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Air quality — Validation of air quality measurement methods in the standardization process

Qualité de l'air — La validation des méthodes de mesure de la qualité de l'air dans le processus de normalisation

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Foreword

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

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This document was prepared by Technical Committee ISO/TC 146, *Air quality*, Subcommittee SC 4, *General aspects*.

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

Introduction

ISO/IEC 17025 defines expectations for verification and validation of test methods. These expectations are based on definitions in ISO/IEC Guide 99 and aim to ensure that test methods are suitable for their intended use and that test results have a known, documented level of quality.

This document describes protocols that have been used within ISO/TC 146 and other technical committees on air quality to verify and validate measurement methods. It also establishes guidance intended to be used for method validation. This document seeks to establish a consistent framework for method validation within ISO/TC 146 and its subcommittees.

Air quality — Validation of air quality measurement methods in the standardization process

1 Scope

This document provides an overview of the validation of air quality measurement methods in the standardization process.

This document deals with robustness testing and interlaboratory testing as the two main steps of partial and full validation. It applies to the different inter-related elements of air quality measurement methods, covering e.g. sampling, sample preparation, storage and transportation of the sample, extraction, analysis or quantification of a measured component and reporting.

Consequently, this document focuses on the "why" and "what" of validation tasks in direct relation to the different steps of the standardization process. This document is focused on the validation tasks for measurement methods either for the whole measurement process or for one of its constituent parts.

Given the informative aim of this document, it does not contain detailed procedures for performing the validation tasks, such as number of laboratories, number of samples, etc.

This document is relevant to measurement methods in ISO/TC 146 and all of its subcommittees.

2 Normative references

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

ISO 4225, *Air quality — General aspects — Vocabulary*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 4225 and the following apply.

ISO and IEC maintain terminology databases for use in standardization at the following addresses:

- ISO Online browsing platform: available at https://www.iso.org/obp
- IEC Electropedia: available at https://www.electropedia.org/

3.1
verification
provision of objective evidence that a given item fulfils specified requirements

[SOURCE: ISO/IEC Guide 99:2007, 2.44]

3.2
validation
verification, where the specified requirements are adequate for an intended use

[SOURCE: ISO/IEC Guide 99:2007, 2.45]

3.3
method
measurement procedure
detailed description of a measurement according to one or more measurement principles and to a given measurement method, based on a measurement model and including any calculation to obtain a measurement result

[SOURCE: ISO/IEC Guide 99:2007, 2.6, modified — Notes to entry omitted]

3.4
measurement method
method of measurement
generic description of a logical organization of operations used in a measurement

[SOURCE: ISO/IEC Guide 99:2007, 2.5, modified — Note to entry omitted]

3.5
reference method
RM
measurement method taken as a reference, which gives the reference value of the measurand

Note 1 to entry: A reference method is fully described.

Note 2 to entry: A reference method can be a manual or an automated method.

3.6
alternative method
AM
measurement method which complies with the criteria given by the reference method

Note 1 to entry: An alternative method can consist of a simplification of the reference method.

Note 2 to entry: Alternative methods can be used if equivalence to the reference method has been demonstrated.

3.7
evaluation
<analytical chemistry> examination of validation data to determine suitability for intended use(s)

3.8
sensitivity
<analytical chemistry> change in instrument response which corresponds to a change in the measured quantity

3.9
selectivity
<analytical chemistry> extent to which the method can be used to determine particular analytes in mixtures or matrices without interferences from other components of similar behaviour

3.10
linearity
<analytical chemistry> ability to use a straight line to describe the relationship between a measurement result and concentration of the analyte of interest

3.11
robustness
<analytical chemistry> measure of the capacity of an analytical method to remain unaffected within specified limits by small, but deliberate variations in method parameters

3.12
repeatability
measurement repeatability
measurement precision under a set of repeatability conditions of measurement

[SOURCE: ISO/IEC Guide 99:2007, 2.21]

3.13
repeatability condition
repeatability condition of measurement
condition of measurement, out of a set of conditions that includes the same measurement procedure, same operators, same measuring system, same operating conditions and same location, and replicate measurements on the same or similar objects over a short period of time

[SOURCE: ISO/IEC Guide 99:2007, 2.20, modified — Notes to entry omitted]

3.14
reproducibility
measurement reproducibility
measurement precision under reproducibility conditions of measurement

[SOURCE: ISO/IEC Guide 99:2007, 2.25, modified — Note to entry omitted]

3.15
reproducibility condition
reproducibility condition of measurement
condition of measurement, out of a set of conditions that includes different locations, operators, measuring systems, and replicate measurements on the same or similar objects

Note 1 to entry: The different measuring systems can use different measurement procedures.

[SOURCE: ISO/IEC Guide 99:2007, 2.24, modified — In Note 1 to entry, "may" changed to "can"; also, Note 2 to entry omitted]

4 Abbreviated terms

For the purposes of this document, the following abbreviated terms apply.

AAS	atomic absorption spectrometry
AM	alternative method
CRF	controlled release facility
FAIR	findable, accessible, interoperable and reusable
FID	flame ionisation detector
FTIR	Fourier-transform infrared
ICP	inductively coupled plasma
ICP-AES	inductively coupled plasma atomic emission spectrometry
ICP-MS	inductively coupled plasma mass spectrometry
LDAR	leak detection and repair
LIDAR	light detection and ranging
LOD	limit of detection

LOQ	limit of quantification
LV	limit value
MSD	mass selective detector
NPL	National Physical Laboratory
OELV	occupational exposure limit values
OGI	optical gas imaging
P-AMS	portable automated measuring systems
QA/QC	quality assurance and quality control
RDM	reverse dispersion modelling
RH	relative humidity
RM	reference method
SOF	solar occultation flux
ST-OELV	short-term occupational exposure limit values
STEL	short-term exposure limits
TDL	tuneable diode laser
TEM	transmission electron microscopy
TDLAS	tuneable diode laser absorption spectroscopy
TWA	time-weighted average concentration
UV	ultra-violet
VOC	volatile organic compounds
WP	work package

5 Purposes for validation

Validation is the process of defining an analytical requirement and confirming that the method under consideration has capabilities consistent with what the application requires in view of the measurement objective(s). This is often referred to as the method being fit for its intended purpose. An important part of this process is determining the uncertainty of the measurement results and whether this is suitable for the intended use, e.g. a maximum specific limit. It is also important to determine if it provides sufficient confidence in conclusions to be drawn from the measurement results.

Often, validation campaigns are designed to determine both an uncertainty associated with the entire measurement method and individual uncertainty components (i.e. various bias and precision terms) associated with individual components of the method. Either selectivity, limit of detection or limit of quantification, or a combination, can also be relevant. This supports the elaboration of the measurement method in terms of providing confidence that any maximum permissible uncertainty that is required for the entire method is fit for the intended application. It also supports the specification of any uncertainty requirement for individual components of the measurement method. Furthermore, validation campaigns confirm that reliable measurement results can be achieved by competent end users. Subsequently, this also serves to ensure that fit for purpose and achievable requirements are set by proficiency testing providers (and equally importantly local competent authorities and national accreditation bodies) in assessing the competence of end users.

In the absence of full or partial validation, requirements in the measurement method are based on expert opinion. With no evidential data there is therefore a higher level of uncertainty at a given level of confidence that the measurement method has capabilities consistent with what the application requires, and that requirements placed upon end users by the measurement method are realistic and achievable.

6 Objectives for validation

The main objectives of validation are confirming that:

- the measurement method meets the requirements specified in the measurement objective;
- the measurement method specified in the standard is clearly described and practicable, or if collecting of improvement proposals is needed;
- the results are comparable when different testing laboratories or institutes use the measurement method for the same task.

NOTE Comparability can be quantified by e.g. repeatability and reproducibility.

Method validation is a process to verify that a measurement method fulfils specified requirements that are adequate for an intended use.[2] It is a series of actions, following development of a method but preceding routine implementation of the method, that demonstrates and documents the fitness of the method for the intended use.

The principal benefit of validation is to provide confidence that measurements made by using the measurement method provide data which can be relied upon by the end user(s) for making correct decisions in one or more of the following areas:

- process control;
- policy making;
- compliance with regulatory requirements (e.g. limit values for emissions or occupational exposure);
- suitability of modelling (e.g. atmospheric modelling).

Measurement methods contained in documents prepared by technical committees on air quality are intended for use in a variety of locations and with a variety of sampling and laboratory equipment. It is expected that a standard method, when properly used, provides consistent measurement results wherever it is used. Additionally, since ISO/IEC 17025 recommends the use of standard methods when available, it is incumbent for those who establish such methods (e.g. ISO/TC 146) to ensure a sufficient degree of validation to support their use in this manner.

