



DEMONSTRATION OF EQUIVALENCE OF AMBIENT AIR MONITORING METHODS

Report by an EC Working group on
Guidance for the Demonstration of Equivalence

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1 INTRODUCTION

One of the objectives of the European Directive 96/62/EC ('Air Quality Framework Directive', ref.1) is to 'assess the ambient air quality in Member States on the basis of common methods and criteria'.

The European Air Quality Directives ('Daughter' Directives) associated with this Framework Directive, which relate to limit or target values for specified atmospheric pollutants, are Directives 1999/30/EC, 2000/69/EC, 2002/3/EC and 2004/107/EC [2-5]. These specify the principles of the reference methods to be used for the measurement of concentrations of these pollutants. In addition, they specify *Data Quality Objectives* that have to be met for the performance of specific measurement tasks. These data quality objectives include minimum requirements for:

- expanded uncertainties of measurement results at the limit or target value(s) set for each pollutant
- time coverage of the measurements in relation to the reference period of the limit or target values
- data capture when using the measurement method, i.e., effective measurement time.

CEN Technical Committee (TC) 264, the Committee for Air Quality Measurement Methods, has produced, or is producing, Standard Methods to satisfy these directives. CEN TC 264's remit was to ensure these were validated against the data quality objectives given in the relevant Directives. In order to harmonize the approaches of the various ambient air Working Groups, in particular for the assessment of the measurement uncertainties, a CEN Report was prepared in which the principles for these uncertainty assessments are laid down (report CR 14377).

A Member State (MS) when implementing the Directives should use the Standard Methods, but the directives allow Member States the possibility to 'use any other method which it can demonstrate gives results equivalent to the above (standard) method'.

This Report describes the principles and methodologies to be used for the demonstration of the equivalence of alternative methods to the EN Standard Methods. It is intended for use by laboratories nominated by National Competent Authorities (see Directive 96/62/EC [1]) to perform the tests relevant to the demonstration of equivalence of ambient-air measurement methods. The building blocks of the equivalence demonstration procedure are presented in Figure 1 below.

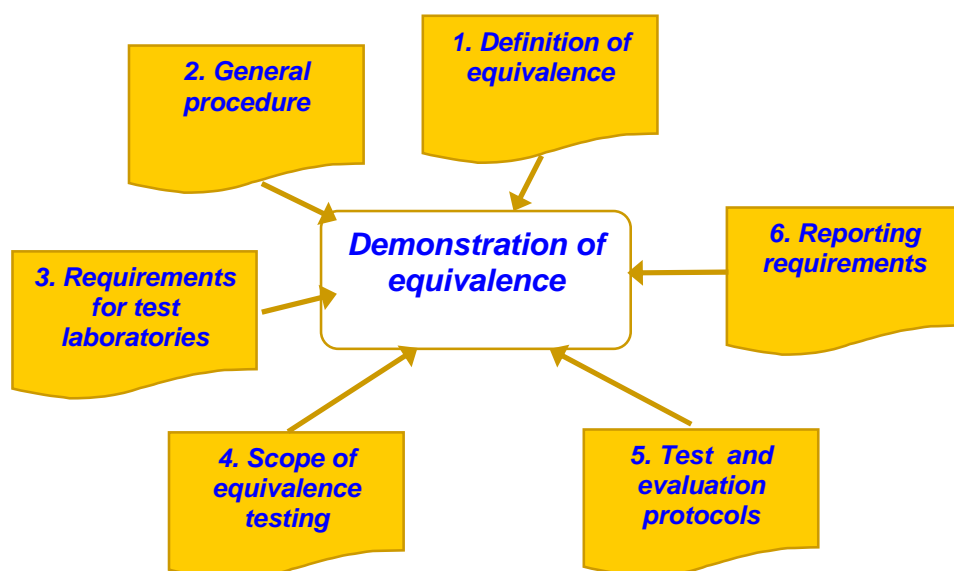


Figure 1. Building blocks for equivalence demonstration

2 REFERENCES TO NORMS

This clause incorporates by dated or undated reference, provisions from other publications. These normative references are cited at the appropriate places in the text and the publications are listed hereafter. For dated references, subsequent amendments to or revisions of any of these publications apply to this only when incorporated in it by amendment or revision. For undated references the latest edition of the publication referred to applies.

EN 12341		Air Quality – Determination of the PM ₁₀ fraction of suspended particulate matter – Reference method and field test procedure to demonstrate reference equivalence of measurements
ENV 13005	1999	Guide to the expression of uncertainty in measurement
EN-ISO 17025	1999	General requirements for the competence of testing and calibration laboratories
CR 14377	2001	Approach to uncertainty estimation for ambient-air measurement methods
EN-ISO 14956	2001	Air quality – Evaluation of the suitability of a measurement method by comparison with a stated measurement uncertainty
EN 13528 pt1	2002	Ambient air quality – Diffusive samplers for the determination of gases and vapours – Requirements and test methods – Part 1: General requirements
EN13528 pt2	2002	Ambient air quality – Diffusive samplers for the determination of gases and vapours – Requirements and test methods – Part 2: Specific requirements and test methods.
EN13528 pt3	2003	Ambient air quality – Diffusive samplers for the determination of gases and vapours – Part 3: Guide to selection, use and maintenance.
ISO 6142	2000	Gas analysis. Preparation of calibration gas mixtures – Gravimetric methods
ISO 6143	2000	Gas analysis. Comparison methods for the determination of calibration gas mixtures
ISO 6144	2002	Gas analysis. Preparation of calibration gas mixtures – Static volumetric methods
ISO 6145		Gas analysis. Preparation of calibration gas mixtures – Dynamic volumetric methods. All Parts

3 TERMS, DEFINITIONS AND ABBREVIATIONS

3.1 *Terms and definitions*

3.1.1	Automated (Measurement) Method/System	A measurement method or system performing measurements or samplings of a specified pollutant in an automated way
3.1.2	Candidate Method	A measurement method proposed as an alternative to the relevant Reference Method for which equivalence has to be demonstrated
3.1.3	Continuous Measurements	Measurements performed at a fixed site on a continuous basis.
3.1.4	Equivalent Method	A method other than the Standard Method for the measurement of a specified air pollutant, that meets the Data Quality Objectives for continuous or fixed measurements specified in the relevant air quality directive.
3.1.5	Fixed Measurements	Measurements performed at a fixed site. [1]
3.1.6	Limit value	A level fixed on the basis of scientific knowledge, with the aim of avoiding, preventing or reducing harmful effects on human health and/or the environment as a whole, to be attained within a given period and not to be exceeded once attained. [1]
3.1.7	Manual (Measurement) Method	A measurement method by which sampling is performed on site, with sample analysis performed in the laboratory.
3.1.8	National Competent Authority	Authority or body designated by a Member State as responsible for the approval of measuring devices (methods, equipment, etc.). [1]
3.1.9	Reference Method	The principle of a method established by EC legislation for the measurement of a specified ambient air pollutant
3.1.10	Standard Method	A method standardized by CEN enacting a Reference Method for a specified ambient air pollutant
3.1.11	Target value	A level fixed with the aim of avoiding more long-term harmful effects on human health and/or the environment as a whole, to be attained where possible over a given period. [1]

3.2 *Abbreviations*

AMS	Automated Measurement System
CM	Candidate Method
CRM	Certified Reference Material
DQO	Data Quality Objective
EC	European Commission
EU	European Union
IR	Infrared
MM	Manual Method
MS	Member State
NCA	National Competent Authority
PM	Particulate Matter
PSM	Primary Standard Material
PT	Proficiency Testing
RM	Reference Method
UV	Ultraviolet

4 DEFINITION OF EQUIVALENCE

There are two different ways of defining an Equivalent Method:

1. A measurement method that meets the requirements set from the viewpoint of fitness-for-purpose for the intended use of the reference method [6]
2. A measurement method giving results that do not differ from those of the Reference Method within a specified statistical uncertainty [7].

The application of one or other definition requires a considerably different approach to the evaluation of equivalence:

The first definition implies that a Candidate Method should fulfil the data quality objectives set for the Reference Method specified in the relevant directive.

The second definition implies that the results obtained with both methods should be determined to be statistically insignificantly different, for example at the 95% confidence level. It does not automatically imply compliance with the uncertainty data quality objectives. In addition, a combination of low 'random' uncertainties of both methods with a systematic difference in results between methods may lead to rejection of a Candidate Method, which according to the first definition would be acceptable.

It should also be noted that, although not specifically stated in the air quality directives or their associated explanatory documents – on the basis of consultations with various experts in the monitoring field – the intended application of the Reference Methods specified in these directives is for continuous or fixed measurements.

Within the framework of air quality measurements, this choice of definition has already been made in the Document specifying 'Terms of Reference for CEN/TC 264 Ambient-air Standards' (see e.g. Report CR 14377 Annex C). These Terms of Reference state that methods other than the Reference Method may be used for the implementation of the directives provided that they fulfil the minimum data quality objectives specified in the relevant directive. Hence, for the current document the principles of first definition apply.

Therefore, considering the intended use of the reference methodologies, the following definition will be used for the demonstration of equivalence:

'An Equivalent Method to the Standard Method for the measurement of a specified air pollutant, is a method meeting the Data Quality Objectives for continuous or fixed measurements specified in the relevant air quality directive'

NOTE 1. The use of the Standard Methods is not restricted to continuous or fixed measurements.

NOTE 2. Where a Candidate Method fails to meet the uncertainty data quality objective of the Standard Method, it may still be able to meet the uncertainty data quality objective for indicative methods.

NOTE 3. For automated measurement systems for gases (Section 8) all relevant uncertainty sources must be assessed and the Candidate Method must pass all the prescribed individual performance criteria, in addition to the overall uncertainty criteria, in order to conform with all the requirements of the relevant EN Norms.

NOTE 4. Equivalence may be granted for regional situations within a Member State, but also for situations encompassing more than one Member State where equivalence can be fully demonstrated using the required procedures to be valid across that complete region. The latter case provides an incentive for 'inter-Member State' consultation prior to the performance of equivalence testing. However, this large regional-scale equivalence may be more difficult to demonstrate for some pollutants than others.

Tables 1a and 1b give an overview of limit or target values, data quality objectives, Reference Methods and EN Standard Methods for compounds under existing or proposed EU legislation.

Table 1a. Limit values, data quality objectives, Reference Methods and EN Standard Methods.

Compound	Limit value ($\mu\text{g.m}^{-3}$)	Reference period	Data Quality Objective		Principles of Reference Method as specified by Daughter Directives	EN Standard Method (or working documents)
			Expanded Uncertainty (%)	Data Capture (%)		
Sulphur dioxide	350	1 h	15	90	Ultraviolet-fluorescence	EN 14212
	125	24 h	15	90		
	20	1 y	15	90		
Nitrogen oxides	200 (NO_2)	1 h	15	90	Chemiluminescence	EN 14211
	40 (NO_2)	1 y	15	90		
	30 (NO_x)	1 y	15	90		
Carbon monoxide	10 mg.m^{-3}	8 h	15	90	Non-dispersive infrared spectrometry	EN 14666
Benzene	5	1 y	25	45	Pumped sampling + analysis by gas chromatography	EN 14662 parts 1-3
PM ₁₀	50	24 h	25	90	PM ₁₀ reference sampler (EN 12341)	EN 12341
	40	1 y	25	90		
Lead	0,5	1 y	25	90	PM ₁₀ reference sampler + analysis by atomic spectrometry	EN 14902

Table 1b. Target values, data quality objectives, Reference Methods and EN Standard Methods.

Compound	Target value ($\mu\text{g.m}^{-3}$)	Reference period	Data Quality Objective		Principles of Reference Method as specified by Daughter Directives	EN Standard Method (or working documents)
			Expanded Uncertainty (%)	Data Capture (%)		
Ozone	120	8 h	15	90/75	Ultraviolet photometry	EN 14665
Benz[a]pyrene	1 ng.m^{-3}	1 y	50	90	PM ₁₀ reference sampler + analysis by liquid chromatography – fluorescence or gas chromatography – mass spectrometry	
Arsenic Cadmium Nickel	6 ng.m^{-3} 5 ng.m^{-3} 20 ng.m^{-3}	1 y	40	90	PM ₁₀ reference sampler + analysis by atomic absorption spectrometry or inductively-coupled plasma – mass spectrometry	EN 14902

NOTES

1. Limit/target values are in $\mu\text{g.m}^{-3}$ unless otherwise stated, expressed at 20 °C and 101,3 kPa for gases and vapours; for PM, metals and benz[a]pyrene they are expressed at ambient conditions
2. The expanded uncertainty is defined at the 95% confidence level.
3. The uncertainty of the Reference Method, which is derived for a shorter averaging period used during laboratory and field validation trials, applies to the longer averaging times specified in the directives (CR 14377).

5 PROCEDURE FOR DEMONSTRATION OF EQUIVALENCE

5.1 Flow scheme

A flow scheme depicting the procedure for equivalence demonstration is given in Figure 2.

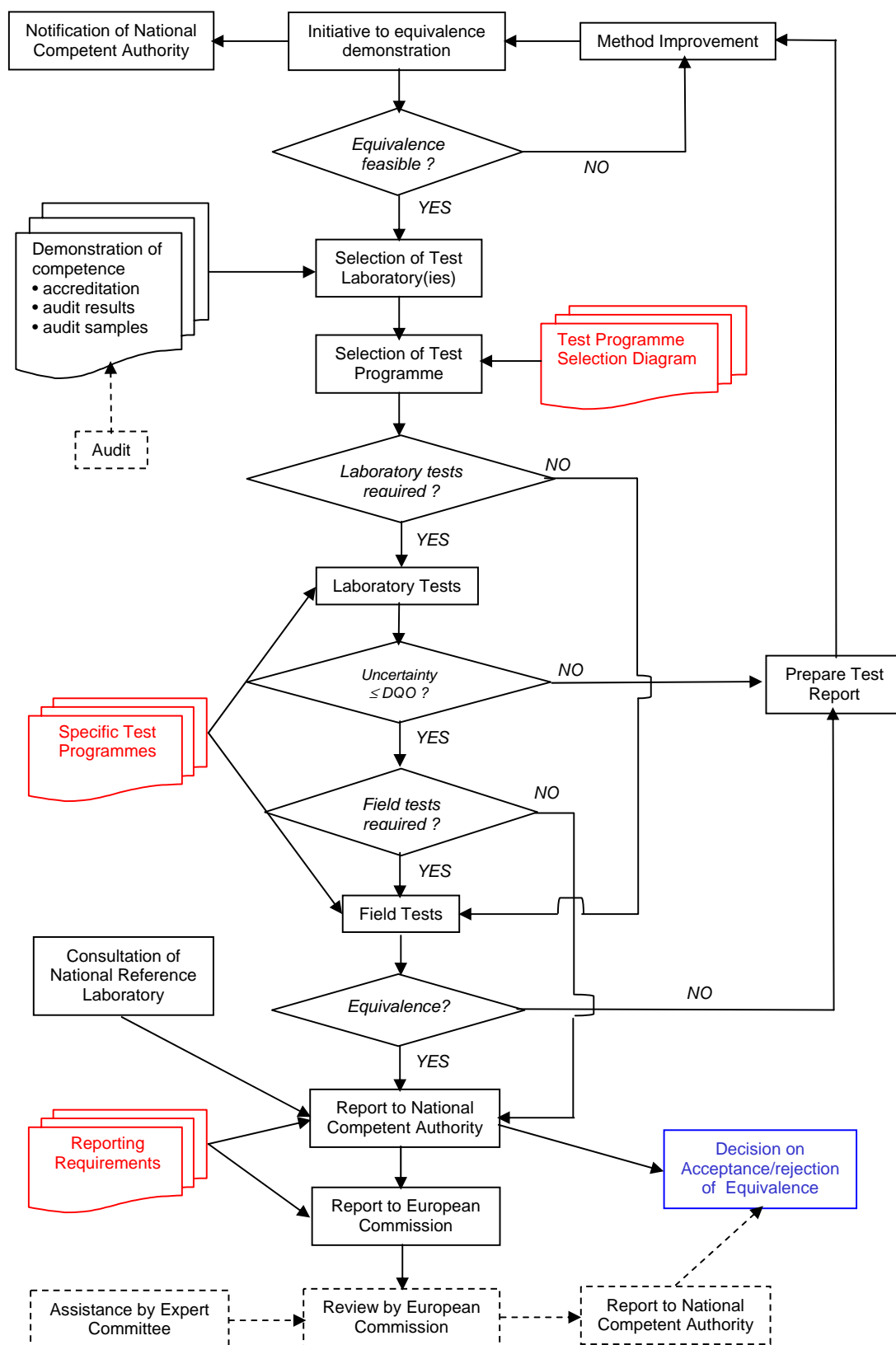


Figure 2. Flow scheme of the procedure for demonstration of equivalence

5.2 General

A Member State may propose methods that deviate from the Reference Method defined in the Daughter Directives [2-5] and elaborated in the EN Standard Methods [8-18] given in Table 1. Consequently, the responsibility for the demonstration of equivalence of the proposed Candidate Method rests with the National Competent Authority. This authority bears responsibility for the quality of national air quality monitoring data. In the process of demonstrating equivalence (see Figure 2) the National Competent Authority (NCA) may delegate its responsibility to a National Reference Laboratory. The NCA remains responsible for the final decision on the acceptance or rejection of a Candidate Method as equivalent to the EN Standard Method, and for reporting to the European Commission.

The initiative for the use of 'equivalent' methods may arise from a National Competent Authority or from a national or regional laboratory performing air quality measurements related to the implementation of the Daughter Directives. In the latter case, the laboratory proposing the use of a method shall notify its National Competent Authority, and perform a preliminary assessment of the Candidate Method in order to ensure that the method:

- fulfils the requirements of data capture and time coverage set for the continuous/fixed measurements, e.g., a Candidate Method for the measurement of concentrations of nitrogen dioxide for comparison with the 1-hour limit value, shall be able to provide a data capture of 90% or more for hourly averaged measurement results, and
- has the potential for meeting the uncertainty requirement for the Standard Method at the limit value concentration.

When the Candidate Method passes this preliminary assessment, the test and evaluation programme relevant to the Candidate Method can be selected using the flow scheme given in Figure 3.

If at any stage of the test programme the measurement uncertainty of the Candidate Method fails to meet the relevant Directive's uncertainty criterion, then the equivalence evaluation may be terminated, and a report of the results obtained prepared for the Competent Authority. This may be used as a basis to reduce relevant uncertainty sources - after which tests appropriate to these uncertainty sources may be repeated, and the resulting uncertainty again compared with the uncertainty criterion.

Following completion of the relevant test and evaluation programme, the results of these tests and evaluations shall be reported to the Competent Authority. The Competent Authority will then decide on the acceptance or rejection of the Candidate Method as an Equivalent Method. In the case of acceptance, an evaluation report with conclusions should be submitted to the European Commission for review. The European Commission in its review may seek to consult a committee of experts concerning the claim for equivalence.

The European Commission reserves the right to question and to reject the use of a particular method if the equivalence is not sufficiently demonstrated. The methodology presented in this report is an acceptable way of sufficiently demonstrating equivalence. If the Commission produces a negative conclusion on the claim for equivalence, then the Competent Authority should reconsider its decision.

5.3 Requirements for laboratories

The laboratories performing the required tests shall be independent of manufacturers or suppliers of equipment used for implementing the Candidate Method.

The laboratories performing the tests necessary for the demonstration of equivalence shall be able to demonstrate technical competence for these tests. These may be the laboratory/laboratories already using the Candidate and/or Standard Method, but may also be

different laboratories, subject to fulfilment of the requirements for laboratories. It is strongly recommended that laboratories work in full compliance with the requirements of EN-ISO 17025, as demonstrated through a formal accreditation.

In the absence of a formal accreditation, compliance with the requirements of EN-ISO 17025 should be demonstrated through an independent audit performed by an auditor with specific experience in the use of the relevant Standard and Candidate Methods. A demonstration of competence by achieving acceptable performance in a suitable Proficiency Testing (PT) scheme is considered useful additional information. In the absence of such a scheme, measurements of a series of appropriate test samples with satisfactory results are strongly recommended for demonstrating competence. Test samples shall be such that the concentration(s) of the compound(s) to be measured is (are) traceable to primary standard materials (PSM) or certified reference materials (CRM).

Note: for the purpose of the supply of suitable test samples, the National Competent Authority may consult an appropriate National Reference Laboratory and/or accreditation body.

5.4 Scope of equivalence

5.4.1 Limiting conditions

It is possible for equivalence to be granted for specific 'regional' conditions (the composition of ambient air, meteorological conditions etc). However, in order to promote an economy of scale it is recommended that regional or national laboratories consult others prior to equivalence testing, and cooperate in order to broaden the scope of equivalence as far as practical. In all cases, however, where the scope of equivalence is restricted in any way, the Equivalent Method should only be applicable over the pollutant concentration range and conditions that were tested for compliance with the relevant Daughter Directive.

In claims to equivalence, limiting conditions shall be specified where relevant. Such limiting conditions should include:

- Composition of the ambient air, i.e., concentration ranges of the specific pollutant and relevant cross interfering species;
- Meteorological conditions, i.e., ranges of temperature, atmospheric humidity, and wind velocity;
- Geographical conditions, such as at specific locations.

5.4.2 Generalization of equivalence claims

For many methods, equivalence that has been proven using the approach described in this Report can be assumed to be valid anywhere else under ambient conditions. Moreover, the test programmes described here generally attempt to demonstrate equivalence for as wide a range of conditions as possible, including practical 'extremes'.

However, this generalization may not hold for all pollutants. This is particularly the case for PM: The semi-volatile fraction, which depends on location and ambient conditions, is not retained in the sample to the same extent by different measuring methods. In addition, current PM levels being close to the limit values, many Member States are required to perform PM measurements throughout their entire territory or in large parts of it, and thus a variety of types of location and ambient conditions are usually involved. Consequently, it may be that equivalence for PM measurements that is established under the conditions described in 9.4.2 of this Report (taking into account where relevant the appropriate correction factor/term into account – see Clause 9.4.2) is not valid for all sites in the Member State.

The generalization of equivalence to include other locations than those tested, in which the Equivalent Method is used, is a separate and essential component that should be in the report from the Competent Authority to the Commission (Reference [1] Clause 10). Generally, this report

must show that the equivalence demonstrated at the locations where it was established, applies to all monitoring sites that use this Equivalent Method for which results are being provided to the Commission.

Developing a detailed procedure for generalization of equivalence claims is beyond the scope of this Report. There is no objective procedure for delineating the monitoring sites where a demonstrated equivalence is valid and where it is not. Instead, expert judgement, based on the similarities in conditions that prevail at the various relevant locations, is needed for this.

