 The combined performance characteristic would be calculated by summing the results of the relevant performance tests according to the equation given in Section 2.3 (repeated below):

$$u_c = \sqrt{\sum_{i=1}^n u_i^2} \quad \text{eq A1.72}$$

A1.9.22 The individual standard uncertainties u_i should be derived as described in Sections i) to vii) above, and the long-term drift determined in the field tests described in A1.10. Only those performance characteristics which contribute to the overall uncertainty would be combined as follows :

$$u_c = \sqrt{u_{SD}^2 + u_{ZM}^2 + u_{SM}^2 + u_A^2 + u_L^2 + u_I^2 + u_{SP}^2 + u_{ST}^2 + u_{AT}^2 + u_C^2} \quad \text{eq A1.73}$$

A1.9.23 In addition, a separate estimate of u_c would be determined using the uncertainty determined from the field repeatability tests performed during the Field Tests, described in A1.10. This is known as $u_{c'}$. This gives a separate estimate of the combined performance characteristic because field repeatability may directly measure a number of uncertainty sources, namely all those influence variables which vary during the field tests. It does not test these over controlled ranges, neither does it give any indication of the relative effects of these influences. However it does show the performance of the CAM under real conditions with representative correlations between influence variables. $U_{c'}$ would be determined by applying the above equation to the following uncertainty sources:

$$u_{c'} = \sqrt{u_R^2 + u_{ZM}^2 + u_{SM}^2 + u_A^2 + u_L^2 + u_I^2 + u_{SP}^2 + u_{ST}^2 + u_{AT}^2 + u_C^2} \quad \text{eq A1.74}$$

The expanded combined uncertainties U_c and $U_{c'}$ expressed as 95% confidence intervals will be derived from the combined standard uncertainties u_c and $u_{c'}$ by multiplying by coverage factors determined from the total number of degrees of freedom according to GUM and the Welch-Satterthwaite[6] equation. Conformance with the Performance Standards in this document would require the conformance of both $u_{c'}$ and u_c with the combined performance characteristic (Table 4.10a part 1).

A1.10 DEFINITIONS OF PERFORMANCE CHARACTERISTICS FOR BENZENE MONITORING SYSTEMS (FIELD TESTS)

A1.10.1 The candidate CAMs would be operated in the field for a period of three months. The samplers would be located at a site appropriate for the operational category (paragraph 2.4.1) required for product certification, (urban, rural etc), which would be selected in accordance with recognised siting criteria.

A1.10.2 The CAMs would be installed and initially calibrated by the manufacturer. They would be operated continuously for the test period during which the following parameters would be tested.

- Repeatability in the field;
- Maintenance interval;
- Zero Drift;
- Span Drift;
- Zero Signal;
- Availability (data capture).

(i) **Repeatability in the Field**

A1.10.3 Two identical analysers would be co-located at a site specific to the application category (paragraph 2.4.1) as agreed between the CAM manufacturer, or supplier, the Certification Committee and the test house, and both would be set to sample the same atmospheric air. The field repeatability would be determined from the standard deviation of the difference, X_{sd} , between the two measurements made at the same time over the test period. Each measurement will be an average over the period T_r . The mean of the differences, X_{bar} , will also be calculated to show the bias between the two CAMs.

The field repeatability is defined from the measured statistical variations of the CAM during the above test and can be defined as a standard uncertainty:

$$u_R = X_{sd} \quad \text{eq A1.75a}$$

The expanded uncertainty can be calculated from the standard uncertainty using the following formula:

$$U_R = (t_f(0.95)u_R) + \left(\frac{X_{bar}}{\sqrt{3}} \cdot k \right) \quad \text{eq A1.75b}$$

where:

(f + 1) is the number of measured values obtained;
 $t_f(0.95)$ is the statistical Student t-factor for a 95% confidence interval with f degrees of freedom;

The coverage factor $k = 1.65$ should be used to obtain a 95% confidence interval when the distribution is rectangular [ISO Guide to Measurement Uncertainty Annex G p59].