Additional considerations are given in 8.2.

7 Types of validation

7.1 Validation of reference methods

Reference methods (RM) are measurement methods that have been validated and of which the quality of the measurement method is, given a specific field of application, fit for its intended purpose and accepted by experts and users. Knowledge on and documentation of the quality of the measurement method is essential to define it as a RM. Validation is therefore an essential step in the standardization process.

RM can be used as a legal reference in either legislation, regulation or in contracts between two or more parties, or a combination thereof. They need, therefore, to be self-supportive. RM are not necessarily of the highest metrological quality. However, experts define a reference method as "reliable" and a good basis for decisions. In general, RM are "fit for purpose" in view of the measurement objective.

Validation of measurement methods is generally performed in two steps including performance characteristics relevant for the considered measurement method:

- robustness testing;
- interlaboratory testing.

As the first step is based on a first draft of the standard and each of the validation steps result in a revised draft standard, the implementation of validation in the standardization process normally relates to three different draft standards, the last one of which is published as a standard.

Cases can occur where the current state of the art is not sufficient for the efficient further development of the envisaged standard. In such a case, a so-called pre-normative research can be needed prior to any standardization with validation.

The robustness testing is generally performed by one or more competent laboratories which ideally already have experience with the new measurement method. The performance characteristics of the measurement method are determined through inter-laboratory experiments. Both steps are needed and contribute to the evaluation of the uncertainty of the measurement results.

The comparability of measurement results obtained by the standardized measurement method is ensured by metrological traceability of the measurement results by means of a documented unbroken chain of calibrations, each contributing to the measurement uncertainty, linking them to an appropriate reference.

Metrological traceability to the International System of Units (SI) can be achieved through:

- calibration provided by a competent laboratory; or
- certified reference materials with a stated metrological traceability to the SI units; or
- direct realization of the SI units.

When metrological traceability to the SI units is not technically possible, the metrological traceability can be ensured by use of an appropriate reference, e.g.

- reference materials without a stated metrological traceability to the SI units;
- results of RM, specified methods or consensus standards that are clearly described and accepted as providing measurement results fit for their intended use and ensured by suitable comparison.

Unfortunately, there is a clear disadvantage with certified reference materials as these are only available for a limited number of components and matrices and are, in general, so expensive that it is not financially possible to use certified reference materials for validation or routine checks. Therefore, it is important to specify in the standardized measurement method the appropriate reference.

The uncertainty of the measurement results obtained by the standardized measurement method consists of the uncertainty contributions resulting from the unbroken chain of calibrations. Therefore, it is important to specify in the standardized measurement method the minimum requirements for these uncertainty contributions.

In specific cases the introduction of a new RM results in the withdrawal of a previous RM. For example, due to the general application of new analytical instruments, the old RM is in practice no longer applicable. Validation of the new RM and cross-comparison of the results of both the old and the new RM allows the continuous use of data collected in the past (the "historical" data).

When a Technical Committee (TC) or Subcommittee (SC) starts a work item, this is generally given to a dedicated working group (WG). The aim of the work is to harmonize as far as possible the practices on a specific topic. Through a series of steps, consensus among the experts is achieved resulting in a first draft standard that, to the opinion of the experts, reflects the state of the art (in terms of standardization) and is assumed to be fit for purpose.

This first draft standard is used as a starting point for the validation work, or, if funds or means for validation are not sufficiently available, can be adopted by the TC or SC members and published as a Technical Specification (TS). When published as a TS, the document states that the measurement method has not been validated.

In general, at least the following different levels of validation can be distinguished:

- full validation by sufficient funding, which means that robustness testing and inter-laboratory testing (e.g. repeatability and reproducibility) as well as evaluation of the uncertainty are acceptably performed;
- partial validation in cases where results of a full validation are not available due to lack of funding, but a set of validation data provided e.g. by at least one member country or one testing laboratory, on the basis of current investigations being available and that expert assessment justifies the validity of these data;
- validation on the basis of existing historical data provided e.g. by at least one member country where the measurement method has been validated on a national level and expert assessment justifies the validity of these data.

7.2 Validation of alternative methods

In specific cases it can be necessary to standardize an alternative method (AM) to the already existing RM, e.g. if a simplification of the RM is desirable or a different measurement technique is available. The scope of the AM can be limited in comparison with the scope of the reference method, but is covered by the scope of RM.

With respect to validation, an AM is treated as outlined in 7.1 for the RM, but often with a limited scope in comparison with the RM. In addition, the equivalence of the AM with the RM is demonstrated for the scope of the AM. The three steps for demonstration of equivalence are:

- description of the AM and setting of the field of application;
- determination of the performance characteristics of the AM and calculation of the expanded uncertainty where appropriate and check of compliance with the maximum expanded uncertainty allowed for the RM;
- check of repeatability and lack of systematic deviation of the AM in comparison with the RM.

Guidance on demonstration of equivalence is given in EN 14793 for stationary source emission measurement methods and in the “Guide to the demonstration of equivalence of ambient air monitoring methods” for ambient air quality measurement methods[5].

The field of application of an AM can partially or completely cover the field of application of the RM. However, if it covers the fields of application of several RM (horizontal method), several evaluations of each RM are needed, e.g. in the case of multi-component measurement methods like FTIR.

The definition of the field of application depends entirely upon the body specifying the AM and the knowledge acquired during the development of the method. It is sometimes preferable to segment a field of application rather than to attempt to validate an overly general method. In this case, a validation file for each field of application is compiled.

7.3 Validation in the absence of certified reference materials

While metrological traceability of a measurement method to the SI is typically accomplished by use of certified reference materials, in some situations a certified reference material might not be available. In these situations, alternative approaches can include one or more of the following:

- inter-laboratory studies;
- recovery experiments using spiked samples;
- comparison with results obtained from another measurement method for the same measurand.

These alternatives do not necessarily establish metrological traceability.

8 Objective, design and documentation of a validation study

8.1 General

A validation study generally includes, at a minimum, the following aspects:

- objective(s) of the validation study (8.2);
- design of the validation study (8.3);
- documentation of the validation study (8.4).

NOTE Guidance on design and documentation of the validation study is also given in Eurachem documents.

8.2 Objective of a validation study

8.2.1 General

The initial step in the validation process is the analysis of the measurement objective (measurement task) and the associated measurement method to identify the specific elements and associated requirements of the measurement method. The validation concerns the following elements of the measurement method, for example:

- sampling;
- sample preparation including e.g. sample transfer and storage;
- analysis;
- performance characteristics;
- determination of the result of measurement and the associated measurement uncertainty;
- documentation and reporting.

8.2.2 Purpose(s) for performing the measurement

Because the objective of validation is to demonstrate fitness for purpose in view of the measurement objective, it is necessary to establish the purpose(s) for performing the measurement so that validation activities can be properly designed to establish that the measurement method is fit for the intended purpose(s). If the measurement method is to be fit for a single, narrow purpose, validation activities can be more narrowly defined. If, however, the purposes are broad or numerous, or both, validation activities also need to be sufficiently broad to address the full range of purposes for which the measurement method is intended to be suitable. For example, validation activities for a measurement method intended to measure a single air pollutant might not need to be as extensive as for a method intended to measure concentration of multiple metals in an air sample.

8.2.3 Representative sampling

It is important to develop sampling strategies that result in samples that reflect the properties of interest of the overall population being sampled. If this is not accomplished, even a reference method might not be able to produce reliable results for decision making. Method validation needs to include consideration for collecting representative samples.

8.2.4 Sample preparation

For many measurement methods, some preparation of the sample is necessary in advance of analysis.

8.2.5 Analysis

The analysis can be carried out in-situ or remotely in the laboratory.

Key considerations include assessment of the performance of the analytical method.

8.2.6 Performance characteristics

The performance characteristics of the measurement method determined in the validation process can include:

- required detection sensitivity;
- limits of detection and quantification;
- selectivity (i.e. ability to measure the analyte of interest in the sample matrix);
- interferences;
- linearity;
- repeatability and reproducibility;
- measurement uncertainty;
- robustness.

8.2.7 Determination of the result of measurement and the associated measurement uncertainty

It is important that the procedures for the determination of the result of measurement and the associated measurement uncertainty are fit for purpose and are giving correct results.

The measurement uncertainty expressed as an expanded uncertainty requires that the level of confidence and the associated coverage factor are properly specified.

8.2.8 Documentation and reporting

It is important that the documentation and reporting procedures specified for the measurement method meet the measurement objective.