There are several relevant ways of describing the sites where a demonstrated equivalence is valid. The sites may be classified in similar groups of locations using *station types* (that are characterized primarily by the nearby sources). The validity range of a demonstrated equivalence can also be described by listing the *regions* (parts of the Member State) of validity. A *combination of station types and regions* (e.g. rural stations in regions A, B and C) may also be a useful way. From this description, a *list of stations with the correction factors applied (or equations used)* can be derived and tabled in the report to the Commission (Reference [1] Clause 10).

5.4.3 *Extent of tests required*

Within this Report, the extent of equivalence testing is specified on the basis of degree of differences between the Standard Method and the Candidate Method.

These differences can – in principle – be separated into two groups (defined subsequently in this Report as ‘variations on a theme’ and ‘different methodologies’).

5.4.3.1 *Variations on a theme*

Minor parts of the Standard Method can be modified resulting in ‘variations on a theme’.

Examples of ‘possible variations’:

- The use of different converters to transform nitrogen dioxide into nitric oxide in chemiluminescence analysers;
- The use of different scrubbers for ozone;
- The use of different sampling media/substrates, e.g., sorbents and filter types;
- The use of different procedures for analyte recovery, e.g., for recovery of benzene from sorbent tubes, and metals and poly-cyclic aromatic hydrocarbons (PAH) from PM samples;
- The use of calibration procedures differing in the number and/or analyte contents of calibration standards, the type of calibration function and its establishment and the re-calibration frequency;
- The use of different analytical procedures, e.g., modifications to the chromatographic separation for benzene and PAH analysis, and to the atomic spectrometric conditions for metals analysis;
- The use of different PM₁₀ filter storage procedures;
- The use of automated filter changers for manual PM₁₀ samplers.

5.4.3.2 *Different methodologies*

A Candidate Method may be based on a different measurement principle. Possible examples of different principles are:

- Automated Measurement Systems for benzene using ultraviolet spectrometry as the detection technique;
- Sampling of particulate matter using a sampling inlet with size and shape differing from those specified in PM₁₀ and PM_{2.5} norms for the reference sampler;
- Measurement of particulate matter using automated methods, e.g., based on β -ray attenuation or on oscillating microbalances;
- Use of in-situ optical measurement techniques for particulate matter;
- Use of different analytical techniques for the measurement of relevant compounds in sample extracts, e.g., liquid chromatography for benzene, inductively-coupled plasma – optical emission spectrometry for metals;
- Measurement of gases and vapours using diffusive sampling instead of pumped sampling or automated methods;
- Automated measurement of gases based on a different spectrometric technique, e.g., fourier-transform infrared spectrometry (FTIR) for sulphur dioxide;
- Measurement of gases using pumped sampling instead of automated methods.

5.4.3.3 *Practical implications*

In practice, the possible use of different methodologies is limited. Based on practical potential/current applications, the following may be considered as relevant examples:

Sulphur dioxide, nitrogen dioxide, carbon monoxide, ozone

The Reference Method is continuous spectrometry. Candidate Methods of practical value include:

- diffusive sampling with subsequent sample analysis;
- 'flow-through' spectrometric techniques using different principles than the reference technique.

Benzene

The Reference Method is pumped sampling (automated or non-automated) followed by sample analysis using gas chromatography. Candidate Methods of practical value are:

- diffusive sampling with subsequent sample analysis;
- 'flow-through' spectrometry;
- automated measurement using ultraviolet spectrometry after sample enrichment.

EN Standard Methods exist for the measurement of benzene by diffusive sampling and analysis by gas chromatography after thermal or solvent desorption of benzene samples (prEN 14662 parts 4 and 5; refs. 16,17). These methods have been evaluated within the frame of the validation of all EN Standard Methods for the measurement of benzene (prEN 14662 part 1-5, refs. 13-17).

Particulate matter

The Reference Method is manual pumped sampling onto a filter substrate using a pre-specified aerosol classifier followed by gravimetric analysis. Candidate Methods may be based on:

- use of automated methods, i.e., β -ray attenuation or (tapered-element) oscillating microbalance;
- use of aerosol samplers with inlet specifications differing from those of the reference sampler.

Metals, benz[a]pyrene

The Reference Method is based on sampling of the PM₁₀ aerosol fraction of the total suspended particulate matter in ambient air, with subsequent analysis using atomic absorption spectrometry or inductively-coupled plasma mass spectrometry (metals), or gas or liquid chromatography (benz[a]pyrene). The Candidate Methods may be based on:

- use of alternative analytical techniques;
- use of alternative aerosol samplers (see under particulate matter).

5.5 Practical approach to equivalence testing

In principle, the approach to equivalence testing described in this report comprises 4 phases, i.e.:

- An initial non-experimental pre-assessment to check whether the Candidate Method has the potential for fulfilling the Data Quality Objectives in the directives on data capture and measurement uncertainty
- Assessment of the uncertainty of the Candidate Method using an approach based on the principles of ENV 13005 (clause 8) in a series of laboratory tests
- The performance of a series of field tests for confirmation of the findings of the laboratory tests in which the Candidate Method is tested side-by-side to the Reference Method; The 'lack-of-comparability' between the two methods then is tested on the basis of the performance of linear regression with symmetric treatment of both variables, i.e., with uncertainties attributed to both variables
- The evaluation of the resulting uncertainties by comparisons of
 - laboratory uncertainty and the uncertainty data quality objective
 - field uncertainty and laboratory uncertainty
 - field uncertainty and the uncertainty data quality objective.

This approach has the advantage that – in the case of 'variations on a theme' – only those contributions to uncertainty that arise from the variation need to be assessed. For example, if a new extraction agent is used, the uncertainty contributions to be tested are the extraction efficiency, blank levels and analytical selectivity. This implies *a priori* knowledge of the uncertainty contributions of all relevant uncertainty sources in the Standard Method. In addition, for manual Candidate Methods for which only the analytical principle but not the sample preparation component differs from the Standard Method (e.g., the use of ICP-OES for the analysis of metals) only the contributions relevant to the use of the different analytical method need to be quantified.

An exception to this is made for the CEN Norms covering automated measurement systems for gases; for these, all relevant uncertainty sources must be assessed in order to avoid the use of the equivalence procedure as an route for monitors that have failed the test criteria of the EN Norms for automated measurement systems for these species being accepted as equivalent.

In general, for particulate matter the test programmes are restricted to field tests only [8].

It should be noted that measurement procedures based on separate sampling and analysis may be open to 'variations' in parts of the procedure that can lead to systematic differences in measurement results produced by different laboratories on 'identical' air samples. This has been shown to introduce a significant additional contribution to measurement uncertainty –that due to inter-laboratory variability. Consequently, where necessary, the test procedure shall involve more than one laboratory in order to evaluate the contributions to uncertainty from 'between-laboratory' variations.

It should also be noted that application of the approach described in this Report is not mandatory. Other approaches that are in conformity with the requirements of ENV 13005 can also be used, provided that the user can prove the validity of the alternative approach.

5.6 Operation of the Candidate Method

The practical operation of the Candidate Method – and possible subsequent Equivalent Method – shall be subject to an appropriate regime of ongoing quality assurance/quality control (QA/QC). This regime shall be documented in the Standard Operating Procedure describing the operation of the method.

Minimum requirements for ongoing QA/QC shall be as reliable as the requirements given in appropriate EN Norms for automated or manual methods [8-18].

In addition, it is recommended that field tests are performed periodically (e.g. at least every 5 years, and when the atmospheric conditions change significantly so that the previous field test programme is no longer valid) by operating Reference and Equivalent Methods in parallel, in order to check whether the measurement results remain equivalent.

6 SELECTING A TEST PROGRAMME

The selection and outline of test programmes is given below.

6.1 General

Figure 3 gives a flow scheme for selection of the appropriate test programme for any Candidate Method. Four different test programmes have been elaborated for four distinct situations. The distinctions are based in principle on whether:

1. There are 'stated references' that exist for the establishment of measurement traceability, or the extent to which it is possible to quantify all contributions to measurement uncertainty from comparisons starting from primary measurement standards (ENV 13005).
2. The measurement methodology is automated or manual, i.e., based on separate sampling and analysis.

The consequences of these distinctions are explained below.

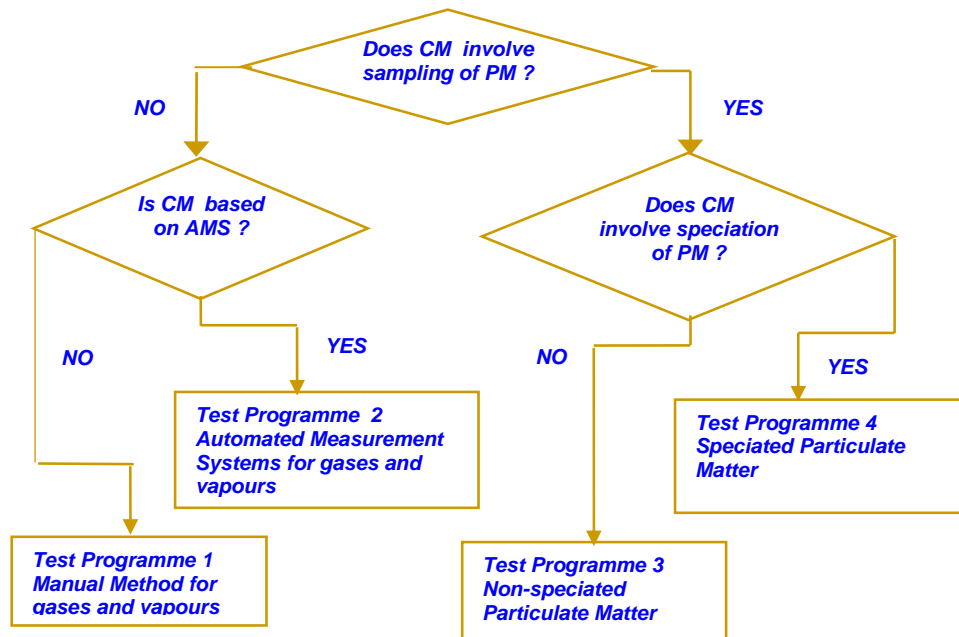


Figure 3. Flow scheme for selection of test programme

6.2 Measurement methodology

Test procedures will differ for automated and manual methods for the measurement of gases; for automated methods the method will be tested more or less as a complete measurement system (e.g., [9]); for manual methods separate steps in the measurement procedure will be subject to uncertainty evaluation in the laboratory tests (e.g., [13]).

6.3 Measurement traceability

The structure and contents of the test programmes given here are determined by the extent to which measurement results can be made traceable to SI units. The existence of primary measurement standards or certified reference materials enable laboratory tests to be performed in which these standards and materials can be used to evaluate measurement bias.

For gaseous and vaporous compounds measurement results can be made fully traceable to SI units through existing primary measurement standards prepared in accordance with ISO 6142, ISO 6144 or ISO 6145. This situation applies to continuous measurements of sulphur dioxide, nitrogen oxides, carbon monoxide and benzene.

For ozone, UV photometry is defined, by convention, as an 'absolute' measurement methodology. A UV photometer of which the measurement uncertainty has been evaluated from first principles may be termed a 'reference' photometer.

For measurements of benzene using pumped sampling methods, reference materials and standards exist through which both the results of the sampling and the analysis can be made fully traceable to SI units.

For heavy metals and benz[a]pyrene reference materials are available which provide traceability for the analytical component of the measurement procedure. However, these generally have sample matrices and measurand concentrations that differ considerably from those relevant to the implementation of the EU Directives. For example, available reference materials for speciated PM measurements – such as NIST SRM 1648 and 1649a – differ in the matrix (bulk sample instead of filter), the particle size (up to 125 µm) and the composition, from those of better representative reference materials that would be required. Representative reference materials currently do not exist.

For the measurement of particulate matter a more complicated situation exists as no relevant metrological standards or reference materials exist for establishing the traceability of PM₁₀ and PM_{2.5} measurements to SI units. Results of measurements of sample volume and sampled mass of particulate matter can be made traceable to SI, but there is no suitable primary standard available to assess the contribution of other uncertainty components of the measurement method. The uncertainty of any Candidate Method therefore has to be determined with reference to a PM reference sampler (e.g., High-Volume Samplers or Low-Volume Samplers as specified in EN 12341 for PM₁₀), assuming these 'reference samplers' to be unbiased with respect to the applied particle-size convention.

6.4 Specification of test programmes

Test Programme 1 refers to manual methods for gases and vapours (benzene, carbon monoxide, sulphur dioxide, nitrogen dioxide and ozone).

- Test Programme 1A: Laboratory test programme for variations on the Standard Method; laboratory and field test programme for pumped sampling alternatives to Standard Methods for other gaseous pollutants
- Test Programme 1B: Laboratory and field test programmes for diffusive sampling analogous to test programmes of EN 13528.

Test Programme 2 refers to alternative automated measurement systems for gases and vapours, (benzene, carbon monoxide, sulphur dioxide, nitrogen dioxide and ozone) e.g., using other spectrometric techniques.

Test Programme 3 refers to alternative methodologies for the monitoring of non-speciated particulate matter. Test programme 3 includes testing of a size selective inlet, when this differs from that of the PM reference sampler.

Test Programme 4 refers to the determination of speciated particulate matter (metals and benz[a]pyrene in samples of particulates).

7 TEST PROGRAMME 1 - MANUAL METHODS FOR GASES AND VAPOURS

7.1 General

This test programme describes a procedure for determining whether a Candidate Method (CM) is suitable to be considered equivalent to an EN Standard Method based on one of the Reference Methods for the measurement of gases and vapours in ambient air [9-15], using manual measurement methods (with separate sampling and analysis). The EN Norms [9-15] have been developed to meet the Data Quality Objectives of the Air Quality Framework Directive and its relevant Daughter Directives. Therefore CMs will similarly have to meet these Directives' requirements.

This test programme is suitable for evaluating:

- pumped and diffusive sampling methods as alternatives for automated methods for the measurement of sulphur dioxide, nitrogen dioxide, carbon monoxide, ozone and benzene
- diffusive sampling methods and modified pumped sampling methods as alternatives for benzene.

7.2 Overview of the test procedures

The EN Norms for the Reference Methods specify procedures to determine the expanded uncertainty of the method from the determination of uncertainty components obtained during the specific tests. This expanded uncertainty is compared with the expanded uncertainty criterion given in the relevant Daughter Directive.

Testing for equivalence will normally be carried out in two parts: a laboratory test in which the contributions of the different uncertainty sources to the measurement uncertainty will be assessed, and a field test in which the Candidate Method will be tested side-by-side with the relevant Standard Method.

If a CM is a modification to an existing EN Standard Method, then only the laboratory performance characteristics that are affected by the modification shall be tested and their standard uncertainties calculated. The standard uncertainties associated with the affected performance characteristics shall then be used together with these existing standard uncertainties for the other characteristics, to determine again the combined measurement uncertainty, u_c .

If a CM utilises a measurement method that is different to a Standard Method, then all of the tests shall be performed.

In both cases the results of existing studies, when demonstrably obtained according to the requirements of this test procedure, may be used to determine standard uncertainties.

The CM should be tested in a way that is representative of its practical use; for example, the frequencies of tests (e.g., response drift) and re-calibrations (e.g., flow rates) that are used in practice should be applied in the test programmes.

For diffusive sampling methods for benzene, information on uncertainty sources exists in EN Norms [16,17]; these norms should be consulted when alternative diffusive sampling methods are considered as Candidate Methods. For diffusive sampling of inorganic gases, no such information is currently available in this form. It is necessary to compile and evaluate this information in the course of the validation of diffusive sampling methods for these gases.

Test Programme 1 consists of a laboratory and field test programme. The Laboratory Test Programme is separated into two parts (1A and 1B), covering methods for which the volume of air sampled can be made traceable to SI units (pumped sampling) and to methods for which this is not possible (diffusive sampling).

Candidate Methods must pass the criteria for the Laboratory Test programme, and also pass the criteria for the Field Test programme. Only Candidate Methods that pass the Laboratory Test Programme shall proceed to the Field Test Programme.

7.3 Laboratory Test Programme

In the laboratory test programme, the uncertainty sources listed in Table 7.1 are considered and assessed, where appropriate.

Table 7.1. Laboratory Test Programme 1: Uncertainty sources

Uncertainty source	Symbol	
	Pumped sampling	Diffusive sampling
1 Sample volume	V_{sam}	
1.2 Sample flow / uptake rate	ϕ	v
1.2.1 calibration and measurement		
1.2.2 variation during sampling		
1.3 Sampling time	t	t
1.4 Conversion to standard temperature and pressure		
2 Mass of compound in sample	m_{sam}	m_{sam}
2.1 Sampling efficiency	E	*
2.2 Compound stability	A	A
2.3 Extraction/desorption efficiency	D	D
2.4 Mass of compound in calibration standards	m_{CS}	m_{CS}
2.5 Response factors		
2.5.1 lack-of-fit of calibration function	F	F
2.5.2 analytical repeatability		
2.5.3 drift between calibrations	d	d
2.6 Selectivity	R	R
3 Mass of compound in blank	m_{bl}	m_{bl}

* For diffusive sampling, sampling efficiency will be incorporated in the uptake rate.

The uncertainty sources that require assessment depend on the differences between Candidate and Standard Methods as follows:

Is the Candidate Method based on a different measurement principle?

In that case, the full Test Programme needs to be performed.

Does the sampling principle of the Candidate Method differ from that of the Standard Method (e.g. diffusive instead of pumped sampling)?

In this case, uncertainty source 1.2 needs to be assessed.

Does the analytical principle of the Candidate Method differ from that of the Standard Method, with the sampling being the same?

In this case, the uncertainty sources under 2.5, 2.6 and 3 need to be assessed.

Is the Candidate Method a modification of the Standard Method?

In this case, the uncertainty sources relevant to the modification need to be investigated, e.g.

- 2.1, 2.2, 2.3 and 3 for alternative sorbents

- 2.3 and 2.6 for alternative extraction solvents
- 2.5 and 2.6 for alternative analytical configurations.

7.3.1 Test programme 1A: pumped sampling

7.3.1.1 Sampled volume of air

The sampled volume of air shall be sufficient to allow reliable quantification of the pollutant concentration at the lower end of the measurement range (10% of the limit value).

In practice, the sampled volume of air may be determined in two ways:

- on the basis of a sample flow rate measured before sampling as

$$V_{sam} = \varphi_{start} t \quad (7.1a)$$

- on the basis of measuring the sample flow rate directly before and after sampling as

$$V_{sam} = \frac{(\varphi_{start} + \varphi_{end})}{2} t \quad (7.1b)$$

in which

φ_{start} = sample flow rate before sampling, calculated as the average of ≥ 3 consecutive measurements

φ_{end} = sample flow rate after sampling, calculated as the average of ≥ 3 consecutive measurements

t = sampling time.

The first situation will occur in monitoring networks in which sequential samplers are used that are only checked or re-calibrated after prolonged intervals (e.g. 6 months). These samplers mostly use mass-flow controllers.

The uncertainty in the volume of air sampled is made up of contributions from

- the measurements of the flow rates before, or before and after, sampling
- the measurement of the sampling time
- flow rate drift, or variations in the flow rate during the sampling period.

For the two cases given in eq. (7.1a) and (7.1b) the uncertainty of the sampled volume $u(V)$ may be derived:

$$\frac{u^2(V_{sam})}{V_{sam}^2} = \frac{u^2(\varphi_{start})}{\varphi_{start}^2} + \frac{u^2(t)}{t^2} + \frac{\Delta^2 \varphi}{3 \varphi_{start}^2} \quad (7.2a)$$

$$\frac{u^2(V_{sam})}{V_{sam}^2} = \frac{u^2(\varphi_{start}) + u^2(\varphi_{end})}{(\varphi_{start} + \varphi_{end})^2} + \frac{u^2(t)}{t^2} + \frac{\Delta^2 \varphi}{\left[12 \frac{(\varphi_{start} + \varphi_{end})}{2}\right]^2} \quad (7.2b)$$

where

$\Delta \varphi$ = flow rate drift. i.e. the difference between two flow subsequent rate measurements:

$$\Delta \varphi = \varphi_{start} - \varphi_{end} \quad (7.3)$$

$u(\varphi_{start})$ is the standard uncertainty in the measurement of the flow before sampling (see 7.3.1.1.1)

$u(\phi_{\text{end}})$ is the standard uncertainty in the measurement of the flow after sampling (see 7.3.1.1.1)

$u(t)$ is the standard uncertainty in the measurement of the time (see 7.3.1.1.2)

In the situation where only the flow rate before sampling is measured, the drift in flow rate over the period of unattended operation should have been established in a test programme preceding the practical use of the sampler.

Because conversion to standard temperature and pressure (STP) is prescribed in the relevant 'Daughter Directive', uncertainty contributions for this conversion are to be taken into account. These contributions will depend on whether mass-flow controlled or volume-controlled sampling devices are used. The calculation of individual uncertainty contributions is given in 7.3.1.1.3.

7.3.1.1.1 Sample flow calibration and measurement

The uncertainty in the measurement of the flow rates before and after sampling is calculated from the uncertainty in the readings of the flow meter used which can be derived from calibration certificates, assuming the calibration is fully traceable to primary standards of flow, and the uncertainty of the actual flow rate measurement results, as

$$\frac{u^2(\phi)}{\phi^2} = \frac{u_{\text{cal}}^2 + \frac{s_{\text{meas}}^2}{n}}{\phi^2} \quad (7.4)$$

where

$u(\phi)$ is the standard uncertainty in the measurement of flow

u_{cal} = uncertainty due to calibration of the flow meter

s_{meas} = standard deviation of individual flow measurements, determined from ≥ 3 measurements

n = number of flow measurements performed under practical conditions of use.

7.3.1.1.2 Sampling time

The sampling time t should be measured to within $\pm 0,5$ min. Then for a sampling time of 8 hours or more the relative uncertainty due to the measurement of t is negligible.

7.3.1.1.3 Conversion of sample volume to STP

Mass-flow controlled sampling devices

For mass-controlled sampling devices a conversion of the sample volume to STP may be affected by direct conversion of measured flow rates to values at STP. For conversion, the following equation is used:

$$\phi_{\text{STP}} = \phi \frac{P}{101,3} \frac{293}{(T + 273)} \quad (7.6)$$

where

ϕ_{STP} = sample flow converted to STP

ϕ = actual measured sample flow

P = actual air pressure during the flow measurements (in kPa)

T = actual air temperature during the flow measurements (in °C).