(ii) **Maintenance Interval**

A1.10.4 The maintenance interval is defined as the time in the operating environment in the field over which the CAM's zero and span drifts remain within the limits specified in this document. This would serve as an indication of the level of maintenance which would be required operationally. It may be necessary to replace consumables (eg desiccants or sample inlet filters) within the maintenance interval, as specified by the manufacturer, to ensure proper CAM performance. In this case a maintenance period will also be defined which will be the maximum period between the replacement of consumables. During the tests on the maintenance interval, the CAM's calibration and maintenance will be carried out using documented procedures, and no adjustments will be made which will alter the response of the CAM. The minimum allowable maintenance period will be as defined in Table 4.11a.

A1.10.5 The test CAM would be operated according the manufacturer's instructions over a three-month period. The maintenance period would be determined by repeated

injections of span and zero gas at two weekly intervals, as described under the long term drift tests in Section A1.10 v and viii below.

(iii) Zero-drift Tests

A1.10.6 Zero drift is defined as the change which takes place in the CAM's response to a certified zero gas over a specified period of time. The different times over which zero drift should be tested are given below.

(iv) Twenty-four Hour Zero Drift

A1.10.7 A gas certified to be free of the measured pollutant and interferences would be supplied to the CAMs under test for the recommended averaging period of the CAM, T_a . The twenty-four hour zero drift would be calculated as the difference between the average of two stable zero values made on two consecutive days, averaged over the period.

$$X_{24hr} = \frac{1}{2} \cdot (Z_{1a} + Z_{2a}) - \frac{1}{2} \cdot (Z_{1b} + Z_{2b}) \quad \text{eq A1.76}$$

Where:-

- Z_{1a} = 1st Zero reading on Day 1;
- Z_{2a} = 2nd Zero reading on Day 1;
- Z_{1b} = 1st Zero reading on Day 2;
- Z_{2b} = 2nd Zero reading on Day 2;

(v) Long-term Zero Drift

A1.10.8 A gas certified to be free of the measured pollutant and interferences would be supplied to the CAM and two stable measurements taken over consecutive periods equal to the recommended averaging period of the CAM, T_a , would be made. This would be repeated every two weeks. Long-term zero drift X_{2M} would be calculated as the difference between the average of two stable zero readings made at the beginning and end of the maintenance interval, where the maintenance interval would be determined as defined in Section A1.10 ii above.

$$X_{2M} = \frac{1}{2} \cdot (Z_{1a} + Z_{2a}) - \frac{1}{2} \cdot (Z_{1b} + Z_{2b}) \quad \text{eq A1.77}$$

Where :-

- Z_{1a} = 1st Zero reading at start of maintenance interval;
- Z_{2a} = 2nd Zero reading at start of maintenance interval;
- Z_{1b} = 1st Zero reading at end of maintenance interval;
- Z_{2b} = 2nd Zero reading at end of maintenance interval;

The standard uncertainty due to zero drift u_{ZM} would be calculated from:

$$u_{ZM} = \frac{X_{ZM}}{\sqrt{3}} \quad \text{eq A1.78a}$$

The expanded uncertainty can be calculated from the standard uncertainty using the following formula:

$$U_{ZM} = u_{ZM} \cdot k \quad \text{eq A1.78b}$$

The coverage factor $k = 1.65$ should be used to obtain a 95% confidence interval when the distribution is rectangular [ISO Guide to Measurement Uncertainty Annex G p59]. This component of the measurement uncertainty of the CAM would be included into the determination of the combined performance characteristic (paragraphs 2.3.2 and 2.3.3).

(vi) Span-drift Tests

A1.10.9 Span drift is defined as the change which takes place in the CAM's response to span gas over a specified period of time. The different times over which span drift should be tested are given below.