8.3 Design of the validation study

The validation study is designed on the basis of the results obtained in 8.2.

The following factors are considered when designing a validation study:

- an understanding of how the method will be used and what is required to demonstrate fitness for purpose;
- applicable requirements derived from either the measurement objective, legislation or regulation, or a combination thereof;
- amount and types of data that need to be collected, and how that will be accomplished;
- reference materials to be used (see 7.1) or, in the absence of reference materials, an acceptable alternative (see 7.3);
- time to complete the validation study;
- cost and financing of the validation study;
- whether samples can or cannot be replicated, and how that impacts the validation study;

- whether the true value is or is not known, and how that impacts the validation study.

The validation plan details the elements described above and specifies the organization plan and planning of the validation experiments.

The organization plan includes the following tasks:

- coordination of the entire validation programme;
- specification of the number of experiments and the number of participants;
- selection of the participating testing laboratories and communication with them;
- designing the validation experiments:
  - organizing an inter-laboratory test for the validation experiments in the laboratory;
  - planning and preparation of the validation experiments in the field;
- cost calculations;
- reporting requirements.

The planning of the validation experiments covers the design of the laboratory and field tests. This includes the specification of the number of testing laboratories and the number of tests to be performed with respect to the subsequent statistical analysis of the data.

8.4 Documentation of the validation study

8.4.1 Report on the validation study

In the documentation of the results of the validation study including the underlying raw data the following elements are included, if applicable:

- field of application;
- measurement method;
- measured component;
- measurand;
- cross-sensitivities;
- measuring range;
- performance characteristics and acceptance criteria;
- measurement uncertainty;
- validation range.

8.4.2 Storage of results of the validation study

Storage of the results of the validation study including the underlying raw data following the principles of FAIR (findable, accessible, interoperable and reuseable) allows future use of these data.

9 Examples of validation procedures for specific types of measurement method

9.1 General

In the following sub-clauses, the key parameters of relevance for each type of measurement method (by subcommittee) and references to the corresponding annexes for the additional details and examples are presented for:

- stationary source emissions (9.2);
- workplace atmospheres (9.3);
- ambient atmospheres (9.4);
- meteorology (9.5);
- indoor air (9.6).

9.2 Stationary source emissions

9.2.1 General

A validation for emission measurement methods depends on the type of the measurement method, e.g. manual or automated method, and on the compound of interest, e.g. gaseous or particulate measured component.

General issues are described in 9.2.2 to 9.2.6.

Examples for the validation of emission measurement methods are presented in Annex A.

9.2.2 Manual measurement methods

The validation of the analytical method is essential for manual measurement methods. This usually includes the use of calibration standards and samples in different concentrations and solutions containing interfering substances, if appropriate, in inter-laboratory studies. It also includes stability tests of samples. These tests are often carried out with samples prepared under controlled conditions and with known properties, distributed to the participating testing laboratories. If the measurement method includes different analytical methods, each of the analytical methods is included in the tests.

9.2.3 Automated measurement methods

The validation of the measuring principle of automated measurement methods includes the application of corresponding analysers by use of test or calibration gases with known properties in different concentrations and compositions. It also includes tests for cross-interferences caused by chemical interfering components and physical influence quantities such as temperature and pressure. The tests are often carried out at appropriate test benches. If the measurement method includes different measuring principles, each of the measuring principle is included in the tests.

9.2.4 Test bench validation

Test bench experiments are carried out under controlled conditions with different pollutant concentrations, different humidity (but without droplets) and different interfering substances. All participants use the measurement method described e.g. in the draft standard. If the measurement method includes different analytical methods or measuring principles, each of them is included in the tests. The evaluation of the test results of the complete measurement method provides information on possible implications for the field tests.

9.2.5 Field test validation

Field tests with the complete measurement method are carried out at real industrial sites with e.g. different influence parameters and waste gas abatement systems. If the measurement method includes different analytical methods or measuring principles, each of them is included in the tests. The evaluation of the test results of the complete measurement method provides information on the applicability of the method in the field.

9.2.6 Final evaluation

The final evaluation of the entire validation programme provides the results as per 8.4 for the specification of the measurement method within the standardization work.

9.3 Workplace atmospheres

Annex B provides an example of method validation for workplace air measurements prepared by ISO/TC 146/SC 2, *Workplace atmospheres*. Key aspects of the validation process for these measurement methods include the following (see Figure B.1 for details):

- determination of basic properties of the substance to be analysed, including physical properties (e.g., gas/vapour, particulate, or semi-volatile) and any applicable occupational exposure limit values;
- selection of the analytical method and sampling method to be used;
- determination of the conditions for sampling, transport, and storage;
- determination of the sample preparation and analytical conditions;
- performance testing to determine analytical recovery, limits of detection and limits of quantification;
- calculation of the components of method uncertainty;
- compilation of the results as described in ISO 20581.

9.4 Ambient atmospheres

Currently none of the measurement methods elaborated by ISO/TC 146/SC 3 have been validated by intra-laboratory or inter-laboratory testing. Details of selected measurement methods are provided in Annex C.

9.5 Meteorology

To date, ISO/TC 146/SC 5 meteorology standards have not been subject to intra-laboratory or inter-laboratory precision testing validation. However, regarding wind measurements, ISO 17713-1 specifies wind tunnel test methods for rotating anemometer performance. It contains well formulated and specified acceptance testing. Annex D presents details.

9.6 Indoor air

The standards work in ISO/TC 146/SC 6 primarily concern indoor air (ISO 16000 series) and the vehicle indoor air quality (ISO 12219 series, under a Joint Working Group with ISO/TC 22). These series cover organic and inorganic gases and particulates as well as odours.

In the two primary methods for organic gases, ISO 16000-3 and ISO 16000-6 validation is generally referenced as voluntary and an internal function of the testing laboratory, with mention of external validation as a suggestion. Where data are presented in the informative annex of the standard, it is usually reprinted from published technical papers that are referenced in the bibliography for the measurement method.

Validation of particulate and odour measurement methods is not generally referenced. Where data related to the measurement method are included in the informative annex of the standard, those data are reprinted from published technical papers.

For a more detailed discussion of the validation recommendations in ISO/TC 146/SC 6 refer to Annex E.

Annex A
(informative)

Stationary source emissions

A.1 General

This annex provides three emission measurement method validation examples:

- planning a validation programme for the full validation of a manual formaldehyde emission measurement method (see A.2);
- presentation of a summary of the results of a validation study for a manual emission measurement method (see A.3);
- presentation of a summary of the results of a validation study for an automated emission measurement method (see A.4);
- presentation of a validation programme for diffuse emission measurement methods (see A.5).

References specific to this annex are given in A.6.

A.2 Example for planning a validation programme for the full validation of a manual formaldehyde emission measurement method

A.2.1 Background

For the determination of formaldehyde concentrations in stationary source emissions different analytical methods are used worldwide. These methods have been bundled in one Technical Specification CEN/TS 17638 elaborated by European Standardization Organization (CEN). The conversion of the TS to a European Standard (EN) requires the validation of the measurement method described in the TS.

The principle of this manual measurement method is at first sampling and absorbing formaldehyde from waste gas in water samples and subsequent analysis of the samples with analytical methods in the laboratory. These analytical methods are calibrated with analytical standards.

The planning of the validation program is described in the following. Additional information on the validation of the measurement method can be found at [93].

A.2.2 Validation programme

A.2.2.1 General

The validation program starts with the validation of the described analytical methods. The next step is a test bench validation where test gases are sampled and analysed. Finally, a sampling of real waste gases with subsequent analysis of the samples completes the validation programme.

The validation programme is structured as follows:

- specification of the organization plan;
- analytical method validation;
- test bench validation;

- field test validation;
- final evaluation of the validation programme.

A.2.2.2 Organization plan

The organization plan includes the following tasks:

- coordination of the entire validation programme;
- specification of the number of required experiments and the number of participants;
- selection of the participating testing laboratories and communication with them;
- design of measurements:
  - organization of an inter-laboratory test for the validation of the analytical methods including a time frame;
  - selection of the analytical methods for the bench and field tests based on the results of the analytical method validation;
  - planning and preparation of the test bench validation experiments with the test bench owner and with the participants of the validation programme; schedule for the test bench experiments;
  - selection of suitable industrial plants for the field test validation;
  - planning and preparation of the field test validation experiments and agreements with the plant operators; schedule for the field test experiments;
- reporting.