By modification of Eq. (7.1) through substitution of ϕ with ϕ_{STP} , the sample volume converted to STP is:

$$V_{\text{sam,STP}} = \phi_{\text{start,STP}} t \quad (7.7a)$$

$$V_{sam,STP} = \frac{(\varphi_{start,STP} + \varphi_{end,STP})}{2} \cdot t \quad (7.7b)$$

The uncertainty contribution for mass-flow controlled sampling devices can then be obtained by extending equation (7.4) to:

$$\frac{u^2(\varphi_{STP})}{\varphi_{STP}^2} = \frac{u_{cal}^2 + \frac{s_{meas}^2}{n}}{\varphi^2} + \frac{u^2(P)}{P^2} + \frac{u^2(T)}{T^2} \quad (7.8)$$

where

φ_{STP} = sample flow corrected to STP

$u(\varphi_{STP})$ = uncertainty in the sample flow corrected to STP

u_{cal} = uncertainty due to calibration of the flow meter

s_{meas} = standard deviation of individual flow measurements, determined from a minimum of 3 measurements

n = number of flow measurements performed under practical conditions of application

$u(T)$ = uncertainty of the actual air temperature value during the flow measurements

$u(P)$ = uncertainty of the actual air pressure value during the flow measurements

P = actual air pressure during the flow measurements

T = actual absolute air temperature during the flow measurements.

By substitution of φ and $u(\varphi)$ by φ_{STP} and $u(\varphi_{STP})$, respectively, in Eq. (7.2), the uncertainty of the sample volume, converted to STP, when employing mass-flow controlled sampling devices is obtained directly as:

$$\frac{u^2(V_{sam,STP})}{V_{sam,STP}^2} = \frac{u^2(\varphi_{start,STP})}{\varphi_{start,STP}^2} + \frac{u^2(t)}{t^2} + \frac{\Delta^2 \varphi_{STP}}{3\varphi_{start,STP}^2} \quad (7.9a)$$

$$\frac{u^2(V_{sam,STP})}{V_{sam,STP}^2} = \frac{u^2(\varphi_{start,STP}) + u^2(\varphi_{end,STP})}{(\varphi_{start,STP} + \varphi_{end,STP})^2} + \frac{u^2(t)}{t^2} + \frac{\Delta^2 \varphi_{STP}}{\left[12 \frac{(\varphi_{start,STP} + \varphi_{end,STP})}{2}\right]^2} \quad (7.9b)$$

Volume-controlled sampling devices

When using volume-flow controlled sampling devices, knowledge is required of the mean ambient temperature and pressure that occurs during sampling. These are used as follows for the conversion:

$$V_{sam,STP} = V_{sam} \frac{\bar{P}}{101,3} \frac{293}{(\bar{T} + 273)} \quad (7.10)$$

where

\bar{P} = average air pressure during the sampling period (in kPa)

\bar{T} = average air temperature during the sampling (in °C).

Uncertainties in values of \bar{T} and \bar{P} used for conversion may be obtained from

- actual measurements, taking into account the uncertainty in the temperature and pressure measurements
- knowledge of extremes of temperature and pressure during sampling, assuming these to be uniformly distributed.

For example, if the temperature extremes are known to be T_{\min} and T_{\max} the uncertainty in \bar{T} may be calculated from

$$u^2(\bar{T}) = u_{\text{cal}}^2 + \frac{(T_{\max} - T_{\min})^2}{12} \quad (7.11)$$

where

u_{cal} = uncertainty due to calibration of the temperature meter.

Generally, the first term will be negligible compared to the second.

The above uncertainty contributions are then combined to give the uncertainty in the sample volume converted to STP for volume-controlled sampling devices as:

$$\frac{u^2(V_{\text{sam,STP}})}{V_{\text{sam,STP}}^2} = \frac{u^2(V_{\text{sam}})}{V_{\text{sam}}^2} + \frac{u^2(\bar{T})}{\bar{T}^2} + \frac{u^2(\bar{P})}{\bar{P}^2} \quad (7.12)$$

7.3.1.2 Mass of compound sampled

The mass of a compound sampled may be expressed as:

$$m_{\text{sam}} = \frac{m_{\text{meas}}}{E \cdot A \cdot D} \quad (7.13)$$

where

E = sampling efficiency

A = compound stability in the sample

D = extraction/desorption efficiency

m_{meas} = measured mass of compound in the analytical sample (extract, desorbate) before correction.

A correction for extraction/desorption efficiency shall be applied when D is significantly different from 1 (see 7.3.2.1.3).

7.3.1.2.1 Sampling efficiency

For the sampling medium to be used the breakthrough volume shall be determined under reasonable worst-case conditions. In practice, these conditions will consist of a combination of a high concentration, high temperature, high air humidity, and the presence of high levels of potentially interfering compounds. As the worst-case conditions will vary between sample locations, test conditions may be adapted to these local conditions.

The sample volume shall be less than half the experimentally established breakthrough volume.

In that case the sampling efficiency will be 100% and will not contribute to the uncertainty in m_{sam} .

7.3.1.2.2 Compound stability

The stability of the compound shall be established experimentally through storage under conditions (time, temperature, environment) that are typical of those in the individual monitoring network. Tests shall be performed at a compound level corresponding to the ambient air limit or target value.

At times $t=0$ and $t=t$, n samples shall each be analysed under repeatability conditions ($n \geq 6$). For both times the samples shall be randomly selected from a batch of representative samples in order to minimize possible systematic concentration differences. As a test of (in)stability, a t-test will be performed (95% confidence, 2-sided). The t-test must show no significant difference between results obtained at the start and end of the stability test.

The uncertainty of the stability determination consists of contributions from:

- extraction/desorption (random part of extraction/desorption efficiency)
- calibration (random part of calibration)
- analytical precision
- inhomogeneity of the sample batch.

However, the uncertainty contribution of the determination of stability will already be covered by contributions determined in Clause 7.3.1.2.3 and it therefore does not need to be taken into account separately.

7.3.1.2.3 Extraction/desorption efficiency

The extraction/desorption efficiency of the compound from the sample and its uncertainty are typically obtained from replicate measurements on Certified Reference Materials (CRMs). The uncertainty due to incomplete extraction/desorption for the level corresponding to the limit value is calculated from contributions of

- the uncertainty in the concentration of the CRM
- the standard deviation of the mean mass determined

as:

$$\frac{u^2(D)}{D^2} = \frac{u^2(m_{CRM}) + \frac{s^2(m_D)}{n}}{m_{CRM}^2} \quad (7.14)$$

where

m_{CRM} = certified mass in the CRM

$s(m_D)$ = standard deviation of the replicate measurement results of the mass determined

n = the number of replicate measurements of the CRM.

When D is significantly different from 1 (at the 95% confidence level), the measurement result shall be corrected accordingly (see eq. (7.1)).

The value of $s(m_D)$ is used as an indicator of the relative uncertainty due to analytical repeatability w_{anal} :

$$w_{anal}^2 = \frac{s^2(m_D)}{m_D^2} \quad (7.15)$$

7.3.1.2.4 Corrections to the measured mass of the compound

The uncertainty in the measured mass of a compound is determined by

- the uncertainty in the concentrations of the calibration standards used
- the lack-of-fit of the calibration function
- drift of detector response between calibrations
- the precision of the analysis
- the selectivity of the analytical system used.

Calibration standards

The uncertainty of the concentration of a compound in the calibration standards used will depend on the type of calibration standard used. For a tube standard prepared by sampling from a standard atmosphere it will depend on:

- the uncertainty of the concentration in the generated standard atmosphere; uncertainty assessments for this parameter can be found in ISO 6144 and 6145 [19,20]
- the uncertainty of the sampled volume of the standard atmosphere.

The uncertainty is calculated as:

$$\frac{u^2(m_{cs})}{m_{cs}^2} = \frac{u^2(C_{sa})}{C_{sa}^2} + \frac{u^2(V)}{V^2} \quad (7.16)$$

where

$u(m_{cs})$ = uncertainty in the mass in the calibration standard (m_{cs})

$u(C_{sa})$ = uncertainty in the concentration in the standard atmosphere (C_{sa})

$u(V)$ = uncertainty in the volume of the standard atmosphere sampled (V).

For calibration standards consisting of solutions the uncertainty will be built up of contributions from:

- the purity of the compound used as calibrant; as the compounds under study are generally available in purities > 99%, the contribution of the purity may be considered insignificant
- when gravimetry is used to prepare the calibration solutions: the uncertainties in the weighings of compounds and solutions
- when volumetric techniques are used to prepare the calibration solutions: the uncertainties in the calibrated volumes of glassware and syringes used.

Note: Examples of calculations of uncertainties can be found in refs. [21] and [22].

For tube standards prepared by spiking from a solution and subsequent purging of the solvent, the uncertainty is composed of the uncertainties of the compound concentration in the solution, the spiking volume, the sampling efficiency and possible selectivity effects due to the presence of residual solvent.

Lack-of-fit of calibration function

The relative uncertainty due to lack-of-fit of the calibration function can be calculated for the relevant concentration (corresponding to the mass of benzene sampled at the limit value) from parameters obtained by a least-squares linear regression ($r = a + b \cdot m_{cs}$), weighted in the concentration of the calibration standard.

Note: Options for the calculation of the uncertainty are given in ref. [21].

As a worst-case approach, the relative uncertainty shall be estimated as:

$$w_F^2 = \frac{u^2(m_r)}{m_r^2} = \frac{u^2(r) + s^2(a) + s^2(b)m_r^2}{b^2 m_r^2} \quad (7.17)$$

where

m_r = mass calculated from the regression equation at response r

$u(r)$ = the uncertainty of the response r

b = slope of calibration function

a = intercept of calibration function

s = standard deviation of parameter between parentheses.

Response drift between calibrations

Normally, the current response factor will be used until a new one is established. In the interval between the re-establishment of its uncertainty, response checks – and, when necessary, adjustments of response factors - shall be performed as an element of ongoing quality control.

In the interval before the next checks response drift may occur. The relative uncertainty due to response drift for the period between subsequent adjustments of response factors shall then be estimated from data on the relative differences in responses between subsequent checks, as

$$w_d^2 = \frac{(r_n - r_{n-1})^2}{3 \left(\frac{r_n + r_{n-1}}{2} \right)^2} \quad (7.18)$$

where r_n is the detector response for a calibration standard corresponding closest to the mass representing a sample at the limit value. This approach assumes that no correction is applied for response drift, e.g., by averaging of subsequently determined response factors.

Selectivity

The analytical system used shall be optimized in order to minimize uncertainty due to the presence of potential interferences. Tests shall be performed with typical interferences at levels corresponding to 5 times the limit value of the compound under study. The uncertainty due to interferences may be obtained from ISO 14956 [23] as

$$w_R^2 = \frac{(r_+ - r_0)^2}{3r_0^2} \quad (7.19)$$

where r_+ represents the response with interferent, and r_0 represents the response without.

7.3.1.2.5 Combined uncertainty in the sampled mass

The contributions given above are combined to give the uncertainty of the mass of compound in the air sample as

$$\frac{u^2(m_{sam})}{m_{sam}^2} = \frac{u^2(m_{cs})}{nm_{cs}^2} + w_{anal}^2 + w_F^2 + w_d^2 + w_R^2 \quad (7.20)$$

where

n = number of calibration standards used to construct the calibration function (≥ 5)

w_R = relative uncertainty due to (lack of) selectivity of the analytical system.

7.3.1.3 Mass of compound in sample blank

The mass of compound in a sample blank is determined by analysis under repeatability conditions of a series of sample blanks; a minimum of 6 replicate analyses should be performed.

The uncertainty is then calculated using the slope of the calibration function extrapolated to the blank response level as

$$u^2(m_{bl}) = \frac{s_{bl}^2}{nb_{bl}} \quad (7.21)$$

where

s_{bl} = standard deviation of the replicate blank analyses

n = number of replicate analyses

b_{bl} = slope of the calibration function at the blank response level.

When the blank response is less than 3 times the noise level of the detector, then the blank level and its uncertainty shall be calculated from the detector noise level using the slope of the calibration function extrapolated to zero response assuming a uniform distribution, as

$$m_{bl} = \frac{3r_0}{2b_0} \quad (7.22)$$

$$u^2(m_{bl}) = \frac{9r_0^2}{12} \quad (7.23)$$

where

r_0 = noise level

b_0 = slope of calibration function at zero response.

7.3.1.4 Combined uncertainty

The combined relative uncertainty of the compound concentration in the air sampled is obtained by combination of contributions given in Clauses 7.3.1.1-7.3.1.3 as

$$w_{CM,lab}^2 = \frac{u_c^2(C_m)}{C_m^2} = \frac{u^2(V_{sam,SPT})}{V_{sam,SPT}^2} + \frac{u^2(m_{sam}) + u^2(m_{bl})}{(m_{sam} - m_{bl})^2} \quad (7.24)$$

7.3.1.5 Expanded uncertainty

The expanded relative uncertainty of the Candidate Method resulting from the laboratory experiments, $W_{CM,lab}$ at the 95% confidence level is obtained by multiplying $W_{CM,lab}$ with a coverage factor appropriate to the number of degrees of freedom of the dominant components of the uncertainty resulting from the performance of the test programme. This can be calculated by applying the Welch-Satterthwaite equation (ISO-GUM, H2). For a large number of degrees of freedom, a coverage factor of 2 is used.

Note: as a first approximation, the number of degrees of freedom may be based on that of an uncertainty contribution covering more than 50% of the variance budget.

7.3.1.6 Evaluation of results of the laboratory tests

The resulting $W_{CM,lab}$ is compared with the expanded relative uncertainty based on the data quality objective for the relevant species W_{dqo} .

If $W_{CM,lab} \leq W_{dqo}$, the field test programme can be performed; if not, the Candidate Method shall first be improved, and relevant changes tested in the laboratory test programme.

7.3.2 Test Programme 1B. Diffusive sampling

7.3.2.1 Reduced test programme

For general information about testing of diffusive samplers, the reader is referred to EN Norms EN 13528 parts 1-3 [24-26].

As a first estimate, the diffusive sampling flow (uptake rate) v and its uncertainty can be determined under 2 sets of extreme conditions [27]. Extreme conditions for diffusive sampling are characterized by extremes of

- Temperature (low and high): these will depend on prevailing local or regional conditions and will differ between member states. Member states must cover prevailing regional extremes.
- Relative humidity (as for temperature)
- Air velocity: this should always be within the range required for proper functioning of the sampler. This range shall be established beforehand; in practice, adherence to the maximum velocity shall be ensured through use of appropriate wind shields (see EN 13528 part 3, [25]). In the tests, a default level of approximately $0,5 \text{ m s}^{-1}$ is applied
- Concentrations of interferents: interferents will either affect the concentration of the compound of interest or compete for sorption sites with the compound of interest. Interferents and maximum extremes will depend on prevailing local or regional conditions. Member states must cover prevailing regional extremes in their test programmes.

Test conditions consist of:

- Extreme 1: A combination of high temperature, high relative humidity and high concentrations of interferents
- Extreme 2: A combination of low temperature, low relative humidity and low concentrations of interferents.

In each test, a minimum of 6 samplers is exposed for the exposure period considered.

The resulting characteristics to be derived are v_{high} , s_{high} , v_{low} and s_{low} .

The effective sampling (uptake) rates and their uncertainties are calculated as follows:

$$v_{eff} = \frac{v_{high} + v_{low}}{2} \quad (7.25)$$

$$u^2(v_{eff}) = \frac{\left[(v_{high} - v_{low}) + 2 \frac{s_{high}}{\sqrt{n_{high}}} + 2 \frac{s_{low}}{\sqrt{n_{low}}} \right]^2}{24} \quad (7.26)$$

where

s_{high} is the standard deviation of the determination of the uptake rate under conditions Extreme 1
 s_{low} is the standard deviation of the determination of the uptake rate under conditions Extreme 2
 n represents the number of samplers exposed in each situation.

The uncertainty calculated in this way is based on the assumption of a triangular distribution of values of v and provides a 'first' uncertainty estimate. The uncertainty assessment can be refined – if necessary – through the performance of extended tests.

7.3.2.2 *Extended test programme*

In the extended test programme, the factors affecting the sampling rate (see above) are varied in 2-level (high/low) or 3-level (high/medium/low) experimental designs. The number of experiments to be performed can be based on an orthogonal or 'Taguchi' design. For the 3-factor/2-level approach a minimum number of 4 experiments suffices, for a 3-factor/3-level design 9 experiments are needed.

The resulting average sampling (uptake) rate and its uncertainty can be evaluated by applying analysis of variance.

7.4 **Field test programme**

7.4.1 *General*

Field tests shall be performed in which the Candidate and Reference Method are compared side-by-side. The measurements will serve to assess

- 'between-sampler' uncertainty of the Candidate Method through the use of replicate samplers
- 'comparability' of the Candidate and Reference Methods.

Generally, results of existing studies, when demonstrably obtained according to the requirements of this test procedure, may be used to determine standard uncertainties. This is particularly relevant to the estimation of between-sampler/instrument uncertainties.

In order to assure proper functioning of the Reference Method, two reference samplers or instruments may be used. In this case the mean squared difference of the results of both reference samplers/instruments can be used as an estimate of the (random) uncertainty of the reference method.

The number of replicate samplers needed to determine the between-sampler uncertainty of the Candidate Method will depend on

- the averaging period of the measurement
- the practicability of performing multiple measurements in parallel
- whether the analysis part of the Candidate Method is to be carried out by more than one laboratory.

Each laboratory carrying out analysis for the Candidate Method shall provide at least two samplers.

When more than one laboratory will carry out the analysis, the field tests shall also be used to evaluate between-laboratory contributions to the uncertainty of the measurement results.

7.4.2 *Experimental conditions*

Test sites shall be representative of typical conditions for which equivalence will be claimed, including possible episodes of high concentrations. A minimum of 4 comparisons shall be performed with particular emphasis on the following variables, if appropriate:

- Composition of the air, notably high and low concentrations of the measured compound and potential interferents
- Air humidity and temperature (high and low) to cover any effects on sampling efficiency or desorption efficiency
- Wind speed (high and low) to cover any dependency of sampler performance due to deviations from ideal behaviour.

A minimum of 40 measurement results for the Candidate Method per comparison shall be collected over a minimum of 8 sampling periods covering a minimum of 20 days (e.g. 2 samplers and 20 periods, 5 samplers and 8 periods).

Samplers and instruments shall be positioned in such a way that the effect of spatial inhomogeneities in the compound concentration in the sampled air are negligible in comparison with other uncertainty contributions.

Both methods shall be operated under conditions reflecting practical application in the field, e.g., calibration intervals, flow checks, analysis of blank samples.

During the tests, the following information shall be collected and recorded

- Calibration procedures, equipment and intervals
- (Results of) quality checks
- Temperature and pressure of the sampled air
- Other conditions relevant for the measurements performed (e.g., air humidity)
- Particular events/situations that may be of influence on measurement results.

7.4.3 Evaluation of the field test data

7.4.3.1 Conversion of measurement results to STP

For the measurement of gaseous pollutants under Directives 1999/30/EC, 2000/69/EC and 2002/3/EC a conversion is required of measurement results to conditions of standard and pressure (STP, 20 °C, 101,3 kPa). Clause 7.3.1.1.3 describes the conversion and the assessment of the resulting uncertainty contribution.

7.4.3.2 Suitability of the dataset

Of the full dataset at least 20% of the results shall be greater than or equal to the upper assessment threshold specified in the relevant Daughter Directive.
Data shall only be removed from the data set when sound technical reasons can be found for doing so. All valid data shall be used for further evaluation.

Note: Indications of outlying data within replicate sets may be obtained using Grubb's tests on the individual single-period variances. Tests are to be performed at the 99% level.

7.4.3.3 Calculation of performance characteristics

7.4.3.3.1 Between-sampler/instrument uncertainty

If the Standard Method is based on an AMS, the results for each measurement period i are averaged first to give 24-hour values y_i .

The relative between-sampler uncertainty for individual laboratories w_{bs} is calculated from the differences of results of the candidate samplers/instruments operated in parallel as:

$$w_{bs}^2 = \frac{\sum_{i=1}^n (y_{i,1} - y_{i,2})^2}{2ny^2} \quad \text{for duplicate samplers} \quad (7.27)$$

where

$y_{i,1}$ and $y_{i,2}$ are the results of parallel measurements for a single period i

y = average of all measurement results of the Candidate Method

n = number of measurement results.

$$w_{bs}^2 = \frac{\sum_{i=1}^n \sum_{j=1}^p (y_{i,j} - \bar{y}_i)^2}{n(p-1)\bar{y}^2} \text{ for replicate samplers with } p > 2 \quad (7.28)$$

where

y_{ij} = result of measurement j for a single period i

\bar{y}_i = mean result for period i

p = number of replicates for period i .

Where more than one analytical laboratory is participating, equation 7.28 shall be used to calculate the between-laboratory w_{bs} .

The w_{bs} between sampler uncertainty component for each individual laboratory and the between-laboratory w_{bs} (if relevant) shall comply with the criteria given in Annex A.

If the performance of a single laboratory causes a method implemented by more than two laboratories to fail the criteria, then the results for this laboratory may be excluded, if sound technical grounds exist for doing so.

7.4.3.3.2 Comparison with Standard Method

First, the performance of the standard samplers/instruments is checked by calculation of the relative between-sampler/instrument uncertainty as in eq. (7.27) or (7.28). This relative uncertainty shall be $\leq 3\%$.

For the comparison of the Candidate Method with the Standard Method, first the results of replicate measurements are averaged to give data pairs 'Candidate Method – Standard Method' with equal measurement periods.

For the evaluation of the uncertainty due to the 'lack of comparability' (differences in the concentrations measured) between the Candidate and Standard Methods, it is assumed that the relationship between measurement results of both methods can be described by a linear relation of the form

$$y_i = a + bx_i \quad (7.29)$$

where x_i is the average result of the Standard Method over period i .

The relation between the average results of the Candidate Method and those of the Standard Method is established using a regression technique that leads to a symmetrical treatment of both variables. A commonly applied technique is orthogonal regression [7,28].

The uncertainty due to lack of comparability will be a function of the concentration of the measurand.

The general relationship describing the dependence of u_{C-S} on x_i is given by

$$u_{C-S}^2(y_i) = \frac{RSS}{(n-2)} - u^2(x_i) + [a + (b-1)x_i]^2 \quad (7.30)$$

where

RSS = the sum of (relative) residuals resulting from the orthogonal regression

$u(x_i)$ = random uncertainty of the Standard Method; as such, the value of u_{bs} calculated for the application of the Standard Method in these tests may be used.

Note: The above equation is used in all the equivalence test programmes in this Report for the field evaluation of a CM against the RM. It can be seen that it corrects for the random uncertainty component arising from the implementation of the RM, and thus if this is implemented badly, in parallel with the operation of a high performance CM, small or negative results may be obtained for the uncertainty of the CM using this equation.