(vii) Twenty-four Hour Span Drift

A1.10.10 A test gas with a known concentration value, which is nominally 80% of C_{max} , would be supplied to the CAM and readings would be averaged over the period T_a . The twenty-four hour span drift (X_{S24}) would then be calculated as the difference between the averaged values of the stable output indicator readings obtained on two consecutive days expressed as a percentage of the limit value:

$$X_{S24} = \frac{S_n - S_{n-1}}{C_{test}} \times C_{limit} \quad \text{eq A1.79}$$

Where:

S_n = Average of two stable span readings on Day 2 - average of two stable zero readings on Day 2;

S_{n-1} = Average of two stable span readings on Day 1 - average of two stable zero readings on Day 1;

C_{test} = Test gas concentration;

(viii) Long-term Span Drift

A1.10.11 A test gas with a known value, nominally 80% of C_{max} , would be supplied to the CAM and two stable measurements taken over consecutive periods equal to the recommended averaging period of the CAM, T_a , would be made. This would be repeated every two weeks. The long-term span drift X_{SM} would be calculated the difference between the average of two stable of stable span readings made at the

beginning and end of the maintenance interval, where the maintenance interval would be determined as defined in Section A1.10 ii above.

$$x_{SM} = \frac{S_n - S_{n-1}}{C_{test}} \times C_{limit} \quad \text{eq A1.80}$$

Where:

S_{n-1} = Average of two stable span readings at start of maintenance interval - average of two stable zero readings at start of maintenance period;

S_n = Average of two stable span readings at end of maintenance interval - average of two stable zero readings at end of maintenance period;

C_{test} = Test gas concentration;

The standard uncertainty due to drift u_{SM} would be calculated from:

$$u_{SM} = \frac{x_{SM}}{\sqrt{3}} \quad \text{eq A1.81a}$$

The expanded uncertainty can be calculated from the standard uncertainty using the following formula:

$$U_{SM} = u_{SM} \cdot k \quad \text{eq A1.81b}$$

The coverage factor $k = 1.65$ should be used to obtain a 95% confidence interval when the distribution is rectangular [ISO Guide to Measurement Uncertainty Annex G p59]. This component of the measurement uncertainty of the CAM would be included into the determination of the combined performance characteristic (paragraphs 2.3.2 and 2.3.3).

(ix) Zero Signal of the CAM

A1.10.12 The zero (background) reading of the benzene measuring CAM should not exceed the Performance Standard for detection limit given in Table 4.10a part¹. This shall be determined by using certified zero gas as specified in Appendix 9.

(x) Availability (Data Capture)

A1.10.13 The CAM's availability is defined as the fraction of the total time for which data of acceptable quality which would be suitable for inclusion into national networks, and for reporting to the EU within its Air Quality Directive, is available. Data from the CAM would be collected automatically and total data capture will be determined for the operating period of the field test.