A.2.2.3 Analytical method validation

The analytical method validation includes the following tasks:

- coordination of the analytical method validation;
- stability test of samples;
- interference study: fixation of compounds which can interfere (or cause a cross sensitivity) with the formaldehyde signal of the sample;
- preparation of a standard test sample reporting sheet;
- setting up an inter-laboratory test: preparation and distribution of formaldehyde test samples as aqueous samples with three different formaldehyde concentrations for each selected analytical method and blank samples;
- analysis of each sample three times (triple analysis) and analysis of the blank sample by the participating laboratories (in total four analyses per sample);
- performance of the laboratory analyses directly at the location of the test bench (if possible) or after transfer to the laboratory facilities;
- evaluation of the results and selection of the analytical methods for the bench and field tests.

For statistical reasons 10 testing laboratories are required for each of the 4 analytical methods which leads to the following number of samples required for the laboratory test:

- 4 samples × 4 analytical methods = 16 samples;
- 16 samples × 10 laboratories = 160 samples.

A.2.2.4 Test bench validation

At a test bench, gases with different known concentrations of formaldehyde are fed into a ring line from where the participating laboratories take their samples. These test gases are offered with different humidity and different interfering substances. All participants are using the same non-isokinetic sampling method according to the TS and each of the selected analytical methods is used. At the end, the results obtained by the complete measurement method are evaluated and possible implications for the following field test are defined.

The test bench validation contains the following items:

- operation of a test bench: the test bench provides the different test gases under homogeneous conditions (validated before);
- preparation of the test programme including a time table for the allocation of the different test gases;
- control of the stability of the generation of formaldehyde concentrations;
- simultaneous sampling with a sampling duration of usually 30 min by all participants at the test bench and subsequent analysis in their laboratories using the selected analytical methods;
- transfer of the samples under controlled conditions to the laboratory for chemical analysis;
- double determination (analysis) of each sample in the laboratory.

A.2.2.5 Field test validation

For the field test validation experiments with real waste gases of industrial plants are carried out. If the measurement method is intended for use at plants with completely different waste gas compositions, field tests at different plants are necessary. The sampling method is applied as specified in the Technical Specification. Each of the selected analytical methods is used.

For the field test validation experiments can be performed e.g. at wood panel production plants (at their wood drying systems) and at a biogas engines. At the wood drying plants, high humidity in the waste gases are special challenges.

The field test programme includes the following:

- preparation of the field test validation experiments and agreements with the plant operators; schedule for the field test experiments;
- scheduling a timetable for the experiments;
- transfer of the samples under controlled conditions to the laboratory for chemical analysis;
- double determination (analysis) of each sample in the laboratory.

A.2.2.6 Evaluation of the entire validation programme

The evaluation of the results of the entire validation programme includes:

- statistical evaluation of the validation data of each validation stage;
- determination of performance characteristics and uncertainties;
- final assessment of the methods or parts of it; identification of restrictions for the application in general and for the analytical methods in particular;
- reporting;
- implementation of the results into the standardization work.

A.3 Example for the presentation of a summary of the results of a validation study for a manual emission measurement method

A.3.1 Background

The manual measurement method for the determination of ammonia in stationary source emissions specified in ISO 21877 was validated on the basis of existing validation data provided by one ISO member country where the measurement was validated on a national level. These data were evaluated and accepted by an ISO technical working group.

The following example (A.3.2 and A.3.3) for the presentation of a summary of the results of a validation study comes from ISO 21877, where the results of the validation of the measurement method in the field and the performance characteristics determined in the entire evaluation of validation of the measurement method are shown.

A.3.2 Validation of the measurement method in the field

The measurement method has been validated by comparative measurements, which were carried out on the waste gas of a cement plant, with eight test laboratories (teams) participating. These measurements took place in two campaigns (campaign 1 in Winter 2013, campaign 2 in Autumn 2014), with four participants each. The measurements were carried out as point measurements after a homogeneity test according to ISO 15259. Two different operational conditions were measured at the cement plant at both campaigns to cover a greater range of concentrations.

Sampling was carried out according to ISO 15259. Identical devices were used for the sampling. All the analytical methods specified in ISO 21877:2019, Clause 9, were used during subsequent analysis.

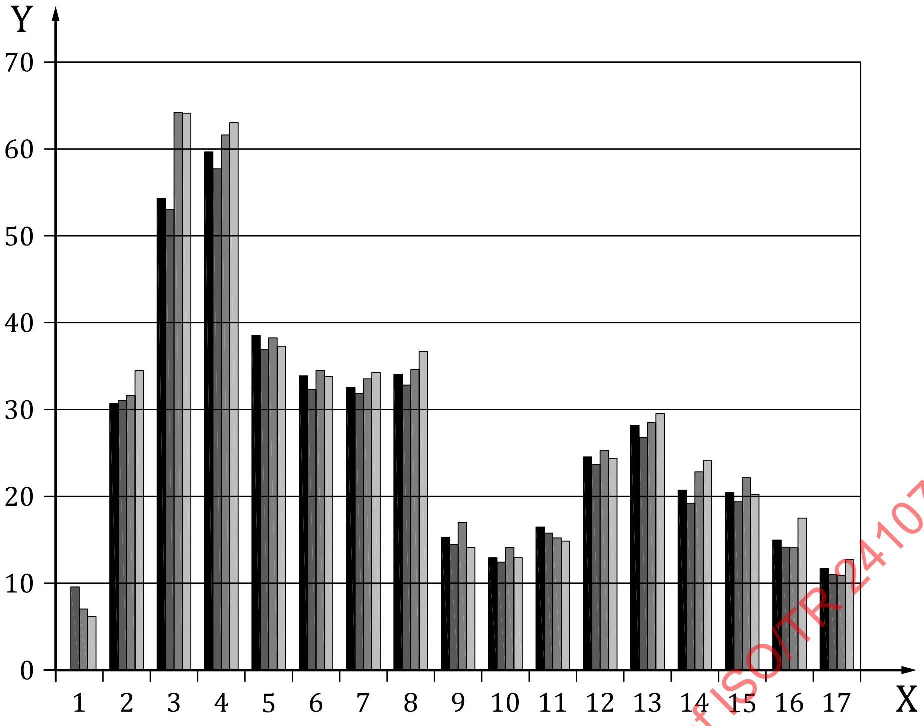
The results of one test laboratory were not included in the analysis based on the results of a Grubbs outlier test and the plausibility assessment of the data. There were thus 165 individual results available for the determination of the performance characteristics.

The measurements cover a concentration range from 7,6 mg/m^3 to 60,5 mg/m^3 (mean value for the individual measurements). Figure A.1 and Figure A.2 show the graphical illustration of the results.

The measurement uncertainty was determined on the basis of the results of the comparative measurements according to ISO 20988 (Experimental design A8 "Parallel measurements with identical measuring systems"). The expanded measurement uncertainty was calculated for a coverage probability of P = 95 %. The results of the comparative measurements are given in Table A.1 and Table A.2.

Based on the results of the measurements of the first campaign, a combined standard uncertainty of 1,6 mg/m^3, an expanded uncertainty of 3,2 mg/m^3 and a relative expanded uncertainty of 12 % have been calculated (see Table A.3).

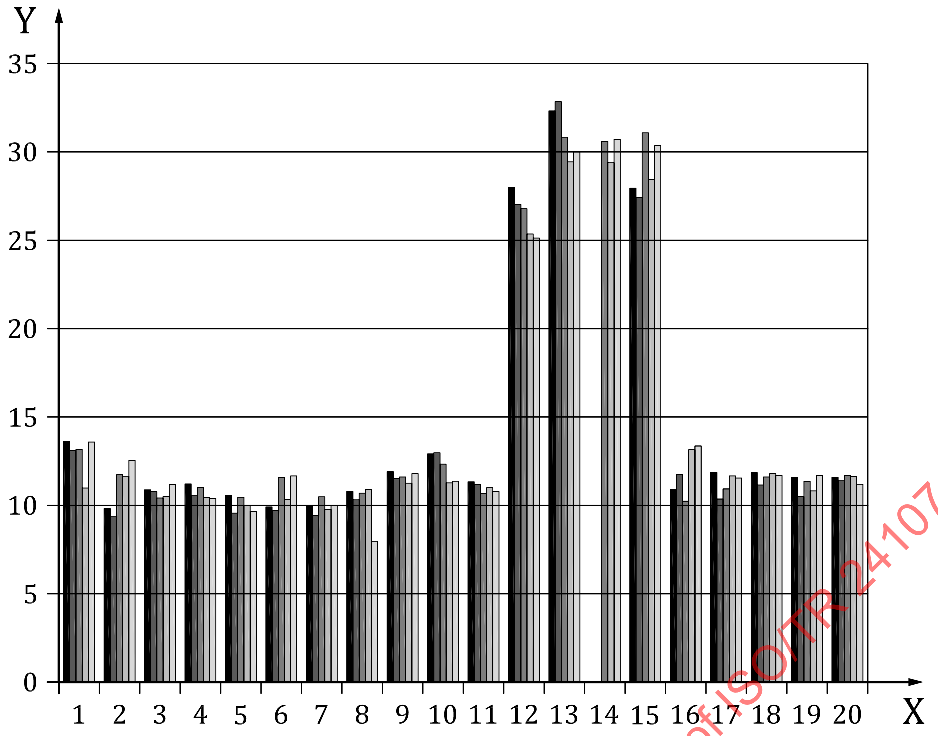
Based on the results of the measurements of the second campaign, a combined standard uncertainty of 0,8 mg/m^3, an expanded uncertainty of 1,6 mg/m^3 and a relative expanded uncertainty of 11 % have been calculated (see Table A.3).