Algorithms for the calculation of a and b and their variances are given in Annex B.

RSS, the sum of (relative) residuals is calculated using eq. 7.31a or 7.32b, depending on whether the residuals or relative residuals are constant.

$$RSS = \sum_{i=1}^n (y_i - a - bx_i)^2 \text{ when } (y_i - a - bx_i)^2 \text{ is constant} \quad (7.31a)$$

$$RSS = (a + bx_i)^2 \sum_{i=1}^n \left(\frac{y_i}{a + bx_i} - 1 \right)^2 \text{ when } \left(\frac{y_i}{a + bx_i} - 1 \right)^2 \text{ is constant} \quad (7.31b)$$

7.4.3.4 Calculation of the combined uncertainty of Candidate Method

The combined relative uncertainty of the Candidate Method $w_{c,CM}$ is calculated as follows:

$$w_{c,CM}^2(y_i) = \frac{u_{c,s}^2(y_i)}{y_i^2} \quad (7.32)$$

In this way, $w_{c,CM}$ is expressed as a function of the compound concentration.

The uncertainty at the limit value w_{CM} is calculated by taking as y_i the concentration at the limit value.

7.4.3.5 Calculation of the expanded uncertainty of Candidate Method

The expanded relative uncertainty of the results of the Candidate Method is calculated by multiplying $w_{c,CM}$ by a coverage factor k reflecting the appropriate number of degrees of freedom resulting from the determination of $w_{c,CM}$ as

$$W_{CM,field} = k \cdot w_{c,CM} \quad (7.33)$$

In view of the large number of experimental results available, a coverage factor $k=2$ can be used for a 95% confidence level.

7.4.4 Evaluation of results of field tests

The resulting uncertainty estimate W_{CM} is compared with the expanded relative uncertainty obtained from the laboratory test programme $W_{CM,l}$ and the expanded relative uncertainty based on the data quality objective for the Standard Method W_{dqo} .

In principle, three cases are possible

1. $W_{CM,field} \leq W_{CM,lab}$: the Candidate Method is accepted as equivalent to the Standard Method

2. $W_{CM,lab} < W_{CM,field} \leq W_{dgo}$: the Candidate Method is accepted conditionally; before final acceptance, the uncertainty evaluation from the laboratory tests should be revisited and corrected such that situation 1 occurs
3. $W_{CM,field} > W_{dgo}$: the Candidate Method is not accepted as Equivalent Method

8 TEST PROGRAMME 2: AUTOMATED MEASUREMENT SYSTEMS FOR GASES

8.1 General

This test programme describes a procedure for determining whether a Candidate Method is suitable to be considered equivalent to the EN Standard Method for the measurement of gases and vapours in ambient air, using automated measurement systems. The EN Standard Methods have been developed to meet the Data Quality Objectives of the Air Quality Framework Directive and its Daughter Directives. Therefore, Candidate Methods will similarly have to meet the directives' requirements.

(Note: In the context of this Section the EN Norms 14211, 14212, 14625, 14626, & 14662 Parts 1-3 are considered as Reference Methods at the time of preparation of this Report)

This test programme covers the requirements for the equivalence testing of an AMS where it is practical to achieve measurements that have full traceability to SI units. These include continuous ambient-air analysers monitoring sulphur dioxide, the nitrogen oxides (NO and NO₂) ozone and carbon monoxide. Analysers measuring benzene in ambient air by sequential automated (quasi-continuous) sampling and subsequent measurements by gas chromatography, are also covered.

The use of similar automated methods for the measurement of precursor 'non-methane hydrocarbons' discussed in EU Directive 2002/03/EC are not included because these measurements are not covered by an EN Standard Method, nor are there yet any assigned uncertainty requirements for such methods.

The methodology specified in this Section for equivalence testing follows very closely the procedures specified in the appropriate EN Norms prepared by CEN Technical Committee 264 'Air Quality'.

8.2 Overview of the test procedures

The EN Norms specify procedures for the type-approval testing of analysers to determine whether their performance (overall measurement uncertainty, data capture etc) conforms with the requirements of the relevant Daughter Directive. These tests define all the individual performance characteristics which contribute to the combined uncertainty of the method (repeatability, linearity lack of fit, responses to cross-interferents etc), and which therefore shall be tested.

These Standard Methods also specify minimum (performance) criteria to which the individual performance characteristics shall conform. In addition, the Standards specify procedures to determine the expanded uncertainty of the method from the component performance criteria obtained during tests, and this expanded uncertainty shall be compared with the expanded uncertainty Data Quality Objective given in the relevant Daughter Directive, in order to assess the performance of the analyser with respect to the Directives' requirements.

Therefore, a Candidate Method will be treated as a complete measurement system (e.g. with sampling system where applicable), as far as possible, and will undergo testing to determine the uncertainties introduced by all the different performance characteristics of the complete measurement system. These separate uncertainties shall then be combined to give an expanded uncertainty, expressed with a level of confidence of 95%, for the CM, which shall then comply with the measurement uncertainty laid down within the relevant EU Directive.

Testing shall be carried out in two parts. A laboratory test in which two instruments of the same pattern will be tested, and a field test in which these two instruments will be tested together against the relevant Standard Method.

If a CM is a modification to an existing type-approved analyser, then only the laboratory performance characteristics that are affected by the modification shall be tested and their standard uncertainties calculated. The standard uncertainties associated with unaffected performance characteristics shall then be used together with these existing standard uncertainties, to determine the combined measurement uncertainty, u_c . An example of such a modification would be a new material for a converter of NO_x to NO within a chemiluminescence NO_x analyzer. Under this modification only the converter efficiency test and the response time test shall be performed in the lab tests. In all cases the field tests shall be performed.

If a CM utilises a measurement method that is different to the EN Standard Method, then all of the tests shall be performed.

The following performance characteristics of the CM will be tested, where applicable:

(i) Laboratory tests

- response time, consisting of rise lag time, rise time, fall lag time and fall time (where applicable – see Section 8.4.2);
- laboratory repeatability standard deviation;
- short-term zero and span drift;
- difference between sample port and calibration port (where applicable);
- detection limit;
- averaging of short-term fluctuations in measurand concentration (where applicable);
- lack of fit (linearity);
- cross-sensitivity to potentially-interfering substances; (Note: if the measuring principle of the CM is different to that of the RM then the choice of the most likely interfering species needs to be made with extreme care, as they may not be the same for both – for guidelines see EN ISO 14156)
- NO_x converter efficiency test (where applicable);
- carry-over (where applicable);
- influence of atmospheric sample pressure and temperature;
- influence of surrounding air temperature
- influence of supply voltage variations.

Both analysers used in the laboratory tests are required to pass all the tests.

(ii) Field tests

- field performance of two CM analysers of the same type(pattern) against one system employing the relevant Standard Method to determine whether systematic differences occur in the measured results;
- field repeatability of two CM analysers;
- long-term zero and span drift;
- availability (maintenance interval).

Both analysers used in the field tests are required to pass all the tests.

The performance characteristics together with their associated performance criteria that are calculated from the tests shall all individually be compared to the specific performance criteria specified in the relevant EN Norms. All the individual performance criteria of the CM shall meet the requirements specified in the relevant EN Norm. The methods for determining the measurement uncertainties associated with these, defined in Table 8.1, are given in this Report and are also explained in more detail in the relevant EN Norms.

From the performance characteristics the following standard uncertainties, where applicable, shall be calculated and then used to calculate the combined expanded measurement uncertainty of the CM:

Table 8.1. Standard uncertainty components to be included in the combined standard measurement uncertainty

<i>Uncertainty Source</i>	<i>Symbol</i>
Repeatability at zero	u_z
Repeatability at 70%-80% of the certification concentration	u_s
Between-instrument uncertainty	u_f
Carry over	u_c
Lack of fit (linearity)	u_l
Difference between sample and calibration port	u_a
Effect of short term fluctuations in concentration	u_{av}
Cross sensitivity to interfering substances	u_{H_2O}, u_{int}
Variation in sample pressure	u_p
Variation in sample temperature	u_t
Variation in surrounding air temperature	u_{st}
Variation in supply voltage	u_v
NO _x converter efficiency	u_{ce}
Comparison with the Standard Method	u_{CM}
Long-term zero drift	u_{zd}
Long-term span drift	u_{sd}

8.3 Definitions applicable to automatic measurement systems

- 8.3.1 Independent measurement An individual measurement that is not influenced by a previous individual measurement, by separating two individual measurements by at least four response times.
- 8.3.2 Individual measurement A measurement averaged over a time period equal to the response time of the analyser.
- 8.3.3 Certification range The concentration range of the measurand over which the CM is to be certified as equivalent (Note: this range is normally chosen to be significantly larger than the value of the shortest term limit or target value, to allow valid measurements of short term fluctuations to be made –see the relevant EN norm)

8.4 Laboratory tests

8.4.1 Test concentrations

Laboratory tests are performed, in principle, over the range of concentrations specified in the EN Norms for the method. A more restricted certification range may be selected by a Member State if judged appropriate. (The CM will then only be applicable to results obtained in this restricted certification range.) Test concentrations specified here for the laboratory tests are based on the maximum of the selected certification range, unless specified otherwise.

8.4.2 Response time

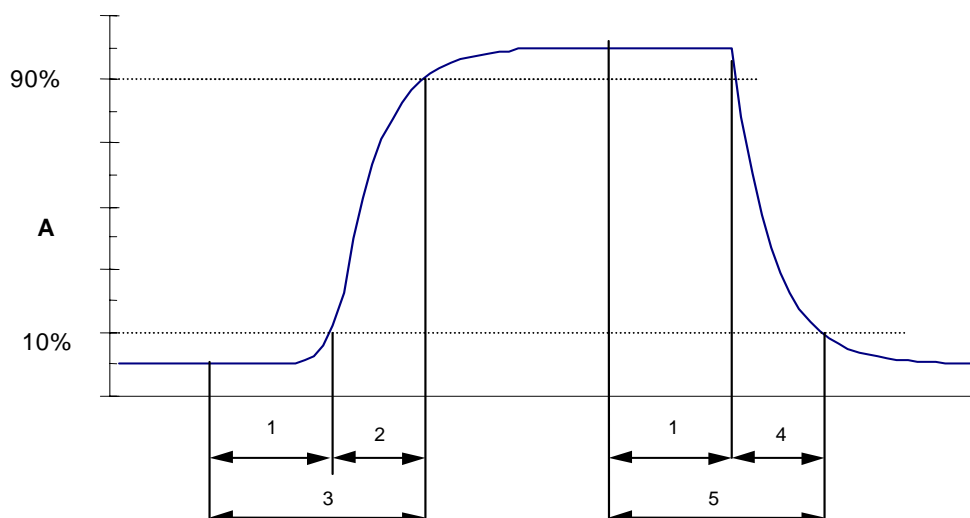
The tests of response time shall be performed on all Candidate Methods that give approximately real-time measurements.

For instruments such as gas chromatographs, the concept of response time is inappropriate and the response time shall be taken to be the time interval of the sampling. For example, if the instrument collects a sample once an hour, then the assumed response time will be one hour. The requirement on response time for this type of CM is that the assumed response time is less than 25% of the required averaging period.

For real-time CMs the following test procedure shall be used:

The determination of the response time shall be carried out by applying a step function in the concentration from less than 20% to about 80% of the maximum of the certification range to the CM and vice versa (see figure 8.1).

The change from the low concentration gas to the high concentration gas needs to be made nearly instantaneously with the use of a suitable valve, or valves. The outlet from this must be applied directly to the inlet of the analyser, and there should be a suitable “oversupply” of the gases that should be vented by using a tee-piece. The gas flows of both the low and the high concentration gases should be selected with these valve(s) in such a way that the dead time for the changeover between the low and high concentrations may be neglected when compared with the measured lag time of the analyser. The step change from low to high concentration gas needs to be timed and this event is the start time ($t = 0$) of the (rise) lag time as shown in Figure 8.1. When the reading corresponding to 98% of the applied concentration has been reached, the gas may be switched back to the low concentration gas. This event is the start time ($t = 0$) of the (fall) lag time. When the reading corresponds to 2% of the applied low concentration has been reached the whole cycle corresponding to figure 8.1 is complete. The response of the CM to the applied step changes of concentration should be recorded and the lag time (the time taken by the CM to indicate 10% of the final concentration value), the response time (the time taken for the CM to indicate 90% of the final concentration value) and the rise time (the difference between the response time and the lag time) should all be determined. Measurements should be made with at least four step changes of concentration in both positive and negative directions. As well as calculating the individual rise and fall response times, the relative differences in response times should also be calculated (see the relevant EN norm). The average values of the four (rise) response times, the four (fall) response times, and the four relative differences, should be calculated. These should be compared with the performance criteria for these characteristics specified in the relevant EN norm (also listed in Annex X).



Key

- A Analyser response
- 1 Lag time
- 2 Rise time
- 3 Response time (rise)
- 4 Fall time
- 5 Response time (fall)

Figure 8.1 — Diagram illustrating the response time

A further requirement is that the response time should be less than 25% of the required shortest averaging period given for the directive's limit or target value. Another requirement is that the relative difference between the average response rise time and average response fall time should be less than or equal to 10% (see the relevant EN Norm).

For CMs measuring NO and NO₂ simultaneously, the response times shall be determined for both NO and NO₂ test gases.

Where the CM uses an adaptive filter for data smoothing, the response times of the CM shall be measured with both the filter enabled and disabled. The maximum response times measured in both these sets of tests shall be compared with the performance criteria in the relevant EN norm.

8.4.3 Short-term drift

The CM is calibrated at both zero concentration and at 70% to 80% of the maximum of the certification range and adjusted as appropriate. It is then supplied with test gas at zero concentration, and after the period equivalent to one independent reading has passed, 20 individual measurements will be recorded of the CM's output. The CM is then supplied with test gas at a concentration around 70% to 80% of the maximum of the certification range and the equivalent measurements recorded.

The CM shall be operated under the laboratory conditions whilst analysing ambient air. After a minimum period of 12 hours the repeatability test is repeated. The averaged values obtained for zero and 70% to 80% of the maximum of the certification range shall be calculated. This test shall be used to show that the 12-hour drift is not the dominant factor in any of the test results.

The short-term drift at zero and at 70% to 80% of the maximum of the certification range shall be calculated as follows:

$$D_{s,z} = (C_{z,2} - C_{z,1}) \quad (8.1)$$

where

$D_{s,z}$ = the 12-hour drift at zero;

$C_{z,1}$ = the average of the zero gas measurements at the beginning of the drift period (just after calibration);

$C_{z,2}$ = the average of the zero gas measurements at the end of the drift period (12 hours).

D_{sz} shall comply with the performance criterion for short term drift at zero given in the relevant EN Standard for the measurand.

$$D_{s,s} = (C_{s,2} - C_{s,1})$$

Span drift now zero drift corrected

$$D_{s,s} = (C_{s,2} - C_{s,1}) - D_{s,z} \quad (8.2)$$

where:

$D_{s,s}$ = the 12-hour drift at the test concentration C_t (nmol/mol);

$C_{s,1}$ = the average of the span gas measurements at the beginning of the drift period (just after calibration) (nmol/mol);

$C_{s,2}$ = the average of the span gas measurements at the end of the drift period (12 hours) (nmol/mol)

$D_{s,s}$ shall comply with the performance criterion for short term drift at span levels given in the relevant EN Norm for the measurand.

8.4.4 Repeatability for continuous measuring CMs

Test gases shall be supplied to the CM at zero concentration and the highest numerical limit or target value specified for the pollutant for a period equivalent to one independent measurement, and then 20 individual measurements of the CM's output are recorded.

From these measurements the repeatability standard deviation (s_i) at zero concentration and at concentration c_i shall be calculated according to:

$$s_i = \sqrt{\frac{\sum (y_i - \bar{y})^2}{n - 1}} \quad (8.3)$$

where:

s_i = the repeatability standard deviation;

y_i = the i th measurement;

\bar{y} = the average of the 20 measurements;

n = the number of measurements, $n = 20$.

The repeatability standard deviation shall be calculated separately for both series of measurements (zero gas and concentration c_i) and the repeatability (r_i) is calculated according to:

$$r_i = t_{n-1, 0.05} \cdot s_i \quad (8.4)$$

where:

$t_{n-1, 0.05}$ = the two-sided Students t-factor at a confidence level of 0,05, with $n-1$ degrees of freedom (for $n = 20$, $t_{n-1, 0.05} = 2,09$);

s_i = the repeatability standard deviation.

r_i shall comply with the performance criteria for repeatability at zero and repeatability at the limit value concentration, respectively, given in the EN Norm for the measurand.

The standard uncertainties u_z and u_s , for repeatability are equal to the repeatability standard deviation, s_i calculated above, for the zero and the limit/target value concentrations.

Note: the above calculation of the repeatability standard deviation is not included in the main body of the text of the relevant EN Norms. Instead it is described in more detail in a normative Annex in the Norms (e.g. see EN14211 Annex G)

8.4.5 Carry over and repeatability for CMs collecting samples onto a sorbent prior to analysis

CMs that collect samples by absorption or other similar means and then subsequently analyse them shall be tested for the carry-over of measurand from one sample to the next. The CM shall be supplied with test gas for one sampling period, at the highest numerical limit or target value specified for the pollutant, followed by one sampling period of zero gas. This procedure shall be repeated 20 times and the results shall be used to calculate both the repeatability standard deviation at the limit value concentration and the carry over standard deviation according to:

$$s_i = \sqrt{\frac{\sum (y_i - \bar{y})^2}{n - 1}} \quad (8.5)$$

where:

s_i = the repeatability / carry-over standard deviation;

y_i = the i th measurement ;

\bar{y} = the average of the 20 measurements;

n = the number of measurements, $n=20$.

The repeatability standard deviation shall be calculated separately for both series of measurements (zero gas and concentration c_i) and the repeatability (r_i) is calculated according to eq. (8.4).

r_i shall comply with the performance criteria for carry over and repeatability specified in the relevant EN Norm respectively.

The standard uncertainties u_c and u_s , for carry over and repeatability are equal to the repeatability standard deviation, s_i calculated above, for the carry over and limit value test concentrations.

8.4.6 Lack of fit (linearity)

The CM shall be adjusted at a concentration of about 90 % of the maximum of the certification range. The linearity of the CM shall then be tested over the range 0 % to 95 % of the maximum of the certification range of the CM using at least 6 concentrations (including the zero point). At each concentration (including zero) at least 5 independent readings shall be performed.

The concentrations shall be applied in the following sequence: 80 %, 40 %, 0 %, 60 %, 20 % and 95 %. The uncertainties in the dilution ratios for the applied concentrations shall be less than 1,5 % with respect to each other.

Note: it is not necessary to know the absolute concentrations of these five test gases - only that the ratios of their concentrations is known to within the specified 1,5%. This can be achieved by a number of means - e.g. by the use of a suitable dynamic gas dilutor

Continuous measuring CMs

After each change in concentration a delay of at least 4 response times shall be taken into account before the next measurement is performed.

Non-continuous measuring CMs

After each change in concentration at least a delay of 1 response time shall be taken into account before the next measurement is performed.

For both, a linear regression function is calculated from the measured mean responses at each concentration. The relative residual for each measured concentration is calculated. The largest

relative residual, ρ_{\max} , and the actual residual at the zero concentration, shall be compared against the performance criterion for lack of fit given in the relevant EN Norm.

The standard uncertainty due to the lack of fit at the limit value concentration, u_l , is calculated according to:

$$u_l = \frac{\rho_{\max} \cdot LV}{\sqrt{3}} \quad (8.6)$$

where:

u_l = the standard uncertainty due to lack of fit at the limit value concentration;

LV = the highest numerical limit or target value specified for the pollutant.

8.4.7 Differences between sample and calibration port

If the CM has different ports for sample gas and calibration gas, the difference in response of the CM when test gas is introduced through the sample or calibration port shall be tested. The test shall be carried out by supplying test gas, with a concentration of 70 % to 80 % of the maximum of the certification range, through the sample port for a time period equal to one independent measurement. Three individual measurements shall then be taken of the CM output. Zero gas is then supplied to the sample port for a time period equal to one independent measurement. This test is repeated with the test gas supplied to the calibration port instead of the sample port. A delay of 4 response times should be left between testing the sample and calibration ports to allow for flushing.

The difference shall be calculated according to:

$$D_{sc} = \left| \frac{y_s - y_c}{c_t} \right| \times 100\% \quad (8.7)$$

where

D_{sc} = the difference sample/calibration port (%);

y_s = the average of the concentrations measured using the sample port;

y_c = the average of the concentrations measured using the calibration port;

c_t = the concentration of the test gas.

D_{sc} shall comply with the performance criterion for the difference between the sample and calibration port in the relevant EN Norm for the compound.

The standard uncertainty due to the difference between the sample and calibration port, u_a , is calculated according to:

$$u_a = \frac{\frac{D_{sc}}{100} \cdot LV}{\sqrt{3}} \quad (8.8)$$

where

u_a = the standard uncertainty due to the difference between the sample and calibration ports, expressed at the highest numerical limit or target value specified for the pollutant.

8.4.8 Effect of short-term fluctuations in concentration (averaging test)

The averaging test gives a measure of the uncertainty in the averaged values caused by concentration variations in the sampled air that are shorter in time scale than that of the measurement process in the analyser. For the determination of the uncertainty due to the averaging the following concentrations are applied to the analyser and readings are taken at each concentration:

- 1) CO, O₃, SO₂ and benzene measuring CMs
 - a constant concentration of the measurand at a concentration that is about twice the highest numerical limit value specified for the pollutant
 - a concentration of the measurand that is stepped in time between zero and about twice the highest numerical limit value specified for the pollutant (see e.g. EN 14625 8.4.12).
- 2) CMs measuring NO and NO₂ simultaneously
 - a constant concentration of NO₂ at a concentration, which is about the hourly limit value;
 - a concentration of NO that is stepped in time between zero and a concentration corresponding to about six times the hourly limit value for NO₂ (see EN14211 8.4.12)

For non-continuously measuring CMs the time period (t_c) of the constant concentration shall be at least equal to a period necessary to obtain two cycle periods (which equals to at least two response times). The time period (t_v) of the varying concentration shall be at least equal to a period necessary to obtain four cycle periods (which equals to at least four response times). The time period (t_D) for the measurand concentration shall be 90 seconds followed by a period (t_{zero}) of 90 seconds of zero concentration.

The change from t_D to t_{zero} shall be within 0,5 seconds. The change from t_c to t_v shall be within one response time of the analyser under test.