APPENDIX 2: MAIN STANDARDS AND CEN ACTIVITIES UNDERPINNING THE PROPOSED MCERTS PERFORMANCE STANDARDS

A2.1 MAIN STANDARDS REVIEWED

Determinand	International Standard used as Basis for Performance Standards
General	<p>ISO 6879 (1995) Air Quality - Performance characteristics and related concepts for air quality measurements</p> <p>ISO 9169 (1994) Air Quality - Determination of performance characteristics of measurement methods. Also Amendment 1 (CD)(1998).</p> <p>BS EN 61207-1 (IEC 1207-1) 1994 Expression of performance of gas analyzers</p>
SO ₂	PrEN "SO ₂ " Ambient air - Measurement method for the determination of the mass concentration of SO ₂ by the means of ultraviolet fluorescence.
CO	ISO/DIS 4224 Ambient air -- Determination of carbon monoxide -- Non-dispersive infrared spectrometric method
NO _x	<p>PrEN "NO_x" version 2 Ambient air - Measurement method for the determination of the concentration of NO_x and NO by chemiluminescence.</p> <p>ISO 7996:1985 Ambient air – Determination of the mass concentration of nitrogen oxides – chemiluminescence method</p>
O ₃	<p>ISO 13964:1998 Air quality – Determination of ozone in ambient air – Ultraviolet photometric method</p> <p>ISO 10313:1993 Ambient air – Determination of the mass concentration of ozone – Chemiluminescence method</p>
Particulates	<p>EN 12341 Air quality - Determination of the PM₁₀ fraction of suspended particulate matter - Reference method and field test procedure to demonstrate reference equivalence of measurement methods</p> <p>ISO/DIS 10473 Ambient air – Measurement of the mass of particulate matter on a filter medium -- Beta-ray absorption method</p>
Lead	ISO 9855:1993 Ambient air – Determination of the particulate lead content of aerosols collected on filters – Atomic absorption spectrometric method
PAH	ISO/DIS 12884 Air quality – Determination of gas- and particle-phase polycyclic aromatic hydrocarbons in ambient air -- Collection on sorbent-backed filters with gas chromatographic/mass spectrometric analysis
Benzene	<p>BS EN 1076:1997 Workplace atmospheres. Pumped sorbent tubes for the determination of gases and vapours. Requirements and test methods</p> <p>VDI 3482 Part 5 Measurement of gaseous emissions - Gas chromatographic determination of aromatic hydrocarbons - sampling by enrichment on activated carbon -desorption with solvent</p>

US EPA Parts 50 and 53 were also considered in the specification of the Performance Standards for NO_x, O₃, CO, SO₂, Particulate matter, and Lead.

**A2.2 CEN TECHNICAL COMMITTEE AND WORKING GROUPS PRODUCING
NEW STANDARDS RELATED TO AMBIENT AIR QUALITY**

CEN Technical Committee and Associated Working Groups	Title
CEN Technical Committee 264	Air Quality
WG 12	Reference methods for SO₂, NO₂, O₃ and CO in Ambient Air
WG 13	Reference methods for Benzene in Ambient Air
WG 14	Reference methods for Pb, Cd, As and Ni in Ambient Air
WG 15	Reference methods for PM_{2.5} measurements in Ambient Air

APPENDIX 3: STANDARD ENVIRONMENTAL OPERATING CONDITIONS

Several existing IEC standards depend upon the first edition of IEC Publication 359, and call for the manufacturer to specify particular values and ranges of influence quantities, according to three degrees of severity known as usage groups I, II and III, as follows:

- I For indoor use and under conditions which are normally found in laboratories and factories and where equipment would be handled carefully.
- II For use in environments having protection from full extremes of environment and under conditions of handling between those of Groups I and III.
- III For outdoor use and in areas where the equipment may be subjected to rough handling.

For testing to the proposed MCERTS performance standards, it would be assumed that CAMs would be operated and tested to class I conditions.

A3.1 CLIMATIC CONDITIONS

A3.1.1 Ambient temperature

Rated ranges of use: +5°C to +40°C

Storage and transport temperature -40°C to +70°C

A3.1.2 Relative humidity of the air

Because extreme values of both temperature and humidity are not likely to occur simultaneously, the manufacturer may specify the time limit over which these may be applied and shall specify the limitations of the combination, if any, for continuous operation.

Rated ranges of use: 20% to 80% excluding condensation;

A3.1.3 Barometric pressure (altitude)

Rated ranges of use: 70.0 kPa to 106.0 kPa
(up to 2200 m altitude)
(525 mm Hg to 800 mm Hg)

A3.1.4 Heating effect due to solar radiation

Rated ranges of use: no direct irradiation;

A3.1.5 Velocity of the ambient air

Rated ranges of use: 0 m/s to 0.5 m/s

A3.1.6 Sand and dust content of the ambient air

Rated ranges of use: negligible content

A3.1.7 Salt content of the air

Rated ranges of use: negligible content

A3.1.8 Contaminating gas or vapour content of the air

Rated ranges of use: specified by the manufacturer

A3.1.9 Liquid water content of the air

Rated ranges of use: negligible contents

A3.2 MECHANICAL CONDITIONS

A3.2.1 Operating position

Rated ranges of use: recommended position $\pm 30^\circ$

A3.2.2 Ventilation

Rated ranges of use: negligibly obstructed

A3.2.3 Vibration

Rated ranges of use: negligible value

A3.3 MAINS SUPPLY CONDITIONS

A3.3.1 Mains supply voltage (considering a distorted waveform)