Key

X	measurement number
Y	NH_3 concentration in mg/m^3
■	team 1/1
■	team 1/2
■	team 2
□	team 3

Figure A.1 — Graphical illustration of the results of the comparative measurements (campaign 1)



Key

X	measurement number
Y	NH_3 concentration in mg/m^3
■	team 4/1
▩	team 4/2
▨	team 5
▧	team 6
□	team 7

Figure A.2 — Graphical illustration of the results of the comparative measurements (campaign 2)

Table A.1 — Results of the comparative measurements conducted on the waste gas of a cement plant (campaign 1)

Measurement number	Number of parallel measurements	Mean value of the ammonia concentration in mg/m^3	Standard deviation in mg/m^3
1	3	7,6	1,8
2	4	31,9	1,8
3	4	58,9	6,1
4	4	60,5	2,3
5	4	37,7	0,8
6	4	33,6	0,9
7	4	33,0	1,1
8	4	34,5	1,6
9	4	15,2	1,3
10	4	13,1	0,7
11	4	15,6	0,7

Table A.1 *(continued)*

Measurement number	Number of parallel measurements	Mean value of the ammonia concentration in mg/m^3	Standard deviation in mg/m^3
12	4	24,5	0,7
13	4	28,2	1,1
14	4	21,7	2,2
15	4	20,5	1,1
16	4	15,2	1,6
17	4	11,6	0,8
Mean value:		27,5	1,6
Bias:		0,9	—

Table A.2 — Results of the comparative measurements conducted on the waste gas of a cement plant (campaign 2)

Measurement number	Number of parallel measurements	Mean value of the ammonia concentration in mg/m^3	Standard deviation in mg/m^3
1	5	12,9	1,1
2	5	11,0	1,4
3	5	10,8	0,3
4	5	10,7	0,4
5	5	10,0	0,5
6	5	10,6	0,9
7	5	9,9	0,4
8	5	10,1	1,2
9	5	11,6	0,2
10	5	12,2	0,8
11	5	11,0	0,3
12	5	26,5	1,2
13	5	31,1	1,5
14	3	30,2	0,7
15	5	29,1	1,6
16	5	11,9	1,4
17	5	11,3	0,6
18	5	11,6	0,3
19	5	11,2	0,5
20	5	11,5	0,2
Mean value:		14,4	0,8
Bias:		0,5	—

Table A.3 — Results of the uncertainty evaluation

	Campaign 1	Campaign 2
Number of degrees of freedom, v:	51	80
Standard uncertainty, u:	1,6 mg/m^3	0,8 mg/m^3
Coverage factor, $k_{0,95}$:	2,0	2,0
Expanded uncertainty, $U_{0,95}$:	3,2 mg/m^3	1,6 mg/m^3
Relative expanded uncertainty, $U_{\mathrm{rel},0,95}$:	12 %	11 %

A.3.3 Performance characteristics

Table A.4 and Table A.5 give an overview of the performance characteristics and the associated performance criteria of the measurement method deduced from the validation study.

Table A.4 shows the performance characteristics and performance criteria of the sampling system.

Table A.4 — Performance characteristics of the sampling system to be determined in the laboratory (L) and in the field (F) and associated performance criteria

Performance characteristic	L	F	Performance criterion
Determination of the volume of the absorption solution		X	≤1,0 % of the volume of solution
Gas volume meter:			
— standard uncertainty of sample volume[b]	X[a]		≤2,5 % of the volume of gas sample[a]
— standard uncertainty of temperature[c]	X[a]		≤1,0 % of the absolute temperature[a]
— standard uncertainty of absolute pressure[c]	X[a]		≤1,0 % of the absolute pressure[a]
Absorption efficiency[d, e]		X	≥95 %
Leak in the sampling line		X	≤2,0 % of the nominal flow rate
Field blank value		X	≤10,0 % of assessment standard

[a] Performance criteria corresponding to the uncertainty of calibration.

[b] The uncertainty of the sampled volume is a combination of uncertainties due to calibration, drift (random drift, drift between two calibrations) and resolution or reading.

[c] The uncertainty of temperature and absolute pressure at the gas volume meter is a combination of uncertainties due to calibration, drift (random drift, drift between two calibrations), resolution or reading, and standard deviation of the mean when several values are used to get the result.

[d] This characteristic is a quality assurance check to quantify the absorption efficiency in the first absorber; but it does not quantify a possible loss of absorption, and therefore it is not included in calculation of expanded uncertainty.

[e] If the criteria for the absorption efficiency for the first absorber cannot be met at very low concentrations, the concentration in the second absorber will be below the analytical limit of quantification.

Because all the components of uncertainty attached to the analysis are difficult to identify and to estimate, the test laboratory can determine the expanded uncertainty due to analysis by taking the repeatability standard deviation determined in an interlaboratory test. A maximum performance criterion is given in Table A.5.

Table A.5 — Performance characteristic of analytical procedure to be determined in the laboratory (L) and associated performance criterion

Performance characteristic	L	Performance criterion
Repeatability standard deviation	X	≤2,5 % of the measured value (value of quantity of NH_4^+ ions in the solution; in milligrams of NH_4^+ per litre of solution)

A.4 Example for the presentation of a summary of the results of a validation study for an automated emission measurement method

A.4.1 Background

This example shows a summary of the results of a validation study for an automated measurement method for the determination of the concentration of gaseous hydrogen chloride (HCl) in waste gases emitted by industrial installations into the atmosphere. The measurement method has been validated during the elaboration of the corresponding EN 16429 on a test bench, on a waste incineration plant and on a large combustion plant. Four different European accredited testing laboratories took part to this validation.

Four different types of portable automated measuring systems (P-AMS) were involved. Two P-AMS used the FTIR technique and two used tuneable diode lasers (TDL) technique. For sample gas conditioning, all P-AMS used configuration 2 specified in EN 16429 (temperature of the sampling line maintained up to the heated analyser).

Only one P-AMS was on the market, which was using FTIR and was certified according to EN 15267-3. Its performance characteristics already determined are fulfilling the criteria fixed by EN 15267-4.

One FTIR and two TDL systems did not always meet the expectations during the field tests. New developments or improvements of the existing systems are necessary. A similar validation work performed with certified instruments would have led, most likely, to much better results.

From observations noticed during the validation campaigns instructions to manufacturers were deduced.

The following example for the presentation of a summary of the results of a validation study comes from EN 16429, where the instructions to manufacturers (A.4.2), characteristics of the reference gases (A.4.3), characteristics of installations (A.4.4) and repeatability and reproducibility in the field (A.4.5) are shown.

Additional information on the validation of the measurement method can be found at [82].

A.4.2 Instructions to manufacturers

The manufacturers were instructed to pay the greatest attention to ensuring that the transfer of the P-AMS from one sampling platform to another one does not affect the rigidity of the connections (between the different parts of the measuring system: probe, heated line, pump, conditioning system, analyser, etc.) and the integrity and efficiency of the associated insulation.

The efficiency of the insulation can be tested by injection a wet span gas.

The manufacturers were instructed to avoid the use of any material that could adsorb or desorb HCl. With some P-AMS using stainless steel (probe, filter, connections) desorption phenomena has been observed when the probe is inserted into the duct that could affect the signal during more than 30 min.

A.4.3 Characteristics of the reference gases

The measurement campaign performed to validate this document has shown that a generator of wet gases instead of a dry gas injection improves the quality of the adjustment. The advantages of a wet adjustment are:

- response times are significantly reduced;
- for Analyser A: from 20 min with a dry gas to 3 min for a wet gas, at the inlet of the probe;
- for Analyser B: from 27 min with a dry gas to 8 min for a wet gas, at the inlet of the probe;
- possibility to use the water vapour generator with an HCl solution instead of a calibration gas bottle and the water vapour generator;
- adjustments with wet gases are more repeatable, which is essential to detect if a drift is significant during the measurement period;

- losses due to cold points in the connections between the probe / filter / heated line / pump / heated line / analyser can be detected during the check of the sampling system using span gas and the appropriate repair carried out.