The averaging effect (X_{av}) is calculated according to:

$$X_{av} = \frac{C_{const}^{av} - 2 \times C_{var}^{av}}{C_{const}^{av}} \times 100\% \quad (8.9)$$

where

X_{av} = the averaging effect (%);

C_{const}^{av} = the average of the at least 4 independent measurements during the constant concentration period (t_c);

C_{var}^{av} = the average of the at least 4 independent measurements during the variable concentration period (t_v).

X_{av} shall comply with the requirements for the measurand in the relevant EN Norm.

For instruments measuring NO and NO₂ simultaneously, X_{av} shall be calculated for both channels and compared with these requirements.

The resulting uncertainty u_{av} is calculated as

$$u_{av} = \frac{X_{av}}{100\sqrt{3}} \quad (8.10)$$

8.4.9 Variation in sample-gas pressure

Measurements are taken at a concentration of about 70 % to 80 % of the maximum of the certification range of the CM at an absolute pressure of about 80 kPa \pm 0,2 kPa and at an absolute pressure of about 110 kPa \pm 0,2 kPa. At each pressure the test gas is supplied for a time period equal to one independent measurement and then three individual measurements will then be taken of the CMs output. From these measurements the averages at each pressure are calculated.

Measurements at different pressures shall be separated by at least 4 response times for continuous measuring CMs and one response time for non-continuous measuring CMs.

The sensitivity coefficient for the influence of sample gas pressure is calculated by:

$$\frac{\Delta C}{\Delta P} = \left| \frac{C_{P_2} - C_{P_1}}{P_2 - P_1} \right| \quad (8.11)$$

where

C_{P_1} = the average concentration of the measurements at sampling gas pressure P_1 ;

C_{P_2} = the average concentration of the measurements at sampling gas pressure P_2 ;

P_1 = the sampling gas pressure P_1 (kPa);

P_2 = the sampling gas pressure P_2 (kPa).

The test parameter b_{gp} to be compared to the test criterion in the relevant EN Norm for the compound investigated is then calculated as

$$b_{gp} = \frac{\Delta C}{\Delta P} \cdot \frac{100}{C_t} \quad (8.12)$$

where C_t is the applied test gas concentration.

The standard uncertainty due sample pressure variation, u_p , is calculated according to:

$$u_p = \frac{\Delta C}{\Delta P} \cdot \left| \frac{P_{max} - P_{min}}{\sqrt{3}} \right| \quad (8.13)$$

where P_{max} and P_{min} are the extremes of pressures encountered in practice.

For calculation of the standard uncertainty from the results of the type-approval test, P_{max} and P_{min} equal P_2 and P_1 , respectively.

8.4.10 Variation in sample-gas temperature

For the determination of the dependence of the sample gas temperature measurements shall be performed at sample gas temperatures of 0 C and 30 C. The temperature dependence shall be determined at a concentration of about 70 % to 80 % of the maximum of the certification range of the CM. At each temperature the test gas is supplied for a time period equal to one independent measurement and then three individual measurements will then be taken of the CM's output.

The sample gas temperature, measured at the inlet of the analyser, shall be held constant for at least 30 minutes before any measurements are taken.

The sensitivity coefficient for the influence of sample gas temperature is calculated as:

$$\frac{\Delta C}{\Delta T_{sg}} = \left| \frac{C_{T_2} - C_{T_1}}{T_2 - T_1} \right| \quad (8.14)$$

where

C_{T_1} = the average concentration of the measurements at sample gas temperature T_1 (°C);

C_{T_2} = the average concentration of the measurements at sample gas temperature T_2 (°C);

T_1 = the sample gas temperature T_1 (°C);

T_2 = the sample gas temperature T_2 (°C).

The test parameter b_{sg} to be compared to the test criterion in the relevant EN Norm for the compound investigated is then calculated as

$$b_{sg} = \frac{\Delta C}{\Delta T_{sg}} \cdot \frac{100}{C_t} \quad (8.15)$$

where C_t is the applied test gas concentration.

The standard uncertainty due sample temperature variation, u_t , is calculated according to:

$$u_t = \frac{\Delta C}{\Delta T_{sg}} \cdot \left| \frac{T_{sg,max} - T_{sg,min}}{\sqrt{3}} \right| \quad (8.16)$$

where $T_{sg,max}$ and $T_{sg,min}$ are the extremes of temperature encountered in practice.

For calculation of the standard uncertainty from the results of the type-approval test, P_{max} and P_{min} equal T_2 and T_1 , respectively.

8.4.11 Surrounding temperature variation

The influence of the surrounding air temperature shall be determined at the following temperatures (within the specifications of the manufacturer):

- the minimum specified temperature ($T_{e,min}$);
- at the laboratory temperature (T_1);
- at the maximum specified temperature ($T_{e,max}$).

For these tests a climate chamber is necessary.

The influence shall be determined at a concentration around 70 % to 80 % of the maximum of the certification range of the CM. At each temperature the test gas is supplied for a time period equal to one independent measurement and then three individual measurements will then be taken of the CM's output. At each temperature measurements at zero and a concentration around 70 % to 80 % of the maximum of the certification range of the CM shall be performed.

At each temperature setting the criteria for warm-up or stabilisation time are to be met.

The measurements shall be performed in the following sequence of the temperature settings:

T_1 , $T_{e,min}$, T_1 and T_1 , $T_{e,max}$, T_1

At the first temperature (T_1) the CM shall be adjusted at zero and at span level (70 % to 80 % of the maximum of the certification range). Then measurements shall be carried out at T_1 , at $T_{e,min}$ and again at T_1 . This procedure shall be repeated at the temperature sequence of T_1 , $T_{e,max}$, and at T_1 .

In order to exclude any possible drift due to factors other than temperature, the measurements at T_1 are averaged, which is taken into account in the following formula for calculation of the sensitivity coefficient for the influence of surrounding temperature:

$$\frac{\Delta C}{\Delta T_e} = \left| \frac{y_T - \frac{y_1 + y_2}{2}}{T - T_1} \right|^{\frac{1}{2}} \quad (8.17)$$

where

y_T = the average of the measurements at $T_{e,min}$ or $T_{e,max}$;

y_1 = the first average of the measurements at T_1 just after calibration;

y_2 = the second average of the measurements at T_1 just before calibration;

T_1 = the surrounding air temperature at the laboratory ($^{\circ}\text{C}$);

T = the surrounding air temperature $T_{e,min}$ or $T_{e,max}$ ($^{\circ}\text{C}$).

For reporting the surrounding air temperature dependence the higher value is taken of the two calculations of the temperature dependence at $T_{e,min}$ and $T_{e,max}$.

This value is then compared to the test criterion in the relevant EN Norm for the compound investigated.

The standard uncertainty due to surrounding temperature variation, u_{st} , is calculated according to:

$$u_{st} = \frac{\Delta C}{\Delta T_e} \cdot \left| \frac{T_{e,max} - T_{e,min}}{\sqrt{3}} \right| \quad (8.18)$$

where $T_{e,max}$ and $T_{e,min}$ are the extremes of surrounding temperature encountered in practice.

For calculation of the standard uncertainty from the results of the type-approval test, $T_{e,max}$ and $T_{e,min}$ are the temperatures used in this test.

8.4.12 Variation due to supply voltage

The influence of changes in the electrical supply voltage shall be determined at both ends of the specified voltage range at zero concentration and at a concentration around 70 % to 80 % of the maximum of the certification range of the CM. At each voltage the test gas is supplied for a time period equal to one independent measurement and then three individual measurements will then be taken of the CMs output. At each voltage measurements at zero and around 70 % to 80 % of the maximum of the certification range shall be performed.

The sensitivity coefficient for the influence of voltage dependence is calculated according to:

$$\frac{\Delta C}{\Delta V} = \left| \frac{C_{V_2} - C_{V_1}}{V_2 - V_1} \right| \quad (8.19)$$

where

C_{V_1} = the average concentration reading of the measurements at voltage V_1 ;

C_{V_2} = the average concentration reading of the measurements at voltage V_2 ;

V_1 = the minimum voltage V_{min} (V) specified by the manufacturer;

V_2 = the maximum voltage V_{\max} (V) specified by the manufacturer.

For reporting the dependence on voltage the highest value of the result at zero and span level shall be taken. This value is then compared to the test criterion in the relevant EN Norm for the compound under investigation.

For an analyser operating on direct current the type approval test of voltage variation shall be carried out over the range of $\pm 10\%$ of the nominal voltage.

The standard uncertainty due to voltage variation, u_v , shall be calculated according to:

$$u_v = \frac{\Delta C}{\Delta V} \cdot \left| \frac{V_{\max} - V_{\min}}{\sqrt{3}} \right| \quad (8.20)$$

where V_{\max} and V_{\min} are the extremes of line voltage encountered in practice.

For calculation of the standard uncertainty from the results of the type-approval test, V_{\max} and V_{\min} equal V_2 and V_1 , respectively.

8.4.13 Cross-sensitivity to interfering substances

The analyser's response to certain interfering substances, which are to be expected to be present in ambient air and which may also interfere with the CMs measurement process shall be tested. These interferents can give a positive or negative response. The test shall be performed at zero and at a test concentration (c_t) similar to the highest numerical limit or target value specified for the pollutant.

The concentration of the mixtures of the test gases with the interferent shall have an uncertainty of less than 5 % and shall be traceable to National Standards, wherever practical. The influence of each interferent shall be determined separately. A correction for the concentration of the measurand shall be made for the dilution effect due to addition of an interferent (e.g. water vapour).

After adjustment of the analyser at zero and 70% to 80% of the maximum of the certification range the analyser shall be fed with a mixture of zero gas and the interferent to be investigated. This mixture will be supplied for a time period equal to one independent measurement, and, following this, three individual measurements will then be taken of the CM's output. This procedure shall be repeated with a mixture of the measurand at concentration c_t and the interferent to be investigated. The influence quantity at zero and concentration c_t are calculated from:

$$Y_{\text{int},z} = y_z \quad (8.21)$$

where

$Y_{\text{int},z}$ = the influence quantity of the interferent at zero;

y_z = the average of the measurements at zero.

and:

$$Y_{\text{int},c_t} = y_{c_t} - c_t \quad (8.22)$$

where

Y_{int,c_t} = the influence quantity of the interferent at concentration c_t ;

y_{c_t} = the average of the measurements at concentration c_t ;

c_t = the concentration of the applied gas at the level of the highest applicable concentration limit value for that pollutant.

The standard uncertainties due to interfering substances, u_{H_2O} and u_{int} , are calculated as follows.

The influence quantity of water vapour is established at a water concentration of 19 mmol/mol, and at a temperature of 20° C \pm 2° C . The uncertainty, however, is to be established at a water concentration of 21.2 mmol/mol. The standard uncertainty due to interference by the presence of water vapour at the highest numerical limit value specified for the pollutant, u_{H_2O} , is therefore calculated according to:

$$Y_{H_2O,z,max} = (21.2 / 19) Y_{H_2O,z} \quad (8.23)$$

$$Y_{H_2O,c_t,max} = (21.2 / 19) Y_{H_2O,c_t} \quad (8.24)$$

$$Y_{H_2O,max} = ((Y_{H_2O,c_t,max} - Y_{H_2O,z,max}) / c_t) \cdot LV + Y_{H_2O,z,max} \quad (8.25)$$

$$u_{H_2O} = \left| Y_{H_2O} / c_{H_2O,max} \right| \cdot \sqrt{(c_{H_2O,max}^2 + c_{H_2O,max} c_{H_2O,min} + c_{H_2O,min}^2) / 3} \quad (8.26)$$

where

$Y_{H_2O,z,max}$ = the influence quantity of an H_2O concentration of 21.2 mmol/mol at zero concentration of the measurand (nmol/mol);

$Y_{H_2O,z}$ = the influence quantity of an H_2O concentration of 19 mmol/mol at zero concentration of the measurand (nmol/mol);

$Y_{H_2O,c_t,max}$ = the influence quantity of an H_2O concentration of 21.2 mmol/mol at the test concentration c_t of the measurand (nmol/mol);

Y_{H_2O,c_t} = the influence quantity of an H_2O concentration of 19 mmol/mol at the test concentration c_t of the measurand (nmol/mol);

Y_{H_2O} = the influence quantity of an H_2O concentration of 21.2 mmol/mol at the hourly limit value (nmol/mol);

c_t = the test gas concentration of the measurand;

LV = the highest numerical limit value specified for the pollutant;

u_{H_2O} = the standard uncertainty due to interference by the presence of water vapour (nmol/mol);

$c_{H_2O,max}$ = the maximum concentration of water vapour (mmol/mol) (= 21.2 mmol/mol);

$c_{H_2O,min}$ = the minimum concentration of water vapour (mmol/mol) (= 6 mmol/mol).

The standard uncertainty due to each interfering compound (other than water vapour) at the highest numerical limit value specified for the pollutant, u_{int} , is calculated according to:

$$Y_{int} = ((Y_{int,c_t} - Y_{int,z}) / c_t) \cdot LV + Y_{int,z} \quad (8.27)$$

$$u_{int} = |Y_{int} / c_{int,max}| \cdot \sqrt{(c_{int,max}^2 + c_{int,max} c_{int,min} + c_{int,min}^2) / 3} \quad (8.28)$$

where

- Y_{int,c_t} = the influence quantity of the maximum concentration of the relevant interfering compound at the test concentration c_t of the measurand;
 $Y_{int,z}$ = the influence quantity of the maximum concentration of the relevant interfering compound at zero concentration of the measurand;
 Y_{int} = the influence quantity of the relevant interfering compound;
 c_t = the test concentration of the measurand at the level of the hourly limit value;
 LV = the highest numerical limit value specified for the pollutant;
 u_{int} = the standard uncertainty due to interference by the presence of a chemical compound;
 $c_{int,max}$ = the maximum concentration of interfering compound;
 $c_{int,min}$ = the minimum concentration of interfering compound.

According to ISO 14956 the summed uncertainties due to the interferents with positive impact and the summed uncertainties of the interferents with negative impact shall be calculated according to:

$$S_{u_{int,pos}} = u_{int,1,pos} + u_{int,2,pos} + \dots + u_{int,n,pos} \quad (8.29)$$

$$S_{u_{int,neg}} = u_{int,1,neg} + u_{int,2,neg} + \dots + u_{int,n,neg} \quad (8.30)$$

Take the highest sum as the representative value for all interferents.

$$u_{int,pos} = \sqrt{(u_{int,1,pos} + u_{int,2,pos} + \dots + u_{int,n,pos})^2} \quad (8.31)$$

$$u_{int,neg} = \sqrt{(u_{int,1,neg} + u_{int,2,neg} + \dots + u_{int,n,neg})^2} \quad (8.32)$$

where

- $u_{int,pos}$ = the sum of uncertainties due to interferents with positive impact;
 $u_{int,1,pos}$ = the uncertainty due to the 1st interferent with positive impact ;
 $u_{int,n,pos}$ = the uncertainty due to the n th interferent with positive impact;
 $u_{int,neg}$ = the sum of uncertainties due to interferents with negative impact ;
 $u_{int,1,neg}$ = the uncertainty due to the 1st interferent with negative impact;
 $u_{int,n,neg}$ = the uncertainty due to the n th interferent with negative impact.

8.4.14 NO₂ converter efficiency

The converter efficiency is determined by measurements with calculated amounts of NO₂. This can be achieved by means of gas-phase titration of NO to NO₂ with ozone.

The test is to be performed at two concentration levels: at 50 % and 95 % of the maximum of the certification range of NO₂.

The NO_x analyser shall be calibrated on the NO and NO_x channel with a NO concentration around 70 % to 80 % of the maximum of the certification range of NO. Both channels shall be set to read the same value and the values shall be recorded.

A known concentration of about 50 % of the maximum of the certification range of NO shall be supplied to the analyser until a stable output signal is achieved. This stabilisation period shall be at least four times the response time of the analyser. Four individual measurements are taken at the NO and NO_x channel. The NO will then be reacted with O₃ to produce the required concentration of NO₂, the NO residue after the gas phase titration reaction shall be 10 % to 20 % of the original NO concentration. This mixture with a constant NO_x concentration shall be supplied to the analyser until a stable output signal is achieved. This stabilisation period shall be at least four times the response time of the analyser.

Four individual measurements are then taken at the NO and the NO_x channel. The O₃ supply shall be switched off and the analyser supplied with only NO until a stable output signal is achieved. This stabilisation period shall be at least four times the response time of the analyser. Then the average of the four individual measurements at the NO and NO_x channel is checked to see whether it is equal within 1 % of the original values.

Repeat the test with a NO test concentration of approximately 95% of the maximum of the certification range of NO₂.

Calculate the converter efficiency from:

$$E_{conv} = \left(1 - \frac{(NO_x)_i - (NO_x)_f}{(NO)_i - (NO)_f} \right) \times 100 \% \quad (8.33)$$

where

- E_{conv} = the converter efficiency in %;
- $(NO_x)_i$ = the average of the four individual measurements at the NO_x channel at the initial NO_x concentration;
- $(NO_x)_f$ = the average of the four individual measurements at the NO_x channel at the resulting NO_x concentration after applying O₃;
- $(NO)_i$ = the average of the four individual measurements at the NO channel at the initial NO concentration;
- $(NO)_f$ = the average of the four individual measurements at the NO channel at the resulting NO concentration after applying O₃.

The lowest value of the two converter efficiencies shall be used to compare with the performance criterion in EN14211 (Table 1). This lowest value shall also be used to calculate the standard uncertainty due to converter efficiency, u_{ce} , according to:

$$u_{ce} = \frac{E_{conv}}{100\sqrt{3}} \cdot LV \quad (8.34)$$

where LV is the highest numerical limit value specified for the pollutant.

8.5 Field test

8.5.1 General

In the field test two CMs of the same type (pattern) are tested for availability (period of unattended operation), between-instrument uncertainty, and long-term drift. The CMs are run in parallel at one and the same sampling point at a selected monitoring station. Operational

requirements are given below for the correct determination of the long-term drift and the between-instrument uncertainty.

One system employing the EN Standard Method will be operated alongside the two CMs, with parallel measurements from one and the same sampling point. From these results any systematic differences between the results obtained by the CM and the Standard Method will be determined.

8.5.2 *Experimental conditions*

Test sites shall be representative for typical conditions for which equivalence will be claimed, including possible episodes of high concentrations. A minimum of 4 comparisons shall be performed with particular emphasis on the following variables, if appropriate:

- Composition of the air, notably high and low concentrations of the measured compound and potential interferents
- Air humidity and temperature (high and low) to cover any effects on sampling efficiency or desorption efficiency
- Wind speed (high and low) to cover any dependency of sampler performance due to deviations from ideal behaviour.

Each comparison shall cover a minimum of one month of uninterrupted monitoring during which hourly-average measurement results shall be collected.

Both methods shall be operated under conditions reflecting practical application in the field, e.g., calibration intervals, appropriate span and zero checks. At the beginning of the test both CMs will be adjusted to read the same value.

During the tests, the following information shall be collected and recorded

- calibration procedures, equipment and intervals
- (results of) quality checks
- temperature and pressure of the sampled air
- other conditions relevant for the measurements performed (e.g., air humidity)
- particular events/situations that may be of influence on measurement results.

8.5.3 *Evaluation of data collected*

8.5.3.1 *Suitability of datasets*

Of the full dataset at least 20% of the results shall be greater than or equal to the upper assessment threshold specified in the relevant Daughter Directive.

Data shall only be removed from the data set when sound technical reasons can be found for doing so. All valid data shall be used for further evaluation.

Note: Indications of outlying data (pairs) may be obtained using Grubb's tests on the individual single-period variances. Outlier tests are to be performed at the 99% level.

8.5.3.2 *Between-instrument uncertainty*

The relative between-sampler/instrument uncertainty defined here as w_{bs} is calculated from the differences of all hourly results of the candidate samplers/instruments operated in parallel as:

$$w_{bs}^2 = \frac{\sum_{i=1}^n (y_{i,1} - y_{i,2})^2}{2ny} \quad (8.35)$$

where

$y_{i,1}$ and $y_{i,2}$ are the results of parallel measurements for a single 1-hour period i

n = number of hourly measurement results

\bar{y} = average of all measurement results of the Candidate Method.

The between-instrument uncertainty shall comply with the relevant criterion given in Annex A.

8.5.3.3 Comparison with the Standard Method

For comparison of the results obtained between the RMs and the CMs, the results of the parallel measurements of the candidate samplers/instruments shall be averaged to give one set of results for x_i and y_i for common measurement periods of equal length.

For the evaluation of the uncertainty due to the 'lack of comparability' (differences in the concentration values measured) between Candidate and Standard Methods it is assumed that the relationship between measurement results of both methods can be described by a linear relation of the form

$$y_i = a + bx_i \quad (8.36)$$

The relation between the average results of the Candidate Method and those of the Standard Method is established using a regression technique that leads to a symmetrical treatment of both variables. A commonly applied technique is orthogonal regression [7,28].

The uncertainty due to lack of comparability will be a function of the concentration of the measurand. The general relationship describing the dependence of u_{C-S} on x_i is given by

$$u_{C-S}^2(y_i) = \frac{RSS}{(n-2)} - u^2(x_i) + [a + (b-1)x_i]^2 \quad (8.37)$$

where

RSS = the sum of (relative) residuals resulting from the orthogonal regression

$u(x_i)$ = random uncertainty of the Standard Method; as such, the value of u_{bs} calculated for the application of the Standard Method in these tests may be used.
(See also the note of equation 7.30)

Algorithms for the calculation of a and b and their variances are given in Annex B.

RSS, the sum of (relative) residuals is calculated using eq. 8.38a or 8.38b, depending on whether the residuals or relative residuals are constant.

$$RSS = \sum_{i=1}^n (y_i - a - bx_i)^2 \text{ when } (y_i - a - bx_i)^2 \text{ is constant} \quad (8.38a)$$

$$RSS = (a + bx_i)^2 \sum_{i=1}^n \left(\frac{y_i}{a + bx_i} - 1 \right)^2 \text{ when } \left(\frac{y_i}{a + bx_i} - 1 \right)^2 \text{ is constant} \quad (8.38b)$$

8.5.3.4 Calculation of the combined 'field' uncertainty to be assigned to the Candidate Method

The combined relative field uncertainty of the Candidate Method $w_{CM,field}$ is calculated as follows:

$$w_{CM,field}^2(y_i) = \frac{u_{C-s}^2(y_i)}{y_i^2} \quad (8.39)$$

The uncertainty at the limit value with the shortest averaging period, $w_{CM,field}$, is calculated by taking as y_i the concentration at the limit value.