	DC and AC (rms) (% of rated voltage)	AC Peak (% of rated voltage)
Rated ranges of use	$\pm 10\%$	$\pm 12\%$
Limit range of operation (called "limiting conditions" in this standard).	Equal to the rated range of use, unless otherwise stated	

A3.3.2 Mains supply frequency

Rated ranges of use: rated value $\pm 5\%$

A3.3.3 Distortion of AC mains supply

The distortion is determined by a factor b in such a way that the waveform is inside an envelope formed by:

$$y_1 = (1 + b) A \sin \omega t$$

and

$$y_2 = (1 - b) A \sin \omega t$$

Rated ranges of use: $b = 0.05$

The values of b are valid when the apparatus is connected to the supply mains.

Notes 1: The above formulae may be applied over a half cycle or a full cycle depending on whether the zero crossings are equally spaced or not.

A3.3.4 Other distortions

Pulses and spikes in an ac mains supply are provisionally covered by Mains supply frequency.

A3.3.5 Ripples of DC supply

Rated ranges in use:	0.5% of the supply voltage
Limit range of operation:	5.0% of the supply voltage

The values given are peak-to-peak values of the ripple voltage expressed as a percentage of the average dc supply voltage.

APPENDIX 4: LIST OF PAHS TO BE CONSIDERED

This list of PAHs is based on those monitored by the DETR's Toxic Organic Micro Pollutants (TOMPs) Network.

Acenaphthene
Acenaphthylene
Anthracene
Benz[a]anthracene
Benzo[a]pyrene
Benzo[b]fluoranthene
Benzo[k]fluoranthene
Chrysene
Coronene
Dibenz[ac]anthracene
Dibenz[ah]anthracene
Fluoranthene
Fluorene
Indeno[123,cd]pyrene
Methylphenanthrene
Phenanthrene
Pyrene

APPENDIX 5: REQUIREMENTS FOR SAMPLING LINE AND SAMPLING MANIFOLD

- A5.1 The sample intake should be constructed in such a way that suction of rain water into the sample line (or CAM system) is prevented. The material of the sample intake as well as the sample line (or CAM system) can influence the composition of the gas in the sampling line. Materials such as polytetrafluoro-ethylene (PTFE), perfluoro-ethylene-propylene (FEP), glass or stainless steel may be used. Copper or copper-based alloys should not be used. If condensation due to high ambient temperatures and/or humidity occurs the sample lines may be moderately heated.
- A5.2 In the case of nitrogen oxide CAMs, in order to avoid disturbance of the nitrogen monoxide-nitrogen dioxide-ozone equilibrium in the sample line (or system), the residence time in the sample system (or line) from the sampling inlet to the monitor should be such that the increase of the nitrogen dioxide content in the sample is less than 2%. The influence of the pressure drop along the complete sampling system including any filter, should be such that it causes an apparent concentration change of less than 1% of the signal output of the analyser.
- A5.3 The increase of the sampled nitrogen dioxide is due to the effect of the reaction of ambient ozone with nitric oxide in the sampling line. By means of the following formula the influence of the residence time on the increase of nitrogen dioxide in the sampling line can be estimated.

$$[O_3]_0 = \frac{b \cdot [O_3]_t}{[O_3]_t - [NO]_t \cdot e^{(b-k)t}} \quad \text{eq A5.1}$$

where:

$[O_3]_0$ ozone concentration at the sample manifold inlet;

$[O_3]_t$ ozone concentration after t seconds of residence time in the sampling line;

$[NO]_t$ nitric oxide concentration after t seconds of residence time in the sampling line;

b the concentration difference between $[O_3]_t$ and $[NO]_t$; $b = [O_3]_t - [NO]_t$
with $b \neq 0$;

k rate constant for the reaction of O_3 with NO : $k = 4.43 \cdot 10^{-4} \text{ ppb}^{-1} \text{ s}^{-1}$ at 25°C;

t residence time in seconds.