A.4.4 Characteristics of installations

The following field tests were performed:

- Field test 1: NPL test bench at Teddington (United Kingdom);

  For each type of the 4 P-AMS selected, two systems A and B were provided by the manufacturer (except for one of the P-AMS).

  For each P-AMS, the tests have been implemented, by a technician of an accredited laboratory with the support of a technician from the manufacturer providing a selected measurement system (P-AMS).

  The first day was dedicated to the installation and adjustment of the P-AMS and the three following days, 14 trails have been performed with HCl concentrations varying from 3 to 61 mg/m^3 simulating an incineration or combustion plant gas matrix. One of the trials was interrupted by a power failure and not processed.
- Field test 2: waste incinerator in Belgium. Two teams took part to the field test and performed measurements simultaneously with the four P-AMS. A total of twelve measurements were performed. The repeatability from the first field test was used to determine the reproducibility;
- Field test 3: coal fired power plant in United Kingdom. Two teams took part to the field test and performed measurements simultaneously with the four P-AMS. A total of twelve measurements were performed. The repeatability from the first field test was used to determine the reproducibility.

An overview of the flue gas characteristics is given in Table A.6.

Table A.6 — Flue gas characteristics during field tests

Field test	Installation	Fuel	Flue gas characteristics						
			T °C	O_2 %	NO_x mg/m^3	SO_2 mg/m^3	CO mg/m^3	H_2O %	HCl mg/m^3
1	Test bench	Mix of gases	≈150	11 to 13	160 to 290	30 to 210	20 to 215	0,3 to 20	3 to 61
2	Waste incinerator	Municipal waste	140 to 150	6,2 to 7,6	40 to 100	3 to 87	0,5 to 4	17 to 20	2,5 to 27
3	Power plant	Coal	130 to 140	5,7 to 6,2	210 to 275	150 to 214	675 to 1 500	10,5 to 11	3 to 5

A.4.5 Repeatability and reproducibility in the field

Repeatability standard deviation $s_{\mathrm{r}j}$ and reproducibility standard deviation $s_{\mathrm{R}j}$ are determined from data obtained during inter-laboratory tests at the three installations. They are mentioned in Tables A.7 to A.9 for the three field tests.

Repeatability in the field r_j (see Formula (A.1)) and confidence interval of repeatability (see Formula (A.2)) are calculated according to ISO 5725-2, from the results of the double measurements implemented by the same laboratory:

$$r_j = \sqrt{2}\, t_{1-\frac{\alpha}{2}} \times s_{rj} \tag{A.1}$$

$$CI_{rj} = \pm t_{1-\frac{\alpha}{2}} \times s_{rj} \tag{A.2}$$

where

s_{rj}	is the repeatability standard deviation;
x_i	is the i^{th} measured signal;
$\overline{x}$	is the average of the measured signals x_i;
$t_{1-\frac{\alpha}{2}}$	is the Student factor for a level of confidence of 95 % and a degree of freedom of n−1 with *n* the number of double measurements;
r_{j}	is the repeatability in the field during the validation of the method at the level of concentration *j;*
Cl_{rj}	is the confidence interval of repeatability.

Reproducibility standard deviation s_{Rj} used to estimate the expanded uncertainty U (see Formula (A.3)), reproducibility in the field R_j (see Formula (A.4)) and confidence interval of repeatability (see Formula (A.5)) are calculated according to ISO 5725-2, from the results of parallel measurements performed simultaneously:

$$U = t_{1-\frac{\alpha}{2}} \times s_{Rj} \tag{A.3}$$

$$R\mathrm{j} = \sqrt{2} \times t_{1-\frac{\alpha}{2}} \times s_{Rj} \tag{A.4}$$

$$CI_{Rj} = \pm t_{1-\frac{\alpha}{2}} \times s_{Rj} \tag{A.5}$$

$$s_{Rj} = \sqrt{{S_{rj}}^2 + {S_{Lj}}^2} \tag{A.6}$$

where

U	is an estimate of the expanded uncertainty;
s_{Rj}	is the reproducibility standard deviation;
S_{Lj}	is the interlaboratory standard deviation
$t_{1-\frac{\alpha}{2}}$	is the Student factor for a level of confidence of 95 % and a degree of freedom of *n*−1; with *n* the number of measurements;
R_j	is the reproducibility in the field during the validation of the method;
Cl_{Rj}	is the confidence interval of reproducibility.

Table A.7 — Repeatability and reproducibility in the field — (NPL test facility)

HCI average concentration mg/m^3 wet at 273K, 101325 Pa	9,0	10,0	10,2	4,7	3,0	2,7	6,2	59,4	40,6	32,3	20,9	20,5	12,0
S_{rj}	0,774	0,515	0,570	0,126	0,259	0,124	0,305	2,026	1,723	1,285	1,102	1,091	1,468
S_{Lj}	0,516	0,576	0,000	1,333	0,893	0,951	1,518	3,634	2,287	1,084	0,000	0,000	4,631
S_{Rj}	0,930	0,772	0,570	1,339	0,930	0,959	1,548	4,161	2,863	1,681	1,102	1,091	4,858
$t_{1-\alpha/2}$	4,303	3,182	4,303	3,182	3,182	3,182	3,182	3,182	3,182	3,182	4,303	4,303	3,182
CI_{rj} rel (in %) = ±	37	16	24	9	28	15	16	11	13	13	23	23	39
CI_{Rj} rel (in %) = ±	44	25	24	91	100	114	80	22	22	17	23	23	129
r rel (in %) = ±	52	23	34	12	39	21	22	15	19	18	32	32	55
R (in %) = ±	63	35	34	129	141	161	112	31	32	23	32	32	183

Table A.8 — Repeatability and reproductibility in the field — (waste incineration)

HCl average concentration mg/m³ wet at 273K, 101325 Pa	4,2	5,5	4,8	3,8	2,6	2,3	2,0	4,2	10,3	12,3	10,9	23,8
Number of results	4	4	4	4	4	5	5	5	4	4	4	4
S_{rj} (6,3 % rel)[a]	0,263	0,346	0,301	0,238	0,162	0,144	0,126	0,266	0,651	0,777	0,687	1,500
S_{Lj}	0,633	0,829	0,606	0,364	0,405	0,262	0,660	1,459	0,500	1,104	0,550	1,136
S_{Rj}	0,685	0,899	0,677	0,435	0,436	0,299	0,672	1,483	0,821	1,350	0,880	1,881
$t_{1-\alpha/2}$	3,182	3,182	3,182	3,182	3,182	2,776	2,776	2,776	2,776	3,182	3,182	3,182
CI_{rj} rel (in %) = ±	20	20	20	20	20	17	17	17	17	20	20	20
CI_{Rj} rel (in %) = ±	52	52	45	37	54	36	93	98	22	35	26	25
r rel (in %) = ±	28	28	28	28	28	25	25	25	25	28	28	28
R (in %) = ±	74	74	64	52	76	51	132	138	31	49	36	36

[a] Reproductibility of P-AMS is calculated considering repeatability information determined on NPL test facility.

Table A.9 — Repeatability and reproducibility in the field — (power plant)