8.5.3.4 Calculation of the expanded field uncertainty of Candidate Method

For each of the datasets the expanded relative uncertainty of the results of the Candidate Method is calculated by multiplying $w_{CM,field}$ by a coverage factor k reflecting the appropriate number of degrees of freedom resulting from the determination of $w_{CM,field}$ as

$$W_{CM,field} = k \cdot w_{CM,field} \quad (8.40)$$

In view of the large number of experimental results available, a coverage factor $k=2$ can generally be used.

8.5.3.5 Long-term drift

After each bi-weekly calibration the drift of the analysers under test must be calculated at zero and at span following the procedures as given below. If the drift compared to the initial calibration exceeds one of the performance criteria for drift at zero or span level, the “period of unattended operation” equals the number of weeks till the observation of the infringement, minus two weeks. For uncertainty calculations the values for “long term drift” are the values for zero and span drift over the period of unattended operation.

The long-term drift is calculated as follows:

$$D_{L,z} = (C_{z,2} - C_{z,1}) \quad (8.41)$$

where

$D_{L,z}$ = the drift at zero;

$C_{z,1}$ = the average of five individual zero gas measurements at the beginning of the drift period (just after the initial calibration);

$C_{z,2}$ = the average of five individual zero gas measurements at the end of the drift period (without any mathematical correction applied to the data).

$$D_{L,s} = \frac{(C_{s,2} - C_{s,1}) - D_{L,z}}{C_{s,1}} \times 100\% \quad (8.42)$$

where

$D_{L,s}$ = the drift at span concentration, %;

$C_{s,1}$ = the average of five individual span gas measurements at the beginning of the drift period (just after the initial calibration);

$C_{s,2}$ = the average of five individual span gas measurements at the end of the drift period (without any mathematical correction applied to the data).

The standard uncertainty due to long-term zero drift, u_{zd} , is calculated according to:

$$u_{zd} = \frac{D_{L,z}}{\sqrt{12}} \quad (8.43)$$

The standard uncertainty due to long-term span drift, u_{sd} , is calculated according to:

$$u_{sd} = \frac{\frac{D_{L,s}}{100} LV}{\sqrt{12}} \quad (8.44)$$

where LV is the hourly limit value or the shortest applicable limit value for that pollutant.

Note: although these uncertainty components are determined in the field, they are included in the total uncertainty determined below (equ.8.46) because they represent an important uncertainty component in the practical implementation of the CM.

8.5.3.6 Period of Unattended Operation

The period of unattended operation is the time period within which the drift is within the performance criterion for long term drift. This is evaluated using the procedure in 8.5.3.5 above and should be reported. It is normally at least two weeks, but is dependent on the specific pollutant concerned, and the specific performance criterion in the relevant EN Norm must be conformed with. If the manufacturer specifies a shorter period for maintenance, then this will be taken as the period of unattended operation.

If one of the analysers malfunctions during the field test, then the field test shall be restarted to show whether the malfunction was coincidental or bad design.

8.5.3.7 Period of availability of the analyser

The correct operation of the CM shall be checked at least every 14 days. It is recommended to perform this check every day during the first 14 days. These checks consists of plausibility checks on the measured values, as well as when available status signals and other relevant parameters. Time, duration and nature of any malfunctioning shall be logged.

The total time period with useable measuring data is the period during the field test during which valid measuring data of the ambient air concentrations are obtained. In this time period the time needed for calibrations, conditioning of sample lines, filters and maintenance shall not be included.

The availability of the analyser is calculated as:

$$A_a = \frac{t_u}{t_t} \times 100 \% \quad (8.45)$$

where

A_a = the availability of the CM;

t_u = the total time period with validated measuring data;

t_t = the time period of the field test minus the time for calibration, conditioning and maintenance.

t_u and t_t shall be expressed in the same units (e.g. hours).

The value obtained for A_a shall be compared to the appropriate performance criterion in the relevant EN Norm

8.6 Determination of the combined measurement uncertainty

The standard uncertainties from Table 8.1, where applicable, are combined by the sum of squares method to give the combined standard measurement uncertainty, u_c , according to:

$$u_{CM,lab} = \sqrt{u_z^2 + u_s^2 + u_c^2 + u_l^2 + u_a^2 + u_{av}^2 + u_{H2O}^2 + u_{int}^2 + u_p^2 + u_t^2 + u_{st}^2 + u_v^2 + u_{ce}^2 + u_{zd}^2 + u_{sd}^2} \quad (8.46)$$

The following are CM specific:

- u_z will only be included for continuous measuring CMs;
- u_c will only be included for non-continuous measuring CMs;
- u_{cv} will only be included for NO_x measuring CMs that use a converter to convert NO_x to NO.

From $u_{CN,lab}$, the relative uncertainty at the limit value is calculated as

$$w_{CM,lab} = \frac{u_{CM,lab}}{LV} \quad (8.47)$$

where LV is either the hourly limit value or the shortest-time limit value of the measurand defined in the relevant directive.

8.7 Calculation of the expanded laboratory uncertainty of Candidate Method

The expanded relative 'laboratory' uncertainty of the results of the Candidate Method is calculated by multiplying $w_{CM,lab}$ by a coverage factor k reflecting the appropriate number of degrees of freedom resulting from the determination of $w_{CM,lab}$ as

$$W_{CM,lab} = k \cdot w_{CM,lab} \quad (8.48)$$

In view of the large number of experimental results available, a coverage factor $k=2$ can be used.

8.8 Evaluation of test results

The resulting uncertainty estimates $W_{CM,lab}$ and $W_{CM,field}$ are intercompared and compared with the expanded relative uncertainty based on the data quality objective for the Standard Method W_{dqo} . Here, 3 situations may occur.

1. $W_{CM,lab} > W_{dqo}$: the Candidate Method is not accepted as an equivalent method
2. $W_{CM,lab} \leq W_{dqo}$ and $W_{CM,field} > W_{CM,lab}$: the Candidate Method is accepted conditionally; before final acceptance, the uncertainty evaluation from the laboratory tests should be re-evaluated and corrected such that situation 3 occurs
3. $W_{CM,lab} \leq W_{dqo}$ and $W_{CM,field} \leq W_{CM,lab}$: the Candidate Method is accepted as equivalent to the Standard Method.

9 TEST PROGRAMME 3 – METHODS FOR PARTICULATE MATTER

9.1 General

This test programme describes a procedure for determining whether a Candidate Method (CM) is suitable to be considered equivalent to the EN Standard Method for the measurement of particulate matter in ambient air, using manual or automated measuring systems.

The EN Standard Methods have been developed to meet the Data Quality Objectives of the Daughter Directives of the Air Quality Framework Directive. The CM will also have to meet the directives' requirements, as explained earlier in the main document.

This test programme is suitable to evaluate CM for monitoring the PM₁₀ or PM_{2.5} fraction of total suspended particulates in ambient air. For example, this methodology may be used to evaluate alternative sample inlets, automated methods such as those based on the use of oscillating microbalances or β -ray attenuation. Also other methods, such as in-situ optical methods may be evaluated for application below the upper assessment threshold specified in the relevant Daughter Directive.

9.2 Overview of the test procedure

The EN Standard Methods specify procedures to determine the expanded uncertainty of the method, e.g., by using a 'GUM' approach. This expanded uncertainty was compared with the expanded uncertainty requirement given in the relevant Daughter Directive, and was shown to fulfil this requirement.

Testing for equivalence will normally be carried out in two parts: a laboratory test in which the contributions of the different uncertainty sources to the measurement uncertainty will be assessed, and a field test in which the Candidate Method will be tested side-by-side with the relevant Standard Method.

For methods for particulate matter laboratory tests are only relevant if the CM is a modification of the existing EN Standard Method, in which case the field test will not be required. Generally, the test procedure will consist of a series of field tests in which the Candidate Method is tested side-by-side with the relevant Standard Method. In general, analysis of filter samples for manual methods will be performed by gravimetric measurement of the mass of particulates collected in conformity with the weighing procedures described in refs. [8] and [29].

When testing Candidate Methods based on the use of sample inlets differing from those applied in the EN Standard Methods, a more sensitive test for equivalence consists of the comparison of the filter contents of the soluble fraction of tracer ions that are suitable for the specific cut-off for PM₁₀ or PM_{2.5}, such as calcium, sodium or magnesium (PM₁₀) or sulphate, ammonium or nitrate (PM_{2.5}) [30].

The Candidate Method should be tested in a way that is representative for its practical use; frequencies of tests and re-calibrations used in practice should be applied in the Test Programme.

Results of existing studies, when demonstrably obtained according to the requirements of this test procedure, may be used to determine standard uncertainties. This is particularly relevant to the estimation of between-sampler/instrument uncertainties as described in 9.5. Results from prior studies may be used provided that they are obtained under conditions in accordance with the requirements of 9.4 and fulfill the criteria given in 9.5.

9.3 Laboratory test programme

9.3.1 General

The laboratory test programme is relevant for the following modifications of the Standard Method:

- Application of automated filter changers leading to filter storage conditions deviating from those prescribed in the EN Standard Methods
- Use of different weighing conditions, e.g., conditions deviating from the requirements set in the EN Standard Methods.

9.3.2 Application of automated filter changers

The assessment of the effect of applying automated filter changers shall be assessed as follows.

Worst-case conditions at monitoring sites shall be established. These must reflect the most unfavourable storage temperatures, using both average day and night time temperatures, for the maximum storage time, in situations when significant fractions of semi-volatile materials are expected on the filters. The storage temperature will depend on a combination of the ambient temperature and the effects of both insulation and local sources of heating and cooling. In general, worst-case effects will not be seen at times of continuously high ambient temperatures, but when storage temperatures are higher than those during sampling. In order to identify worst-case conditions both temperatures to which the sampled filters are exposed and ambient temperatures shall be measured.

A minimum of 40 samples shall be collected in conditions known to produce significant fractions of semi-volatile material on the filter.

These samples shall be removed from the sampler and weighed according to the procedure of the EN Standard Method. Subsequently, the samples shall be exposed to the worst-case conditions of time and temperature established, in a temperature-controlled cabinet, and reweighed according to the procedure of the EN Standard Method.

The largest mass loss observed shall be entered into the uncertainty budget as the 'loss due to storage' u_{storage} by conversion assuming a uniform distribution:

$$u_{\text{storage}}^2 = \frac{(\Delta m)^2}{12} \quad (9.1)$$

where

Δm = the largest mass loss observed for a single sample.

9.3.3 Different weighing conditions

The additional uncertainty arising from the use of weighing conditions outside the range specified in the EN Standard Method shall be assessed both for blank filters and for samples. For the latter, worst-case conditions of particulate composition shall be selected, by consideration of the mass of hygroscopic and semi-volatile materials sampled.

A minimum of 5 blank filters, from at least 2 different batches, for each type of filter to be used in the field, shall be investigated. The mass change of the filters between the extremes allowed by the revised conditions, i.e., the limits of high temperature and high relative humidity, and low temperature and low relative humidity, shall be established. The maximum mass change of the filter shall be entered into the uncertainty budget as the difference due to weighing conditions $u_{\text{w,blank}}$ by conversion assuming a uniform distribution:

$$u_{w,blank}^2 = \frac{(\Delta m)^2}{12} \quad (9.2)$$

where

Δm = the largest mass loss observed for a single blank filter.

A minimum of 40 samples shall be collected in conditions known to produce significant effects on filter mass when weighed under the weighing conditions proposed.

These samples shall first be weighed under conditions fulfilling the requirements of the relevant EN Standard Method, and subsequently under the new weighing conditions proposed.

The largest mass difference observed shall be entered into the uncertainty budget as the difference due to weighing conditions $u_{w,sample}$ by conversion assuming a uniform distribution:

$$u_{w,sample}^2 = \frac{(\Delta m)^2}{12} \quad (9.3)$$

where

Δm = the largest mass loss observed for a single sample.

9.4 Field test programme

9.4.1 General

Field tests shall be performed in which Candidate and Standard Method are compared side-by-side. The measurements will serve to assess

- 'between-sampler/instrument' uncertainty of the Candidate Method through the use of two samplers or instruments
- 'comparability' of the Candidate and Standard Methods.

Generally, results of existing studies, when demonstrably obtained according to the requirements of this test procedure, may be used to determine standard uncertainties. This is particularly relevant to the estimation of between-sampler/instrument uncertainties (see also 9.2).

In order to assure proper functioning of the Standard Method, two samplers or instruments may be used. In this case the mean squared difference of the results of both samplers/instruments can be used as an estimate of the (random) uncertainty of the Standard Method for these tests (see 9.6).

9.4.2 Experimental conditions

Test sites shall be representative for typical conditions for which equivalence will be claimed, including possible episodes of high concentrations. A minimum of 4 comparisons shall be performed with particular emphasis on the following variables, if appropriate:

- Composition of the PM fraction, notably high and low fractions of semi-volatile particles, to cover the maximum impact of losses of semi-volatiles
- Air humidity and temperature (high and low) to cover any conditioning losses of semi-volatiles during the sampling process
- Wind speed (high and low) to cover any dependency of inlet performance due to deviations from ideal behaviour as dictated by mechanical design, or deviations from the designated sampling flow rate.

A minimum of 40 measurement results each averaged over at least 24-hour per comparison shall be collected.

Samplers and instruments shall be positioned in such a way that the effect of spatial inhomogeneities of the compound concentration in the sampled air are negligible in comparison with other uncertainty contributions.

Both methods shall be operated under conditions reflecting practical application in the field, e.g., calibration intervals, flow checks, analysis of blank samples.

During the tests, the following information shall be collected and recorded

- calibration procedures, equipment and intervals
- (results of) quality checks
- Temperature and pressure of the sampled air
- Other conditions relevant for the measurements performed (e.g., air humidity)
- Particular events/situations that may be of influence on measurement results.

9.5 Evaluation of data collected

9.5.1 Suitability of datasets

Of the full dataset at least 20% of the results shall be greater than 50% of the limit value specified in the relevant Daughter Directive.

Data shall only be removed from the data set when sound technical reasons can be found for doing so. All valid data shall be used for further evaluation.

Note: Indications of outlying data (pairs) may be obtained using Grubb's tests on the individual single-period variances. Outlier tests are to be performed at the 99% level.

9.5.2 Calculation of performance characteristics

9.5.2.1 Between-sampler/instrument uncertainty

First, the Candidate Method results for each 24-hour measurement period i are averaged for each sampler/instrument to give 24-hour values y_i .

The between-sampler uncertainty u_{bs} is calculated from the differences of all 24-hour results of the candidate samplers/instruments operated in parallel as:

$$u_{bs}^2 = \frac{\sum_{i=1}^n (y_{i,1} - y_{i,2})^2}{2n} \quad (9.4)$$

where

$y_{i,1}$ and $y_{i,2}$ are the results of parallel measurements for a single 24-hour period i

n = number of 24-hour measurement results.

The between-sampler/instrument uncertainty shall be determined

- for each of the comparisons separately
- for all results together
- for two datasets obtained by splitting the full dataset according to PM concentrations: greater than or equal to, or below 50% of the upper assessment threshold specified in the relevant Daughter Directive.

A between-sampler/instrument uncertainty $> 3 \mu\text{g.m}^{-3}$ is an indication of unsuitable performance of one or both samplers/instruments, and equivalence shall not be declared for the Candidate Method when the criterion of between sampler/instrument uncertainty of $\leq 3 \mu\text{g.m}^{-3}$ is not satisfied.

9.5.2.2 Comparison with the Standard Method

First, the performance of the standard samplers/instruments is checked by calculation of the relative between-sampler/instrument uncertainty as in eq. (9.5). The between-sampler/instrument uncertainty for the Standard Method shall be $\leq 2 \mu\text{g.m}^{-3}$.

For a comparison with the Standard Method the results of the parallel measurements of candidate samplers/instruments are averaged to give one result y_i for each 24-hour measurement period.

For the evaluation of the uncertainty due to the 'lack of comparability' between Candidate and Standard Methods it is assumed that the relationship between measurement results of both methods can be described by a linear relation of the form

$$y_i = a + bx_i \quad (9.5)$$

Note: in practice, the actual relationship between measurement results of manual and automated methods may not always be linear.

The relation between the average results of the Candidate Method and the average results of the Standard Method is established using a regression technique that leads to a symmetrical treatment of both variables. A commonly applied technique is orthogonal regression [7,28].

The regression equation is calculated for

- each of the comparisons separately
- for all results together
- for a dataset representing PM concentrations greater than or equal to 50% of the upper assessment threshold specified in the relevant Daughter Directive.

For further evaluation, the uncertainty in the results of the Candidate Method from comparison with the Standard Method, u_{C-S} , is calculated using a general equation describing u_{C-S} as a function of PM concentration x_i . The use of one general equation avoids having to distinguish between 3 different situations when a and/or b differ from 0 and 1, respectively.

The general relationship describing the dependence of u_{C-S} on x_i is given by

$$u_{C-S}^2(y_i) = \frac{RSS}{(n-2)} - u^2(x_i) + [a + (b-1)x_i]^2 \quad (9.6)$$

where

RSS = the sum of (relative) residuals resulting from the orthogonal regression

$u(x_i)$ = random uncertainty of the Standard Method; as such, the value of u_{bs} calculated for the application of the Standard Method in these tests may be used.
(See also note below Eq. 7.30)

Algorithms for the calculation of a and b and their variances are given in Annex B.

RSS, the sum of (relative) residuals is calculated using eq. 9.7.

$$RSS = \sum_{i=1}^n (y_i - a - bx_i)^2 \quad (9.7)$$

The uncertainty u_{C-S} is calculated for

- each of the comparisons separately
- for all results together

- for a dataset extracted from all results representing PM concentrations greater than or equal to 50% of the upper assessment threshold specified in the relevant Daughter Directive.

9.5.3 Calculation of the combined uncertainty to be assigned to the Candidate Method^{*}

For all 7 datasets the combined relative uncertainty of the Candidate Method $w_{c,CM}$ is calculated as follows:

$$w_{c,CM}^2(y_i) = \frac{u_{c,s}^2(y_i)}{y_i^2} \quad (9.8)$$

For each of the datasets the uncertainty at the daily limit value w_{CM} is calculated by taking as y_i the concentration at the limit value.

9.5.4 Calculation of the expanded uncertainty of Candidate Method

For each of the datasets the expanded relative uncertainty of the results of the Candidate Method is calculated by multiplying $w_{c,CM}$ by a coverage factor k reflecting the appropriate number of degrees of freedom resulting from the determination of $w_{c,CM}$ as

$$W_{CM} = k \cdot w_{CM} \quad (9.9)$$

In view of the large number of experimental results available, a coverage factor $k=2$ can be used.

9.6 Evaluation of results of field tests

The highest resulting uncertainty estimate W_{CM} is compared with the expanded relative uncertainty based on the data quality objective for the Standard Method $W_{d,qo}$. In principle, two cases are possible

1. $W_{CM} \leq W_{d,qo}$: the Candidate Method is accepted as equivalent to the Standard Method
2. $W_{CM} > W_{d,qo}$: the Candidate Method is not accepted as Equivalent Method.

9.7 Application of correction factors or terms

When case 2 in Clause 9.6 occurs, it is permitted to apply a correction factor or term resulting from the regression equation obtained for the full dataset. The corrected values obtained shall the satisfy the requirements for all datasets or subsets (see 9.5.2.2).

However, even when the Candidate Method passes the equivalence test (Case 1 in Clause 9.6) a correction may be applied in order to improve the accuracy of the Candidate Method.

With reference to Clause 9.5.2.2, three distinct situations may arise.

1. The slope b is not significantly different from 1: $|b-1| \leq 2 \cdot u(b)$, the intercept a is significantly different from 0: $|a| > 2 \cdot u(a)$.

In this case, the value of intercept a may be used as a term used to correct all input values y_i as follows:

$$y_{i,corr} = y_i - a \quad (9.10)$$

* Both eqs. (9.6) and (9.7) contain an uncertainty component due to the implementation of the Standard Method.

The resulting values of $y_{i,corr}$ may then be used to calculate by linear regression (eq. 9.5) a new relationship to calculate

$$y_{i,corr} = c + dx_i \quad (9.11)$$

$u_{C_R,corr}$ is then calculated as

$$u_{C_S}^2(y_{i,corr}) = \frac{RSS}{(n-2)} - u^2(x_i) + [c + (d-1)x_i]^2 + u^2(a) \quad (9.12)$$

where $u(a)$ = the uncertainty of the original intercept a , the value of which has been used to obtain $y_{i,corr}$ (see Annex B for calculation of $u(a)$). RSS is calculated using eq. (9.13).

$$RSS = \sum_{i=1}^n (y_i - c - dx_i)^2 \quad (9.13)$$

2. The slope b is significantly different from 1: $|b-1| > 2.u(b)$, the intercept a is not significantly different from 0: $|a| \leq 2.u(a)$.

In this case, the value of the slope b may be used as a factor to correct all input values y_i as follows:

$$y_{i,corr} = \frac{y_i}{b} \quad (9.14)$$

The resulting values of $y_{i,corr}$ may then be used to perform a new linear regression to calculate $u_{C_S,corr}$ as

$$u_{C_S}^2(y_{i,corr}) = \frac{RSS}{(n-2)} - u^2(x_i) + [c + (d-1)x_i]^2 + x_i^2 u^2(b) \quad (9.15)$$

where $u(b)$ is the uncertainty of the original slope b , the value of which has been used to obtain $y_{i,corr}$ (see Annex B for calculation of $u(b)$). RSS is calculated using eq. (9.13).

3. The slope b is significantly different from 1: $|b-1| > 2.u(b)$, AND the intercept a is significantly different from 0: $|a| > 2.u(a)$.

In this case, the values of the slope b and the intercept a may be used to correct all input values y_i as follows:

$$y_{i,corr} = \frac{y_i - a}{b} \quad (9.16)$$

The resulting values of $y_{i,corr}$ may then be used to perform a new linear regression to calculate $u_{C_S,corr}$ as

$$u_{C_S}^2(y_{i,corr}) = \frac{RSS}{(n-2)} - u^2(x_i) + [c + (d-1)x_i]^2 + x_i^2 u^2(b) + u^2(a) \quad (9.17)$$

where $u(b)$ is the uncertainty of the original slope b , the value of which has been used to obtain $y_{i,corr}$ (see Annex B for calculation of $u(b)$), and $u(a)$ is the uncertainty of the original intercept a ,

the value of which has been used to obtain $y_{i,corr}$ (see Annex B for calculation of $u(a)$). RSS is calculated using eq. (9.13).

Note: eq. (9.17) is a simplification because it does not include covariance between slope and intercept. The resulting uncertainty may be higher than when a covariance term is included.