And

$$[O_3]_o - [O_3]_t = [NO]_o - [NO]_t$$

Where

$[NO]_o$ NO concentration at the sample manifold inlet

Example

Assuming a residence time of 2 seconds in the manifold and the following concentrations measured after the sampling manifold:

$$[O_3]_t = 22 \text{ ppb}$$

$$[NO]_t = 100 \text{ ppb}$$

Equation A5.1 will give an ozone concentration at the sample inlet, $[O_3]_o$, of 24.1 ppb and therefore a NO concentration at the sample inlet of 97.9ppb. This would result in an increase of 2.1 ppb of NO_2 due to the reaction of NO and O_3 in the sampling manifold and a loss of 2.1ppb of NO.

APPENDIX 6: RECOMMENDATIONS FOR THE ANALYSES OF HEAVY METAL SAMPLES

- A6.1 All analyses of metal samples collected must be performed by a laboratory which has accreditation to EN45001 for the requisite measurements.
- A6.2 It is recommended that, only if the amount of each metal to be analysed exceeds 1 mg on the filter, should Ion-Coupled Plasma Atomic-Emission Spectroscopy (ICP-AES) be used in the analyses. This is due to the detection limits of ICP-AES being close to the collected masses of metals from ambient samples. If the amounts are smaller than 1mg, then the extra sensitivity achievable using Ion-Coupled Plasma - Mass Spectroscopy (ICP-MS) technique would be required for the analysis of Pb, Cd, and Ni. However, hydride-generation and fluorescence detection should be used for As measurements.
- A6.3 Field blank samples should be prepared and taken through the same procedure as real samples as far as possible, including mounting in the sample unit without using the pump, dismounting and return to the laboratory. Field blanks should be analysed in the same way as ambient samples. The number of field blanks should be at least one percent of the number of real samples taken and not less than six for each sampling exercise.

APPENDIX 7: RECOMMENDATIONS FOR THE ANALYSES OF PAH SAMPLES

- A7.1 All analysis of PAH samples collected must be performed by a laboratory accredited to EN45001 for the appropriate measurements.
- A7.2 At least one field blank per five samples should be taken. If five or more samplers are sampling in parallel at least one blank should be taken during each sampling period. The field blanks should be handled in the same manner as the samples but no ambient air should be drawn through them. This should include the fitting of the sample collecting media to the sampling system, as this is when some contamination may occur. Field blanks should be analysed in the same way as ambient samples.
- A7.3 High values for the blank samples can be caused by contamination in the solvents, reagents, glassware and other sample processing equipment used. Glassware must therefore be thoroughly cleaned and laboratory blanks run with each batch of no more than five samples. For example cleaning may be carried out by acid washing followed by heating to 450°C. All solvents and other materials must be routinely demonstrated to contain insignificant levels of the compounds of interest in comparison to those captured during sampling. Interferences to the analysis may be caused by contaminants that are co-extracted from the sample. Additional clean-up by chromatography may be required.
- A7.4 Exposure to heat, ozone, nitrogen dioxide and ultraviolet light may cause PAH degradation during sampling, storage and processing. These problems should be addressed as part of the standard operating procedure prepared by the manufacturer/user. Sealed sampling containers should be kept cool and protected from light both in the field and during transport (eg with solid carbon dioxide). In the laboratory the sample should be kept refrigerated at 4°C or below for no longer than two weeks prior to extraction. Where possible incandescent or UV-filtered lighting should be used in the laboratory to avoid photodegradation during analysis.
- A7.5 Throughout the analysis of PAH samples appropriate precautions must be taken to minimise exposure to carcinogens during all test work.