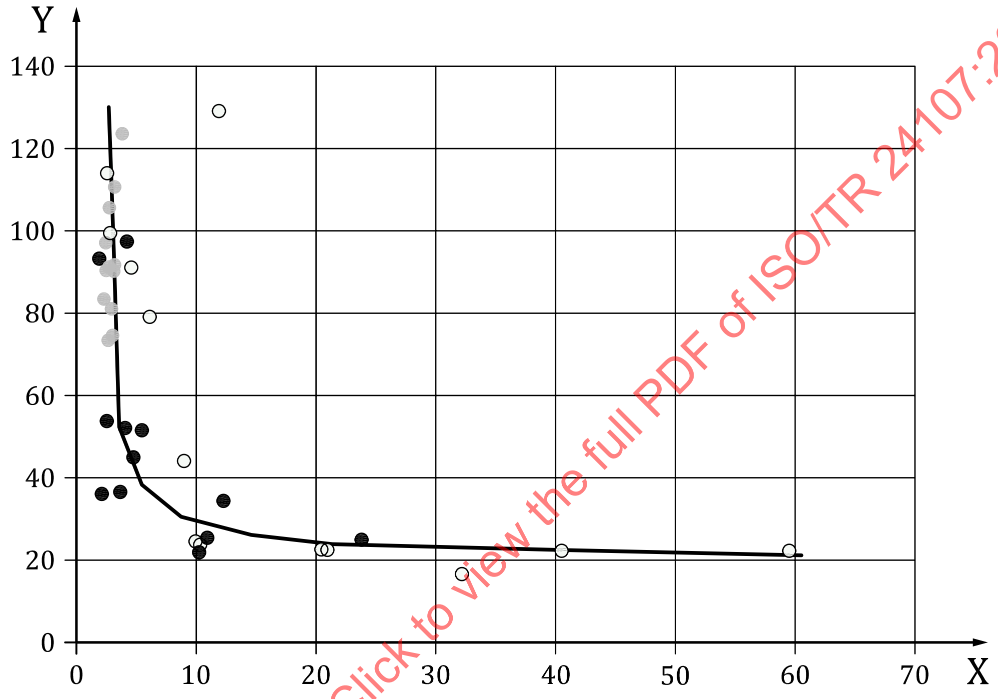
HCl average concentration mg/m³ wet at 273K, 101325 Pa	3,3	3,0	2,8	2,7	2,5	2,4	2,4	3,0	2,8	3,2	3,8	3,4
Number of results	3	4	4	4	4	4	4	3	4	4	4	4
S_{rj} (6,3 % rel)[a]	0,205	0,189	0,174	0,172	0,157	0,151	0,154	0,188	0,173	0,199	0,241	0,212
S_{Lj}	0,649	0,674	0,901	0,763	0,745	0,611	0,676	0,532	0,614	1,084	1,466	0,947
S_{Rj}	0,681	0,700	0,917	0,782	0,762	0,629	0,694	0,564	0,638	1,102	1,485	0,971
$t_{1\text{-}\alpha/2}$	4,303	3,182	3,182	3,182	3,182	3,182	3,182	4,303	3,182	3,182	3,182	3,182
Cl_{rj} rel (in %) = ±	27	20	20	20	20	20	20	27	20	20	20	20
Cl_{Rj} rel (in %) = ±	90	74	106	91	97	84	90	81	74	111	124	92
r rel (in %) = ±	38	28	28	28	28	28	28	38	28	28	28	28
R rel (in %) = ±	127	105	149	129	138	118	128	115	104	157	175	130

[a] Reproductibility of P-AMS is calculated considering repeatability information determined on NPL test facility.

An estimate of the expanded uncertainty can be deducted from Table A.7 to Table A.9. See Figure A.3.

Between 0 mg/m^3 and 10 mg/m^3 the estimates of expanded uncertainty are significantly different from one plant to the other. This can be explained by several reasons:

- the number of available P-AMS has a rather high impact on the level of uncertainty. 7 sets of data were available in NPL test facility, 5 on the waste incineration plant and 4 at the coal power plant. Student coefficient used to expand the uncertainty differs from one campaign to another (t = 3,18 or 4,303 for field test 1, 2,776 or 3,182 for field test 2 and 3,182 or 4,3 for field test 3);
- data from two extra P-AMS (one FTIR and one TDLAS implemented by the laboratory in charge of controls of the plant) reducing the t factor of 40 % (between the coal power plant and the waste incineration plant);
- higher level of interferent gases in the power plant and in some NPL test compared to the waste incineration matrix.



Key

X	HCl concentration in mg/m^3 on wet gas
Y	expanded uncertainty *U* in %
●	waste incineration plant
○	NPL test facility
◍	coal power station

Figure A.3 — Estimate of the expanded uncertainty determined from the results of the three field test campaigns

A.5 Example validation programme for measurement methods for diffuse and fugitive volatile organic compounds (VOC) emissions

A.5.1 General

This annex describes an example validation programme based upon an actual validation carried out for EN 17628 covering measurement of diffuse and fugitive volatile organic compounds (VOC) emissions applicable to measurement techniques including:

- light detection and ranging (LIDAR);

- solar occultation flux (SOF);
- optical gas imaging (OGI) camera;
- tracer gas;
- reverse dispersion modelling (RDM).

The standard was applicable to petrochemicals, oil refining, and chemical industries receiving, processing, storing, and/or exporting of volatile organic compounds (VOC), and included the emissions of VOC from the natural gas processing/conditioning industry and the storage of natural gas and similar fuels, including methane. All large industrial sources of VOC emitted into the atmosphere were in principle within scope, with the exception of transport.

The validation was carried out across two field campaigns. The first was (by design) at a decommissioned refinery plant which enabled a controlled release facility (CRF) to be deployed emitting known reference fluxes from known locations. Embedding the CRF within the decommissioned plant ensured the standardized method and techniques would be challenged with a realistic measurement scene as the site topography would influence the wind field and therefore flux. The second campaign was carried out at an active refinery where diffuse and fugitive emissions were real, i.e. unknown fluxes from unknown locations. Hence, whilst the first campaign involved absolute comparison to known reference values and allowed biases to be determined, the second campaign was a relative comparison but with real-world diffuse and fugitive emissions.

The example programme that follows has been amended and generalised from the actual validation that was carried out in order to provide broader applicability and a more general example for validating diffuse emission measurement methods.

A.5.2 Structure of validation project

The validation programme is structured as follows:

- WP1a: Collation and review of available technical information and stakeholder consultations;
- WP1b: Specifications for the initial performance requirements of the remote monitoring techniques;
- WP2: Coordination of the field measurement programme;
  - WP2a: Appointment of a field coordinator, initial consultation with suitable candidate industrial site operators, and planning;
  - WP2b: Support for the selection of the first industrial site for the specified field validation programme;
  - WP2c: Objectives and specifications of the second field trial;
- WP3: Meteorological measurements (with wind speed and direction);
- WP4: Optical gas imaging camera suitable for field work;
- WP5: Implementation of the remote monitoring techniques and estimation/calculation methods at a site where a controlled release facility providing VOC emissions can be deployed and operated in the field;
- WP6: Implementation of the remote monitoring technologies and estimation/calculation methods at the second industrial site;
- WP7: Complete evaluation of all the monitoring data available after the field trials, including the LDAR/OGI/Other technology data;
- WP8: Comprehensive specifications of the performance requirements for remote monitoring techniques for use with the standard;
- WP9: Reporting on the validation programme and on progress with the European Standard.

A.5.3 Work programme

A.5.3.1 WP1a: Collation and review of available technical information and stakeholder consultations

This work package entails:

- collation and review of technical information from previous field work using the remote monitoring techniques listed above, with a view to defining an appropriate field validation programme;
- consultation with stakeholders with a view to finalising the scope and methodology of the field validation programme, and of the standard;
- delivery of a report covering a review of the available monitoring techniques, examples of field measurement data, and a comprehensive set of references to the available field work.

A.5.3.2 WP1b: Specifications for the initial performance requirements of the remote monitoring techniques

The initial performance requirements of the remote monitoring techniques are specified based on the review of the previous field work carried out above. The first field campaign is planned to test these initial performance requirements with a view to subsequent recommendations being made for finalisation of the draft standard later in the work programme.

This work package entails:

- report on the initial performance characteristics for the remote monitoring techniques;
- presentation of the initial performance characteristics to the WG;
- WG to agree upon a set of initial performance characteristics for planning for the first campaign.

A.5.3.3 WP2a: Appointment of a field coordinator, initial consultation with suitable candidate industrial site operators, and planning

The role of coordinator is carried out by an organisation that has the project management expertise to act as the coordinator of the field measurements, and the technical expertise to provide advice on relevant field measurement tasks. This work package entails the following:

- project management and technical coordination of the entire validation programme;
- identification and discussions with candidate industrial sites for the first and second campaigns;
- identification of any leak detection and repair (LDAR) programmes at the candidate sites as far as is practical, where the sites have active emissions (this is most relevant to the second campaign);
- where there is an LDAR programme in place it is important for the field coordinator to review the use of the monitoring equipment and its calibrations; it is important that the status and the results of the LDAR programme(s) are made available to the WG for review prior to any field tests being carried out using the remote monitoring techniques;
- technique critique of the results from the two campaigns and appropriate checking to ensure robust conclusions are drawn;
- attendance of the coordinator at working group meetings, ensuring progress is reported and key decisions are made in consultation with the WG.