The resulting values for $u_{C_S,corr}$ can then be entered in eq.(9.8) to calculate the combined relative uncertainty of the Candidate Method after correction as

$$w_{c,CM,corr}^2 = \frac{u_{C_S,corr}^2(y_i)}{y_i^2} \quad (9.18)$$

and the expanded relative uncertainty $W_{CM,corr}$ as

$$W_{CM,corr} = k \cdot w_{CM,corr} \quad (9.19)$$

$W_{CM,corr}$ can then be re-evaluated as in Clause 9.6.

9.8 Examples

In annex D some examples are given of results of equivalence testing for AMS for particulate matter according to the above procedures.

9.9 Ongoing QA/QC of the Equivalent Method

There is a requirement for ensuring the ongoing quality of the particulate measurement results obtained using the Equivalent Method. This is particularly important because the equivalence procedure depends on only field tests between the Standard and Equivalent Method, and there is limited QA/QC that can be carried out on a routine basis (flow calibration). In addition, the equivalence tests were necessarily carried out under a limited range of particulate compositions, which may not continue to be representative for the actual conditions. Therefore, it may be necessary that periodic side-by-side comparisons are carried out between the Standard and the Equivalent Methods at the sites where it is judged that the particulate composition is no longer representative of that during the equivalence tests.

10 TEST PROGRAMME 4 – SPECIATED PARTICULATE MATTER

10.1 General

This test programme describes a procedure for determining whether a Candidate Method (CM) is suitable to be considered equivalent to the EN Standard Method for the measurement of speciated substances in particulate matter in ambient air. The EN Standard Methods have been developed to meet the Data Quality Objectives of the Air Quality Framework Directive and its Daughter Directives. Therefore CM will similarly have to meet the directives' requirements, as explained earlier in the main document.

This test programme is suitable to evaluate CM for monitoring metals and PAH.

For example, this methodology may be used to evaluate the alternative analytical technique of inductive-coupled plasma – optical emission spectrometry for the measurement of metals or capillary electrophoresis for the measurement of benz[a]pyrene. Where only a small part of the method has been changed (variation on a theme such as a different extraction technique), then only the part of the method that is different needs to be investigated, by the laboratory tests detailed below.

10.2 Overview of the test procedures

The EN Standard Methods specify procedures to determine the expanded uncertainty of the method from the components performance criteria obtained during tests. This expanded uncertainty was compared with the expanded uncertainty criterion given in the relevant (proposed) Daughter Directive, and was shown to be within the required performance of the method with respect to the Directives' requirements.

Testing for equivalence will normally be carried out in two parts: a laboratory test in which the contributions of the different uncertainty sources to the measurement uncertainty will be assessed, and a field test in which the Candidate Method will be tested side-by-side with the relevant Standard Method.

If a CM is a modification to an existing EN Standard Method, then only the laboratory performance characteristics that are affected by the modification shall be tested and their standard uncertainties calculated. The standard uncertainties associated with the affected performance characteristics shall then be used together with these existing standard uncertainties for the other characteristics, to determine a new standard combined measurement uncertainty, u_c .

If a CM utilises a measurement method that is different to the Standard Method, then all of the tests shall be performed.

In both cases the results of existing studies, when demonstrably obtained according to the requirements of this test procedure, may be used to determine standard uncertainties.

The CM should be tested in a way that is representative for its practical use; frequencies of tests (e.g., response drift) and re-calibrations (e.g., flow rates) used in practice should be applied in the test programmes).

10.3 Laboratory Test Programme

10.3.1 General

In the laboratory test programme, the uncertainty sources listed in Table 3 are considered and assessed.

Table 3. Laboratory Test Programme 4: Uncertainty sources

Uncertainty source	Symbol
1 Mass of compound in sample	m_{sam}
1.2 Compound stability	A
1.3 Extraction/desorption efficiency	D
1.4 Mass of compound in calibration standards	m_{CS}
1.5 Response factors	F
1.5.1 lack-of-fit of calibration function	
1.5.2 analytical repeatability	
1.5.3 drift between calibrations	
1.6 Selectivity	R
2 Mass of compound in blank	m_{bl}

The uncertainty sources that require assessment depend on the differences between Candidate and Standard Methods as follows:

Is the Candidate Method based on a different measurement principle?

In that case, the full TP needs to be performed.

Is the Candidate Method a modification of the Standard Method ?

In this case, the uncertainty sources relevant to the modification need to be investigated, e.g.

- 1.3 and 1.6 for alternative extraction solvents
- 1.5 and 1.6 for alternative analytical configurations.

10.3.2 Test programme

10.3.2.1 Mass of compound sampled

The mass of a compound sampled may be expressed as

$$m_{sam} = \frac{m_{meas}}{E \cdot A \cdot D} \quad (10.1)$$

where

E = sampling efficiency

A = compound stability in the sample

D = extraction/desorption efficiency

m_{meas} = mass of compound measured in the analytical sample (extract, desorbate).

A correction for extraction/desorption efficiency is only applied when D is significantly different from 1 (see 10.3.2.1.3).

10.3.2.1.1 Sampling efficiency

For the purpose of this Test Programme the sampling efficiency is considered to be a part of the sampling procedure and, hence, is not dealt with. There may be problems, for example due to losses or degradation of compounds (e.g., benz[a]pyrene), but these will not affect the equivalence of the part(s) of the method under consideration in this Test Programme.

10.3.2.1.2 Compound stability

The compound stability shall be experimentally established for storage under conditions (time, temperature, environment) typical to the individual laboratory.

Tests shall be performed at a compound level corresponding to the ambient air limit or target value.

At times $t=0$ and $t=t$, n samples each shall be analyzed under repeatability conditions ($n \geq 6$). For both times the samples shall be randomly picked from a batch of representative samples in order to minimize possible systematic concentration differences. As a test of (in)stability a t-test will be performed (95% confidence, 2-sided). The t-test must show no significant difference between the start and end of the stability test.

The uncertainty of the stability determination consists of contributions from

- extraction/desorption (random part of extraction/desorption efficiency)
- calibration (random part of calibration)
- analytical precision
- inhomogeneity of the sample batch.

As such, the contribution of the determination of stability will already be incorporated in other contributions and needs not to be taken into account in the uncertainty.

10.3.2.1.3 *Extraction/desorption efficiency*

The extraction/desorption efficiency of the compound from the sample and its uncertainty are typically obtained from replicate measurements on Certified Reference Materials (CRM). For metals and benz[a]pyrene no CRM exist that are representative for the samples obtained; in the absence of such CRM, NIST SRM for total suspended particulates may be used to evaluate extraction efficiency. A minimum of 6 replicate measurements shall be performed.

The uncertainty due to incomplete extraction/desorption for the level corresponding to the limit value is calculated from contributions of

- the uncertainty in the concentration of the CRM
- the standard deviation of the mean mass determined

as

$$\frac{u^2(D)}{D^2} = \frac{u^2(m_{CRM}) + \frac{s^2(m_D)}{n}}{m_{CRM}^2} \quad (10.2)$$

where

m_{CRM} = certified mass in the CRM

$s(m_D)$ = standard deviation of the replicate measurement results of the mass determined

n = the number of replicate measurements of the CRM.

When D is significantly different from 1 (at the 95% confidence level), the measurement result shall be corrected accordingly (see eq. (10.1)).

The value of $s(m_D)$ is used as an indicator of the relative uncertainty due to analytical repeatability w_{anal} :

$$w_{anal}^2 = \frac{s^2(m_D)}{m_D^2} \quad (10.3)$$

10.3.2.1.4 *Measured mass of compound*

The uncertainty in the measured mass of a compound determined by

- the uncertainty in the concentrations of the calibration standards used
- the lack-of-fit of the calibration function

- drift of detector response between calibrations
- the precision of the analysis
- the selectivity of the analytical system used.

Calibration standards

The calibration standards used will consist of solutions of the analyte; the uncertainty in the concentrations will be built up of contributions from

- the purity of the compound used; as the compounds under study are generally available in purities > 99%, the contribution of the purity may be considered insignificant
- when gravimetry is used to prepare the calibration solutions: the uncertainties in the weighings of compounds and solutions
- when volumetric techniques are used to prepare the calibration solutions: the uncertainties in the calibrated volumes of glassware and syringes used.

Note: Examples of calculations of uncertainties can be found in ref. [21].

Lack-of-fit of calibration function

The relative uncertainty due to lack-of-fit of the calibration function can be calculated for the relevant concentration (corresponding to the mass of benzene sampled at the limit value) from parameters obtained by a least-squares linear regression ($r = a + b \cdot m_{cs}$), weighted in the concentration of the calibration standard.

Note: Options for the calculation of the uncertainty are given in ref. [21], Appendix E3 (equations E3.3 to E3.6).

As a worst-case approach, the relative uncertainty shall be estimated as

$$w_F^2 = \frac{u^2(m_r)}{m_r^2} = \frac{u^2(r) + s^2(a) + s^2(b)m_r^2}{b^2 m_r^2} \quad (10.4)$$

where

m_r = mass calculated from the regression equation at response r

$u(r)$ = uncertainty in the response r

b = slope of calibration function

a = intercept of calibration function

s = standard deviation of parameter between parentheses.

Response drift between calibrations

Normally, the current response factor will be used until a new one is established. In the interval between the re-establishment of its uncertainty, response checks – and, when necessary, adjustments of response factors - shall be performed as an element of ongoing quality control.

In the interval before the next checks response drift may occur. The relative uncertainty due to response drift for the period between subsequent adjustments of response factors shall then be estimated from the relative differences in responses between subsequent checks, as

$$w_d^2 = \frac{(r_n - r_{n-1})^2}{3 \left(\frac{r_n + r_{n-1}}{2} \right)^2} \quad (10.5)$$

where r_n is the detector response for a calibration standard corresponding closest to the mass representing a sample at the limit value. This approach assumes that no correction is applied for response drift, e.g., by averaging of subsequently determined response factors.

Selectivity

The analytical system used shall be optimized in order to minimize uncertainty due to the presence of potential interferents. Tests shall be performed with typical interferents at levels corresponding to 5 times the limit value of the compound under study. The uncertainty due to interferences may be obtained from ISO 14956 [23] as

$$w_R^2 = \frac{(r_+ - r_0)^2}{3r_0^2} \quad (10.6)$$

where r_+ represents the response with interferent, and r_0 represents the response without.

10.3.2.1.5 Combined uncertainty in the sampled mass

The contributions given above are combined to give the uncertainty of the mass of compound in the air sample as

$$\frac{u^2(m_{sam})}{m_{sam}^2} = \frac{u^2(m_{cs})}{nm_{cs}^2} + w_{anal}^2 + w_F^2 + w_d^2 + w_R^2 \quad (10.7)$$

where

n = number of calibration standards used to construct the calibration function (≥ 5)

w_R = relative uncertainty due to (lack of) selectivity of the analytical system.

10.3.2.2 Mass of compound in sample blank

The mass of compound in a sample blank is determined by analysis under repeatability conditions of a series of sample blanks; a minimum of 6 replicate analyses should be performed. The uncertainty is then calculated using the slope of the calibration function extrapolated to the blank response level as

$$u^2(m_{bl}) = \frac{s_{bl}^2}{nb_{bl}} \quad (10.8)$$

where

s_{bl} = standard deviation of the replicate blank analyses

n = number of replicate analyses

b_{bl} = slope of the calibration function at the blank response level.

When the blank response is below 3 times the noise level of the detector, then the blank level and its uncertainty shall be calculated from the detector noise level using the slope of the calibration function extrapolated to zero response assuming a uniform distribution as

$$m_{bl} = \frac{3r_0}{2b_0} \quad (10.9)$$

$$u^2(m_{bl}) = \frac{9r_0^2}{12} \quad (10.10)$$

where

r_0 = noise level

b_0 = slope of calibration function at zero response.

10.3.2.3 Combined uncertainty

The combined relative uncertainty of the compound mass in the air sampled is obtained by combination of contributions given in Clauses 10.3.2.1 – 10.3.2.2 as

$$w_{CM,lab}^2 = \frac{u_{lab}^2(m)}{m^2} = \frac{u^2(m_{sam}) + u^2(m_{bl})}{(m_{sam} - m_{bl})^2} \quad (10.11)$$

10.2.3.4 Expanded uncertainty

The expanded relative uncertainty of the Candidate Method resulting from the laboratory experiments, $W_{CM,lab}$ at the 95% confidence level is obtained by multiplying $w_{CM,lab}$ with a coverage factor appropriate to the number of degrees of freedom resulting from the performance of the test programme. This can be calculated by applying the Welch-Satterthwaite equation (ISO-GUM, H2). For a large number of degrees of freedom, a coverage factor of 2 is used.

Note: as a first approximation, the number of degrees of freedom may be based on that of an uncertainty contribution covering more than 50% of the variance budget.

10.3.2.5 Evaluation of results of the laboratory tests

The resulting $W_{CM,lab}$ is compared with the expanded relative uncertainty based on the data quality objective for the Standard Method W_{dgo} .

If $W_{CM,lab} \leq W_{dgo}$, the field test programme can be performed; if not, the Candidate Method shall first be improved, and relevant changes tested in the laboratory test programme.

10.4 Field test programme

10.4.1 General

When required, field tests shall be performed in which Candidate and Standard Method are compared side-by-side. The measurements will serve to assess

- 'between-sample' uncertainty of the Candidate Method through the use of replicate samples
- 'comparability' of the Candidate and Standard Methods.

For constituents of particulate matter, the sampling is not a part of the equivalence testing. Therefore, sub-samples from high-volume samples with different loadings may be used to obtain the required information. In principle, 8 or more sub-samples may be obtained from one high-volume sample and the homogeneity of compound loadings on the sub-samples has been demonstrated for benz[a]pyrene [31] to be better than < 4 % (coefficient of variation) when applying the Standard Method.

In order to assure proper functioning of the Standard Method, a minimum of two samples shall be analyzed by application of the Standard Method.

The number of replicate samples needed to determine the between-sampler uncertainty of the Candidate Method (Standard Method) will depend on whether the Candidate Method is to be used by more than one laboratory. When used by one laboratory, a minimum of six sub-samples will be analyzed using the Candidate Method.

When used by more than one laboratory, the field test is also used to assess between-laboratory contributions to the uncertainty of the measurement results. For this purpose, each laboratory will analyze a minimum of two samples using the Candidate Method.

10.4.2 Experimental conditions

Samples shall be representative of typical conditions for which equivalence will be claimed, including possible episodes of high concentrations. A minimum of 4 comparisons shall be performed with particular emphasis on the following variables, if appropriate:

- Composition of the air, notably high and low concentrations of the measured compound and potential interferences
- Air humidity and temperature (high and low) to cover any effects on extraction efficiency.

For the Candidate Method a minimum of 20 different high-volume samples per comparison – to be divided into 8 sub-samples each - shall be collected. Alternatively, a minimum of 160 samples obtained using a low-volume Standard sampler may be used.

Samplers and instruments shall be positioned in such a way that the effect of spatial inhomogeneities of the compound concentration in the sampled air are negligible in comparison with other uncertainty contributions.

Both methods shall be operated under conditions reflecting practical application in the field, e.g., calibration intervals, response checks, analysis of blank samples.

During the tests, the following information shall be collected and recorded

- Calibration procedures, equipment and intervals
- (Results of) quality checks
- Other conditions relevant for the analyses performed.

10.4.3 Evaluation of test results

10.4.3.1 Suitability of the dataset

Of the full dataset, at least 20% of the results shall be greater than or equal to the upper assessment threshold specified in the relevant (currently proposed) Daughter Directive.

Data shall only be removed from the data set when sound technical reasons can be found for doing so. All valid data shall be used for further evaluation.

Note: Indications of outlying data within replicate sets may be obtained using Grubb's tests on the individual single-period variances. Tests are to be performed at the 99% level.

10.4.3.2 Calculation of performance characteristics

10.4.3.2.1 Between-sampler/instrument uncertainty

The relative between-sample uncertainty for individual laboratories w_{bs} is calculated for the full dataset from the differences of results of the candidate samplers/instruments operated in parallel as:

$$w_{bs}^2 = \frac{\sum_{i=1}^n (y_{i,1} - y_{i,2})^2}{2ny^2} \quad \text{for duplicate samples} \quad (10.12)$$

where

$y_{i,1}$ and $y_{i,2}$ are the results of parallel measurements for a single period i

\bar{y} = average of all measurement results of the Candidate Method

n = number of measurement results.

$$w_{bs}^2 = \frac{\sum_{i=1}^n \sum_{j=1}^p (y_{i,j} - \bar{y}_i)^2}{n(p-1)\bar{y}^2} \text{ for replicate samplers with } p > 2 \quad (10.13)$$

where

y_{ij} = result of measurement j for a single period i

\bar{y}_i = mean result for period i

p = number of replicates for period i .

When more than one analytical laboratory is participating, equation 10.13 shall be used to calculate the between-laboratory w_{bs} .

The w_{bs} between sampler uncertainty component for each individual laboratory and the between-laboratory w_{bs} (if relevant) shall comply with the criteria given in Annex A.

If the performance of a single laboratory causes a method implemented by more than two laboratories to fail the criteria, then the results for this laboratory may be excluded, if sound technical grounds exist for doing so.

10.4.3.2.2 Comparison with Standard Method

First, the performance of the Standard samplers/instruments is checked by calculation of the relative between-sampler/instrument uncertainty as in eq. (10.12) or (10.13). The relative between-sampler/instrument uncertainty for the Standard Method shall be $\leq 4\%$.

For a comparison with the Standard Method first the results of replicate measurements are averaged to give data pairs 'Candidate Method – Standard Method' with equal measurement periods.

For the evaluation of the uncertainty due to the 'lack of comparability' between Candidate and Standard Method it is assumed that the relationship between measurement results of both methods can be described by a linear relation of the form:

$$y_i = a + bx_i \quad (10.14)$$

where x_i is the average result of the Standard Method over period i .

The relation between the average results of the Candidate Method and those of the Standard Method is established for the full dataset using a regression technique that leads to a symmetrical treatment of both variables. A commonly applied technique is orthogonal regression [7,28].

The uncertainty due to lack of comparability will be a function of the concentration of the measurand.

The general relationship describing the dependence of u_{C-S} on x_i is given by

$$u_{C-S}^2(y_i) = \frac{RSS}{(n-2)} - u^2(x_i) + [a + (b-1)x_i]^2 \quad (10.15)$$

where

RSS = the sum of (relative) residuals resulting from the orthogonal regression

$u(x_i)$ = random uncertainty of the Standard Method; as such, the value of u_{bs} calculated for the application of the Standard Method in these tests may be used.
(See also note below Eq.7.30)

Algorithms for the calculation of a and b and their variances are given in Annex B.

RSS, the sum of (relative) residuals is calculated using eq. 10.16a or 10.16b, depending on whether the residuals or relative residuals are constant.

$$RSS = \sum_{i=1}^n (y_i - a - bx_i)^2 \text{ when } (y_i - a - bx_i)^2 \text{ is constant} \quad (10.16a)$$

$$RSS = (a + bx_i)^2 \sum_{i=1}^n \left(\frac{y_i}{a + bx_i} - 1 \right)^2 \text{ when } \left(\frac{y_i}{a + bx_i} - 1 \right)^2 \text{ is constant} \quad (10.16b)$$

10.4.3.3 Calculation of the combined uncertainty of Candidate Method

The combined relative uncertainty of the Candidate Method $w_{c,CM}$ is calculated as follows:

$$w_{c,CM}^2(y_i) = w_{bs}^2 + \frac{u_{c-s}^2(y_i)}{y_i^2} \quad (10.17)$$

In this way, $w_{c,CM}$ is expressed as a function of the compound concentration.

The uncertainty at the limit value w_{CM} is calculated by taking as y_i the concentration at the limit value.

10.4.3.4 Calculation of the expanded uncertainty of Candidate Method

The expanded relative uncertainty of the results of the Candidate Method is calculated by multiplying $w_{c,CM}$ by a coverage factor k reflecting the appropriate number of degrees of freedom resulting from the determination of $w_{c,CM}$ as

$$W_{CM,field} = k \cdot w_{c,CM} \quad (10.18)$$

In view of the large number of experimental results available, a coverage factor $k=2$ can be used.

10.4.4 Evaluation of results of field tests

The resulting uncertainty estimate $W_{CM,field}$ is compared with the expanded relative uncertainty obtained from the laboratory test programme $W_{CM,lab}$ and the expanded relative uncertainty based on the data quality objective for the Standard Method W_{dgo} .
In principle, three cases are possible

1. $W_{CM,field} \leq W_{CM,lab}$: the Candidate Method is accepted as equivalent to the Standard Method
2. $W_{CM,lab} < W_{CM,field} \leq W_{dgo}$: the Candidate Method is accepted conditionally; before final acceptance, the uncertainty evaluation from the laboratory tests should be revisited and corrected such that situation 1 occurs
3. $W_{CM,field} > W_{dgo}$: the Candidate Method is not accepted as Equivalent Method.

11 REPORTING REQUIREMENTS

Final reports on the Demonstration of Equivalence submitted to the Competent Authority and further to the European Commission should contain – at minimum – the following information.

Title of the method

Executive summary

General information

1. A summary of the principles of the Candidate Method; the full Standard Operating Procedure of the method, including a description of ongoing QA/QC, shall be annexed.
2. The scope of equivalence testing, i.e., the differences between the Candidate Method and the Standard Method that require specific tests to be performed.
3. A description of the conditions for which equivalence with the Reference Method is claimed, e.g., concentration range, environmental conditions, type of location.
4. Sources of uncertainty data for unchanged parts of the EN Norms enacting the Reference Method, where relevant.
5. Names of the laboratories involved in the test programme(s) and the scope of their relevant competences, e.g., ISO 17025 accreditation.

Laboratory test programme (where applicable)

6. The parameters tested in the laboratory programme.
7. A description of the test procedures used, including procedures for the establishment and maintenance of measurement traceability where relevant, and procedures for quality control and quality assurance.
8. The test results, the results of the uncertainty assessment, and the results of their comparison with the relevant Data Quality Objectives including uncertainty or, in the absence of Data Quality Objectives, the results of the comparison between Candidate Method and Standard Method.

Field test programme (where applicable)

9. Full description of the test locations, test periods and conditions (e.g. temperature, humidity, wind velocity, concentration level)
10. A description of the equipment and test procedures used, including procedures for the establishment and maintenance of measurement traceability where relevant, and procedures for quality control and quality assurance.
11. The test results, the results of the uncertainty assessment, and the results of their comparison with the relevant Data Quality Objectives including uncertainty, or, in the absence of Data Quality Objectives, the results of the comparison between Candidate Method and Standard Method.