APPENDIX 8: RECOMMENDATIONS FOR FILTER WEIGHING PROCEDURES

- A8.1 Before use, loose fibre material should be removed from the blank filters. Prior to use the unused filters should be kept for 48 hours in open dust protected sieve trays, in an air conditioned weighing room with a temperature of $(20 \pm 1)^{\circ}\text{C}$ and a relative humidity of $(50 \pm 3)\%$ before weighing. Before weighing a filter, it should be examined for pinholes and other imperfections by backlighting with an area light source similar to a x-ray film viewer.
- A8.2 The balance used for weighing should be permanently installed in the above room and have a resolution of at least $10\mu\text{g}$ and a weighing chamber large enough to accommodate an unfolded filter. After equilibration each filter would be weighed and this tare weight recorded with a unique filter identification number. The filters should then be transported to site either in a petri dish or a cassette.
- A8.3 After sampling the removed filter should be transported back to the laboratory in either a petri dish or cassette. The dust loaded filters should then be equilibrated under the same conditions as above before weighing. Very dry filters (eg field blanks stored close to a central heating radiator) take a considerably longer than 48 hours to reach equilibrium. In order to prevent such problems, field blanks and unused filters should be stored in the weighing room. Also filters soaked during the sampling procedure would not reach equilibrium after 48 hours of conditioning. Extra drying in an oven or desiccator should not be done because of losses of volatile material from the sample. In this case the conditioning period shall be extended for an extra 24 hours.
- A8.4 After conditioning the exposed filters should be weighed and this weight recorded with the unique filter identification number.

APPENDIX 9: REQUIREMENTS FOR CALIBRATION AND TEST GASES

Calibration and test gases are required for the MCERTS test procedures described in this document. These shall have specified accuracies and specifications for impurities - so as to ensure that the uncertainties in their characteristics do not compromise the validity of the tests prescribed in this document (eg the concentration of the calibration gases should be accurate so that they do not give rise to falsely rejecting the CAM in the accuracy test).

A9.1 CALIBRATION AND TEST GASES FOR LABORATORY TESTS

Table 9.1 Maximum Permitted Uncertainties in the Concentration of Calibration Gases used for Accuracy Tests

Calibration Gas ⁽¹⁾	Uncertainty (Relative to limit value)
SO ₂	±1%
CO	±1%
NO	±1%
NO ₂	±3%
O ₃	±1%
Benzene	±2%

⁽¹⁾ Calibration gases shall be traceable to national primary gas concentration standards.

Table 9.2 Specification of the Purity of Zero Gases used for Laboratory Tests

Pollutant	Maximum Absolute Value	Maximum concentration value relative to EU Limit Value
SO ₂	0.1 ppb	0.08%
NO	0.1 ppb	0.1%
NO ₂	0.1 ppb	0.1%
O ₃	0.1 ppb	0.2%
CO	0.02 ppm	0.2%
Benzene	0.05 ppb	0.3%

TABLE 9.3: Maximum permitted uncertainties in concentrations of gases used for cross-interference tests

(i) **NO_x CAM**

Interferent	Category 1 Rural and Remote Concentration	Category 2 Kerbside and Urban Centre Concentration	Required Accuracy of Test Gas
CH ₄	5 ppm	3300 ppm	±5%
C ₂ H ₆	5 ppb	50 ppb	±5%
C ₃ H ₈	5 ppb	50 ppb	±5%
CO ₂	350 ppm	500 ppm	±5%
CO	1 ppm	50 ppm	±5%
H ₂ S	10 ppb	100 ppb	±5%
NH ₃	10 ppb	100 ppb	±5%
SO ₂	200 ppb	400 ppb	±5%
Water vapour	20% to 80% RH	20% to 80% RH	±5%

(ii) **SO₂ CAM**

Interferent	Category 1 Rural and Remote Concentration	Category 2 Kerbside and Urban Centre Concentration	Required Accuracy of Test Gas
CH ₄	5 ppm	3300 ppm	±5%
C ₂ H ₆	5 ppb	50 ppb	±5%
C ₃ H ₈	5 ppb	50 ppb	±5%
CO ₂	350 ppm	500 ppm	±5%
CO	1 ppm	50 ppm	±5%
H ₂ S	10 ppb	100 ppb	±5%
NH ₃	10 ppb	100 ppb	±5%
NO	500 ppb	1 ppm	±5%
NO ₂	200 ppb	500 ppb	±5%
m-Xylene	2.0 ppm	2.0 ppm	±5%
Water vapour	20% to 80% RH	20% to 80% RH	±5%

(iii) **O₃ CAM**

Interferent	Category 1 Rural and Remote Concentration	Category 2 Kerbside and Urban Centre Concentration	Required Accuracy of Test Gas
CH ₄	5 ppm	3300 ppm	±5%
C ₂ H ₆	5 ppb	50 ppb	±5%
C ₃ H ₈	5 ppb	50 ppb	±5%
CO ₂	350 ppm	500 ppm	±5%
CO	1 ppm	50 ppm	±5%
H ₂ S	10 ppb	100 ppb	±5%
NH ₃	10 ppb	100 ppb	±5%
NO	500 ppb	1 ppm	±5%
NO ₂	200 ppb	500 ppb	±5%
SO ₂	200 ppb	400 ppb	±5%
Toluene	100 ppb	1 ppm	±5%
Styrene ²⁾	N/A	10 ppb	±5%
Water vapour	20% to 80% RH	20% to 80% RH	±5%

²⁾Possible sources from industrial plants. (This has a greater than 1 to 1 response.)

(iv) CO CAM

Interferent	Category 1 Rural and Remote Concentration	Category 2 Kerbside and Urban Centre Concentration	Required Accuracy of Test Gas
CH ₄	5 ppm	3300 ppm	±5%
C ₂ H ₄	5 ppb	50 ppb	±5%
C ₆ H ₆	5 ppb	50 ppb	±5%
CO ₂	350 ppm	500 ppm	±5%
H ₂ S	10 ppb	100 ppb	±5%
NH ₃	10 ppb	100 ppb	±5%
NO	500 ppb	1 ppm	±5%
NO ₂	200 ppb	500 ppb	±5%
SO ₂	200 ppb	400 ppb	±5%
Water vapour	20% to 80% RH	20% to 80% RH	±5%

(v) Benzene CAM

Interferent	Category 1 Rural and Remote Concentration	Category 2 Kerbside and Urban Centre Concentration	Required Accuracy of Test Gas
CH ₄	5 ppm	3300 ppm	±5%
C ₂ H ₄	5 ppb	50 ppb	±5%
CO ₂	350 ppm	500 ppm	±5%
CO	1 ppm	50 ppm	±5%
H ₂ S	10 ppb	100 ppb	±5%
NH ₃	10 ppb	100 ppb	±5%
NO	500 ppb	1 ppm	±5%
NO ₂	200 ppb	500 ppb	±5%
SO ₂	200 ppb	400 ppb	±5%
Water vapour	20% to 80% RH	20% to 80% RH	±5%

A9.2 CALIBRATION AND TEST GASES USED FOR FIELD TESTS

Table 9.4 Maximum Permitted Uncertainties in the Concentration of Calibration Gases used for Field Tests

Calibration Gas ¹	Uncertainty
SO ₂	±3%
CO	±1%
NO	±3%
NO ₂	±3%
O ₃	±3%
Benzene	±5%

¹Test mixtures shall be traceable to national primary gas concentration standards.

Table 9.5 Specification of Purity of Zero Gas used for Field Tests

Pollutant	Maximum Absolute Value	Maximum concentration value relative to limit value
SO ₂	0.5 ppb	0.4%
NO	0.5 ppb	0.5%
NO ₂	0.5 ppb	0.5%
O ₃	0.2 ppb	0.4%
CO	0.05 ppm	0.6%
Benzene	0.01 ppb	0.6%