Conclusions

12. Results of the overall testing of the performance of the Candidate Method as compared to the Data Quality Objectives specified in the relevant EU 'Daughter Directive'
13. The overall conclusion about the equivalence including restrictions, if any, in the conditions under which the claim to equivalence is valid or generalizations of the equivalence claim to other relevant conditions. Relevant conditions include concentration ranges, meteorological conditions, geographical locations and/or type(s) of monitoring sites.

12 REFERENCES

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ANNEX A

Table A1. Criteria for between-sampler/instrument and between-laboratory uncertainties for specified compounds

<i>Compound</i>	<i>Required Standard Uncertainty (%) *</i>	<i>Between-sampler/ instrument (%)</i>	<i>Between lab (%)</i>
Sulphur dioxide	7.5	5	5
Nitrogen dioxide	7.5	5	5
Ozone	7.5	5	5
Carbon monoxide	7.5	5	5
Benzene	12.5	3	7.5
Benz[a]pyrene	25	4	15
Nickel	20	5	12.5
Cadmium	20	5	12.5
Lead	12.5	4	7.5
Arsenic	20	5	12.5

* 50% of the data-quality objective expanded uncertainty for continuous or fixed measurements as specified in relevant (proposed) Daughter Directives.

ANNEX B

Algorithms for the calculation of orthogonal regression parameters.

Regression equation: $y = a + b \cdot x$

Slope b:

$$b = \frac{Syy - Sxx + \sqrt{(Syy - Sxx)^2 + 4(Sxy)^2}}{2Sxy}$$

Where:

$$Sxx = \sum (x_i - \bar{x})^2$$

$$Syy = \sum (y_i - \bar{y})^2$$

$$Sxy = \sum (x_i - \bar{x}) \cdot (y_i - \bar{y})$$

$$\bar{x} = 1/n \sum x_i$$

$$\bar{y} = 1/n \sum y_i$$

Intercept a:

$$a = \bar{y} - b \cdot \bar{x}$$

The uncertainties of the slope and intercept (for corrections to PM Candidate Methods):

$$u^2(b) = \frac{Syy - ((Sxy)^2 / Sxx)}{(n-2) \cdot Sxx}$$

$$u^2(a) = u^2(b) \frac{\sum x^2}{n}$$

ANNEX C

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ANNEX D

EXAMPLES OF RESULTS OF EQUIVALENCE TESTING FOR AMS FOR PARTICULATE MATTER

Introduction

This annex contains some examples of results of equivalence testing for automated methods for measurement of PM_{2.5}, and PM₁₀, performed using the algorithms given in Clause 9.5-9.7. In these assessments, a limit value for PM_{2.5} of 35 µg.m⁻³ has been assumed following a recommendation in the Second Position paper on Particulate Matter.

The measurement data used for PM_{2.5} were taken from the validation study carried out by CEN TC 264 WG 15. This annex gives three examples:

- One in which the CM for one location fulfills the requirements for equivalence but may still be improved in accuracy by correction of its results
- One in which the CM for one location does not fulfill the requirements until after correction
- One in which correction of results for one location improve the comparability, but does not lead to acceptance of the CM as an Equivalent Method.

The measurement data used for PM₁₀ were supplied by the Landesumweltamt Nordrhein-Westfalen – LUA-NRW (Germany).

Using the algorithms presented in Clause 9.5 it is relatively easy to judge whether corrections may lead to an improvement beyond meeting the equivalence requirements: unless the slope *b* of the regression equation obtained for uncorrected results is high, a random uncertainty above 12,5% of the limit value concentration (about 4,4 µg.m⁻³ for PM_{2.5} ; about 6,3 µg.m⁻³ for PM₁₀) is an indication that corrections will generally fail to bring the required improvement because of excessive scatter of the results of the Standard and Candidate Methods when compared using regression, unless the slope of the regression equation is considerably higher than 1.

It should be noted that for PM_{2.5} the between-sampler uncertainty for the Standard Method has been calculated from the data actually available from the validation study.

For PM₁₀ a between-sampler uncertainty for the Standard Method of 1,5 µg.m⁻³ has been assumed, based on information supplied by LUA-NRW.

Examples of results – PM_{2.5}

Comparison of CM1 and RM1 – location A

Full dataset (µg.m⁻³, uncorrected)

RM1,1	RM1,2	CM1	RM1,1	RM1,2	CM1	RM1,1	RM1,2	CM1	RM1,1	RM1,2	CM1
20.2	21.4	18.4	18.8	22.0	24.9	15.3	15.4	19.6	19.9	20.5	23.7
15.1	16.5	15.9	17.7	18.4	20.8	22.3	21.7	26.4	22.3	24.2	26.0
17.8	16.8	20.0	17.6	19.0	18.2	22.7	24.2	26.4	25.4	25.8	25.1
20.1	19.3	21.8	23.4	23.5	21.8	22.3	22.5	26.4	20.4	21.5	21.2
24.6	26.7	29.2	23.5	24.3	24.0	19.7	21.3	25.0	18.4	17.8	20.2
30.3	29.9	37.0	17.0	17.0	21.2	17.3	17.9	23.5	19.4	19.8	22.8
24.0	24.2	27.7	16.9	17.1	19.5	23.2		26.0	35.9	37.3	42.2
21.2	21.4	23.4	26.4	27.7	37.9	24.4	25.2	27.2	23.5	24.6	29.2
19.4	20.8	23.3	27.4	28.6	29.5	17.6	17.2	22.4	25.8	26.0	30.8
22.3	21.9	22.7	34.0	36.1	31.8	10.0	10.8	14.9	12.4	12.9	18.0
14.9	15.5	17.0	25.7	26.2	28.1	21.5	26.8	26.7		11.8	15.6
13.2	12.5	15.7	29.3	31.1	31.8	13.5	13.8	12.7	10.7	11.2	15.8
11.0	12.4	12.7	19.2	19.9	22.9	7.8	8.1	9.8	12.6	13.2	17.4
12.1	13.0	14.6	28.2	30.6	28.9	13.5	13.2	16.6			
15.8	16.5	20.5	10.9	11.9	16.0	20.6	21.2	24.0			

Evaluation of uncorrected data for CM1

RESULTS OF REGRESSION		EQUIVALENCE TEST RESULTS	
slope b	0.96	random term	1.89 µg/m ³
uncertainty of b	0.05	bias at LV	-3.32 µg/m ³
intercept a	-1.83	combined uncertainty	3.82 µg/m ³
uncertainty of a	1.13	relative uncertainty	10.9% pass
number of datapairs	58	RM between-sampler uncertainty	1.35 µg/m ³

Evaluation of data for CM1 after correction for intercept

RESULTS OF REGRESSION		EQUIVALENCE TEST RESULTS	
slope b	0.96	random term	2.20 µg/m ³
uncertainty of b	0.05	bias at LV	-1.50 µg/m ³
intercept a	0.00	combined uncertainty	2.66 µg/m ³
uncertainty of a	1.13	relative uncertainty	7.6% pass
number of datapairs	58	RM between-sampler uncertainty	1.35 µg/m ³

Comparison of CM2 and RM1 – location B

Full dataset ($\mu\text{g.m}^{-3}$, uncorrected)

RM1,1	RM1,2	CM2	RM1,1	RM1,2	CM2	RM1,1	RM1,2	CM2	RM1,1	RM1,2	CM2
18.5	17.5	15.7	11.1	11.2	6.2	48.9	48.5	44.0	56.0	56.0	51.2
24.5	25.5	18.4	12.3	12.3	8.9	40.9	40.0	34.4	18.4	19.5	15.3
43.8	43.1	41.5	27.7	27.4	21.4	47.1	47.1	42.4	62.7	62.3	55.7
45.4	45.1	45.3	40.6	41.6	34.4	32.1	33.1	27.3	58.2	59.4	54.0
40.3	40.1	35.9	16.6	16.1	13.6	41.0	41.0	37.7	50.7	48.9	47.2
34.4	32.2	25.7	17.7	16.5	11.1	37.0	36.8	33.3	6.9	6.8	4.0
39.4	38.5	33.1	38.9	38.3	34.0	66.3	67.2	61.4	16.9	16.8	13.1
46.0	46.0	39.0	31.4	30.5	25.4	58.3	56.6	53.3	46.2	45.6	42.4
69.5	68.3	65.1	42.6	41.7	36.0	33.0	31.7	28.3	38.6	35.9	34.5
55.2	54.9	49.9	55.1	53.9	52.3	22.4	22.1	18.6	69.7	69.9	67.8
59.5	59.6	62.0	24.6	24.7	20.0	59.5	59.2	55.3	69.0	68.5	62.7
65.4	67.5	60.1	31.8	31.9	30.8	64.2	63.1	61.1	70.8	70.8	64.3
58.4	58.4	51.2	22.6	23.3	17.7	46.7	45.2	42.1	25.2	25.3	21.2
48.1	48.3	47.2	6.2	6.9	1.6	25.4	25.2	19.5	6.2	6.9	1.8
28.1	31.0	22.2	6.8	7.4	3.2	31.1	30.5	26.3	13.9	13.4	6.6
25.6	24.7	25.9	14.5	15.5	10.0	38.8	38.0	33.3	13.5	13.6	11.0
19.5	19.0	13.3	39.2	38.8	34.7	38.2	39.2	33.7	27.0	25.6	21.3
43.3	42.3	36.3	46.9	47.8	41.1	45.7	45.3	43.4	39.7	39.7	34.0
42.7	42.1	37.0	34.3	33.6	27.4	73.7	72.4	69.8	12.5	12.1	5.7
29.0	28.7	23.3	15.6	14.9	9.0	55.4	55.8	52.6	17.0	16.5	12.1
30.7	29.5	25.1	35.0	34.1	30.7	50.0	50.0	46.3	9.9	9.9	7.1
13.0	12.3	6.9	54.4	54.3	49.5	54.1	52.5	46.5			

Evaluation of uncorrected data for CM2

RESULTS OF REGRESSION		EQUIVALENCE TEST RESULTS	
slope b	1.01	random term	1.29 $\mu\text{g/m}^3$
uncertainty of b	0.01	bias at LV	-4.51 $\mu\text{g/m}^3$
intercept a	-4.91 *	combined uncertainty	4.69 $\mu\text{g/m}^3$
uncertainty of a	0.46	relative uncertainty	13.4% fail
number of datapairs	87	RM between-sampler uncertainty	1.35 $\mu\text{g/m}^3$

* Significant at 95% confidence level.

Evaluation of data for CM2 after correction for intercept

RESULTS OF REGRESSION		EQUIVALENCE TEST RESULTS	
slope b	1.01	random term	1.38 $\mu\text{g/m}^3$
uncertainty of b	0.01	bias at LV	0.40 $\mu\text{g/m}^3$
intercept a	0.00	combined uncertainty	1.43 $\mu\text{g/m}^3$
uncertainty of a	0.46	relative uncertainty	4.1% pass
number of datapairs	87	RM between-sampler uncertainty	1.35 $\mu\text{g/m}^3$

Comparison of CM1 and RM1 – location C

Full dataset ($\mu\text{g.m}^{-3}$, uncorrected)

RM1,1	RM1,2	CM1	RM1,1	RM1,2	CM1	RM1,1	RM1,2	CM1	RM1,1	RM1,2	CM1
14.8	15.1	12.4	33.0	34.8	16.1	16.9	17.0	13.2	8.4	8.2	7.7
4.8	6.2	4.5	23.2	24.4	12.1	10.0	10.1	7.7	10.9	10.8	9.7
19.1	19.8	20.4	20.7	22.6	11.1	7.4	7.6	8.2	14.8	14.8	9.9
13.5	16.1	11.4	14.4	15.4	9.1	12.0	11.8	8.5	38.5	37.3	24.5
18.8	19.9	13.8	8.1	8.6	5.9	10.9	11.0	8.7	40.0	41.1	23.6
22.2	21.5	12.8	7.1	7.2	9.9	22.3	22.6	13.4	17.0	17.8	11.6
7.2	8.2	4.0	10.7	11.3	8.9	17.8	17.8	7.4	16.0	15.5	14.8
16.4	16.0	11.2	13.7	14.1	12.3	8.8	11.2	2.9	27.1	26.5	18.4
43.7	46.1	39.9	22.7	22.8	15.9	5.6	5.7	7.5	25.7	27.2	20.3
37.5	40.2	26.1	12.5	12.6	11.3	10.8	10.0	8.9	35.8	35.8	17.3
48.2	52.0	34.6	8.4	7.3	7.6	6.3	7.2	6.4	13.8	14.1	5.2
44.3	47.4	31.3	6.3	6.2	6.8	6.2	8.0	5.5	18.6	18.6	12.5
25.8	26.9	16.0	11.6	11.6	11.8	6.9	6.9	7.3	33.8	34.1	20.3

Evaluation of uncorrected data for CM1

RESULTS OF REGRESSION		EQUIVALENCE TEST RESULTS	
slope b	0.64 *	random term	2.77 $\mu\text{g/m}^3$
uncertainty of b	0.04	bias at LV	-11.50 $\mu\text{g/m}^3$
intercept a	1.21	combined uncertainty	11.82 $\mu\text{g/m}^3$
uncertainty of a	0.80	relative uncertainty	33.8% fail
number of datapairs	52	RM between-sampler uncertainty	1.35 $\mu\text{g/m}^3$

* Significant at 95% confidence level.

Evaluation of data for CM1 after correction for slope

RESULTS OF REGRESSION		EQUIVALENCE TEST RESULTS	
slope b	1.04	random term	4.89 $\mu\text{g/m}^3$
uncertainty of b	0.06	bias at LV	2.51 $\mu\text{g/m}^3$
intercept a	1.19	combined uncertainty	5.50 $\mu\text{g/m}^3$
uncertainty of a	1.26	relative uncertainty	15.7% fail
number of datapairs	52	RM between-sampler uncertainty	1.35 $\mu\text{g/m}^3$

Examples of results – PM₁₀

Comparison of CM1 and RM – location D

Full dataset ($\mu\text{g.m}^{-3}$, uncorrected)

RM	CM1	RM	CM1	RM	CM1	RM	CM1	RM	CM1	RM	CM1
36.0	35.9	81.2	58.6	22.0	14.7	24.9	23.0	45.5	32.4	24.0	21.8
13.9	15.0	41.8	24.9	21.5	16.7	25.8	21.3	20.9	17.5	39.4	32.0
33.3	24.6	52.5	34.2	19.4	18.2	27.2	25.4	49.5	38.1	50.4	36.7
44.8	31.0	29.7	13.7	21.5	20.3	15.3	13.3	46.2	39.6	22.8	16.9
53.6	43.5	17.4	9.2	25.7	23.1	26.4	22.0	26.6	26.7	30.9	20.9
47.9	30.0	30.2	20.3	30.3	29.5	21.9	19.0	34.0	29.3	24.6	21.5
33.9	19.0	35.5	21.6	24.8	22.3	36.9	35.8	23.3	19.2	33.5	28.1
23.6	14.5	36.8	23.0	26.9	27.9	31.6	24.5	25.3	20.5	33.8	30.6
29.2	18.5	39.3	25.4	29.9	27.1	41.1	30.8	36.0	29.6	34.6	31.5
19.0	11.2	40.9	35.0	27.7	25.1	46.7	40.0	27.5	16.1	38.5	27.4
14.3	11.9	23.8	20.8	15.8	11.4	57.0	53.3	15.8	14.2	37.3	19.6
37.8	27.7	31.2	30.4	26.5	22.5	55.1	52.4	15.9	16.2	66.0	60.8
23.8	21.8	50.2	38.5	21.4	17.0	25.2	21.5	23.5	22.0	38.4	31.5
19.6	15.0	44.1	38.3	18.4	12.9	21.8	22.3	17.4	16.1	23.9	18.3
62.5	49.7	24.0	17.1	29.4	27.0	29.6	22.2	33.8	27.2	46.9	41.4
66.2	52.1	22.4	18.4	19.2	8.6	44.7	39.1	30.4	23.4	39.9	31.1
42.6	31.4	20.5	18.9	31.3	22.5	25.0	22.7	57.6	43.3	8.2	7.7
40.0	29.1	18.0	15.8	34.0	24.0	22.4	19.3	37.0	29.4	22.0	21.7
44.2	38.5	16.2	14.4	26.0	19.4	26.1	20.1	39.6	33.0	41.8	34.8
50.4	42.5	29.2	23.1	33.6	28.0	30.3	18.9	25.5	20.2	38.2	33.6
44.5	34.3	40.8	30.2	51.8	42.7	13.9	12.0	39.8	29.8	14.4	13.7
23.4	16.9	39.9	22.5	22.6	16.9	23.5	21.2	28.2	20.6	27.7	20.4
29.5	25.6	20.8	15.2	27.7	22.2	22.9	20.3	16.5	14.9	18.4	14.3
59.6	44.5	18.3	15.6	21.4	17.3	24.1	24.3	15.3	16.2	11.1	10.4
39.0	21.7	18.7	16.5	31.1	29.4	39.6	27.2	30.5	28.4	23.4	20.7
45.1	25.2	12.2	8.9	24.0	20.8	29.0	18.6	32.0	26.6	43.8	34.2
21.5	16.4										

Evaluation of uncorrected data for CM1

RESULTS OF REGRESSION		EQUIVALENCE TEST RESULTS	
slope b	0.793 *	random term	3.48 $\mu\text{g}/\text{m}^3$
uncertainty of b	0.024	bias at LV	-10.25 $\mu\text{g}/\text{m}^3$
intercept a	0.09	combined uncertainty	10.83 $\mu\text{g}/\text{m}^3$
uncertainty of a	0.81	relative uncertainty	21.7% fail
number of datapairs	157	RM between-sampler uncertainty	1.50 $\mu\text{g}/\text{m}^3$

* Significant at 95% confidence level.

Evaluation of data for CM1 after correction for slope

RESULTS OF REGRESSION		EQUIVALENCE TEST RESULTS	
slope b	1.018	random term	4.74 $\mu\text{g}/\text{m}^3$
uncertainty of b	0.030	bias at LV	0.44 $\mu\text{g}/\text{m}^3$
intercept a	-0.44	combined uncertainty	4.76 $\mu\text{g}/\text{m}^3$
uncertainty of a	1.03	relative uncertainty	9.5% pass
number of datapairs	157	RM between-sampler uncertainty	1.50 $\mu\text{g}/\text{m}^3$

Comparison of CM2 and RM – location E

Full dataset ($\mu\text{g.m}^{-3}$, uncorrected)

RM	CM2	RM	CM2	RM	CM2	RM	CM2	RM	CM2	RM	CM2
10.0	9.8	44.3	36.8	22.1	21.9	35.3	33.6	23.7	23.9	48.1	42.9
21.8	17.0	37.0	35.7	12.1	12.2	20.6	17.7	34.1	23.5	47.6	33.2
31.2	22.4	98.4	79.9	18.4	18.0	24.7	23.8	20.6	19.6	18.8	17.0
35.0	26.9	78.5	58.1	17.7	19.3	24.0	22.4	34.5	26.9	33.2	19.1
66.9	51.7	67.8	55.2	20.1	21.4	29.0	27.6	17.9	20.8	19.7	16.4
72.1	52.7	28.3	25.3	19.1	18.8	20.0	18.9	49.2	41.4	31.3	25.5
35.0	26.2	13.6	11.8	23.4	24.0	24.2	21.5	57.2	54.8	27.1	27.7
38.7	29.5	34.6	28.5	29.7	26.2	19.2	19.7	45.8	44.3	32.9	28.3
29.6	23.4	28.3	24.0	34.9	32.6	37.8	36.5	44.0	39.2	38.9	26.3
10.7	10.2	30.8	27.9	20.1	16.0	23.7	22.9	14.5	13.7	31.1	21.3
10.8	9.5	36.7	28.7	27.0	25.2	30.9	29.5	21.5	21.8	21.6	18.2
30.7	27.4	52.0	45.0	28.5	25.6	46.8	44.2	21.2	20.9	75.0	60.4
43.3	32.7	43.0	37.3	25.1	22.1	54.9	53.7	18.9	16.1	35.4	28.8
13.8	14.0	44.5	41.8	49.1	36.5	62.4	59.1	26.7	21.5	21.5	16.1
26.2	20.6	28.7	27.3	24.2	17.9	47.7	47.9	42.6	33.3	96.4	81.2
16.0	15.6	38.1	34.2	29.7	26.6	19.8	18.5	58.2	43.9	40.3	31.4
63.8	53.6	56.4	55.8	26.8	24.3	20.9	21.2	33.0	25.2	7.2	6.9
45.0	40.8	22.8	21.0	24.5	22.2	27.4	24.2	39.0	30.5	13.4	13.8
38.7	32.9	16.6	13.5	51.4	41.0	44.9	39.6	21.1	15.3	54.4	45.5
56.7	50.9	25.6	24.9	41.7	35.3	27.8	22.3	82.9	69.8	37.0	28.3
61.1	53.4	13.9	12.5	18.3	17.1	24.6	19.2	22.8	15.8	15.8	16.5
58.0	51.9	16.4	14.6	18.9	16.6	20.7	17.0	17.7	11.9	23.4	18.6
85.4	75.0	22.0	17.5	20.5	12.4	24.3	17.2	12.2	12.6	16.3	12.6
18.3	16.8	37.9	29.0	48.1	42.6	15.3	12.0	43.7	38.3	9.3	8.9
37.0	30.0	47.7	36.4	17.0	14.1	15.5	14.3	35.5	24.8	18.1	17.1
79.1	66.2	21.8	18.3	21.1	18.9	27.5	26.8	29.8	23.4	51.0	41.6
52.8	46.0	15.0	13.9	23.6	19.4						

Evaluation of uncorrected data for CM2

RESULTS OF REGRESSION		EQUIVALENCE TEST RESULTS	
slope b	0.829 *	random term	2.70 $\mu\text{g/m}^3$
uncertainty of b	0.014	bias at LV	-7.67 $\mu\text{g/m}^3$
intercept a	0.88	combined uncertainty	8.13 $\mu\text{g/m}^3$
uncertainty of a	0.52	relative uncertainty	16.3% fail
number of datapairs	159	RM between-sampler uncertainty	1.50 $\mu\text{g/m}^3$

* Significant at 95% confidence level.

Evaluation of data for CM2 after correction for slope

RESULTS OF REGRESSION		EQUIVALENCE TEST RESULTS	
slope b	1.004	random term	3.49 $\mu\text{g/m}^3$
uncertainty of b	0.017	bias at LV	1.13 $\mu\text{g/m}^3$
intercept a	0.93	combined uncertainty	3.67 $\mu\text{g/m}^3$
uncertainty of a	0.63	relative uncertainty	7.3% pass
number of datapairs	159	RM between-sampler uncertainty	1.50 $\mu\text{g/m}^3$