A.5.3.4 WP2b: Support for the selection of the first industrial site for the specified field validation programme

A site is selected where it is possible to carry out controlled releases of VOC providing known reference fluxes and know locations enabling the biases of the remote monitoring techniques to be determined. It is important for the site to have characteristics commensurate with the type of industrial areas covered under the draft standard (storage / process areas / VOC handling). Even if the site is not fully active, it is important for it to have:

- suitable locations for installation of the controlled release facility and deployment of the remote monitoring techniques; an ideal location would a disused or de-commissioned part of a site with no active VOC handling and/or storage; the whole area is optimally flat for roughly 500 m × 500 m to allow deployment of the monitoring techniques;
- suitable for the deployment of the gas tracer technique;
- ideally a LDAR or VOC emissions programme with results that have demonstrated credibility;
- Suitable locations to deploy the meteorological equipment that is being defined within the validation programme, in order to provide a first assessment of its capabilities;
- supplementary data, (e.g. appropriate meteorological monitoring, passive sampling, canisters for speciated VOC sampling), or locations exist in the industrial site where these can be effectively installed;
- allow for results from the controlled releases to be unambiguous (e.g. it is best if the site is not too structurally complex).

The relevant advantages and limitations of the identified possible first campaign site(s) will be prepared and presented by the validation coordinator to the WG. The initial performance characteristics provide in WP1b are considered when deciding on the site for the first campaign. The decision of the site for the first campaign is made by the WG.

A.5.3.5 WP2c: Objectives and specifications of the second field trial

A site is selected where there are active emissions to atmosphere with relatively complex industrial operating processes where there are different sources of fugitive and diffuse VOC emissions. The following factors are considered in the selection of the second site:

- an established LDAR programme with results that have credibility and can be assessed beforehand by the WG;
- previous OGI data imaging inaccessible emission sources in support of the LDAR programme;
- suitable access for the remote monitoring techniques;
- suitable for the deployment of the gas tracer technique;
- suitable locations to deploy the meteorological equipment;
- supplementary data, (e.g. appropriate meteorological monitoring, passive sampling, canisters for speciated VOC sampling), or locations exist in the industrial site where these can be effectively installed.

The relevant advantages and limitations of the identified possible second campaign site(s) will be prepared and presented by the validation coordinator to the WG. The decision of the site for the second campaign is made by the WG.

A.5.3.6 WP3: Meteorological measurements (with wind speed and direction)

At least four meteorological sensors are deployed at different elevations (up to 15 m) due to the topography of the two campaign sites, and at different locations covering different site areas. The required sensor characteristics include:

- calibrated to a traceable standard;
- accuracy of 0,1 m/s at wind speeds up to about 10 m/s;
- capability to be deployed at different elevations of up to 15 m above the ground.

A portable wind LIDAR to determine a vertical profile in the 40 m to 200 m range is also deployed, which when combined with the meteorological sensors will enable more accurate vertical wind speed profiling.

A.5.3.7 WP4: Selection of optical gas imaging (OGI) camera for campaigns

An optical gas imaging camera is selected from those commercially available. Consideration is given to the most appropriate spectral wavelengths for the selected VOC to be monitored at the campaign sites, and the required plume detection capabilities in the industrial environments.

Specifications for the optical gas imaging camera will be prepared, including requirements for the validation of the method.

This will be implemented at the selected sites to identify significant emission sources and to support effectively the LDAR programme that is in place at these sites.

A.5.3.8 WP5: First field validation campaign

A validation work programme for the first selected campaign site will be specified from the outputs of the work packages above and includes:

- draft first campaign work plan:
    - identification of the location to be used for the controlled release facility, remote monitoring techniques and meteorological equipment;
    - controlled release facility releases of VOC suitable for testing the remote monitoring techniques with release rates up to 50 kg/h (propane equivalent) and controllable down to about 5 kg/h with known release rates; releases are for periods of at least 30 min;
    - tests over a period of three to four days, with at least five releases per day;
    - plan for deployment of OGI camera specified in WP4;
    - plans for processing and analysis of required data, including paying particular attention to assessing the validity of the initial technique performance characteristics identified in WP1b and determining an updated set of performance characteristics for the techniques;
- pre-campaign visit to the site by qualified scientists, and discussions with the plant owners to ensure that the defined validation work programme is practical and achievable during the selected times and within the allocated time scale;
- finalisation of first campaign work plan post site visit;
- execution of first campaign.

The coordinator will prepare a report for the WG containing results and conclusions from the first field validation campaign.

A.5.3.9 WP6: Work programme for second campaign site

A validation work programme for the second selected campaign site is specified from the outputs of the work packages above and includes:

- draft first campaign work plan:
    - identification of the locations to be used for the remote monitoring techniques and meteorological equipment. The areas to be covered are preferably such that a valid measurement of the total fluxes of emissions from the complete industrial plant is achievable;
    - plan for deployment of OGI camera specified in WP4;
    - plans for processing and analysis of required data, in particular comparing the agreement between the techniques to the updated performance characteristics determined from WP5.
- pre-campaign visit to the site by qualified scientists, and discussions with the plant owners, to ensure that the defined validation work programme is practical and achievable during the selected times and within the allocated time scale;
- finalisation of second campaign work plan post site visit;
- execution of second campaign.

The coordinator will prepare a report for the WG containing results and conclusions from the second field validation campaign.

A.5.3.10 WP7: Campaign data analysis

This work package includes the analysis of all the results acquired over the two validation campaigns. This analysis includes:

- critique of LDAR results where available from the two sites;
- summary of lessons learnt from the OGI camera deployment and how the application of this technique might be improved;
- analysis of advantages and limitation of DIAL, SOF, tracer gas and RDM measurements;
- comparison of DIAL, SOF, tracer gas, RDM and site LDAR data;
- identification of possible improvements that could be made to the draft standard.

A.5.3.11 WP8: Defining performance characteristic requirements and uncertainties

This work package includes reviews of the initial performance characteristics from WP1b and defines performance characteristic requirements for each of the techniques from the data from the two campaigns. Consideration is given to how such performance characteristics might change at different industrial sites within the scope of the draft standard and allowance made for this in the requirements.

In addition to the defined performance characteristics requirements, it is also considered if any additional QA/QC are to be added to the draft standard in order to control the technologies within these requirements on an ongoing basis.

This work package, with reference to the performance characteristic requirements, also provides an evaluation of the uncertainties associated with each technology and define an overall maximum permissible uncertainty for each technology.

The coordinator will summarise the above work in a report and present this to the WG.

A.5.3.12 WP9: Reporting on the validation programme

This work package covers the reporting of the validation work. The following reports are included:

- interim month 12 report covering the analysis of the applicability of the selected methods for monitoring the different fugitive and diffuse emission sources, and a definition of the optimum field validation programme;
- interim month 24 report covering:
  - completion of the first field validation programme and its results and conclusions;
  - status of the second field validation programme;
  - summary of progress with the drafting of the standard;
- interim month 36 report covering:
  - completion of the second validation programme together with its results and conclusions;
  - production of performance specifications for the selected methods used;
  - summary of status on the drafting of the standard;
- report on preparation of the standard.

A.5.4 Validation campaign

For finalised performance characteristics, see Table A.10.

Table A.10 — Tested and validated measurement criteria for main equipment, size (10 m to 50 m) × (10 m to 50 m); emission source localization and quantification

Characteristics	DIAL	OGI	RDM	SOF	TC
Limit of quantification, in kg/h	1	Not applicable	5 (1 not tested)	5 (1 not tested)	1
Achieved uncertainty, at 95 % level of confidence, in %	10 to 20	Not applicable	30[a] to 80	33[b]	30[b]
Number of individual observations	4	Not applicable	> 10	12	12
Time period to achieve quantification with the required uncertainty, in h	1	1; localization only	3 to several days	0,5 to 1 on each of 3 separate days	0,5 to 1 on each of 3 occasions

[a] wind speed > 2 m/s, emission rate 10 kg/h.

[b] validated against the measured data, for repeated releases at 10 kg/h.

Annex B
(informative)

Workplace atmospheres

B.1 General

References specific to this annex are given in B.7.

B.2 Introduction

Measurement methods need to fulfil certain requirements stated in International Standards such as ISO 20581. In the course of a method validation, it is determined how those requirements can be obeyed. Some requirements for the measurement methods are universal as for example the relevant minimum measuring range. Other requirements depend on the state in which the analyte is present, e. g. vapour or particulate, and are described in the related international standardizations. The following international standardizations describe the trials needed for validation:

- gases and vapours: ISO 22065, ISO 23320;
- metals and metalloids: ISO 21832;
- mixture of airborne particles and vapour: ISO 23861.

NOTE Terminology used in this annex is defined in ISO 18158.

Measurement methods are developed in accordance to a limit value which determines the relevant minimum measuring range and the concentration levels for the validation trials and is usually between a tenth and twice the limit value (ISO 20581). The majority of measurement methods consists of two parts: sampling and analysis. During the validation process, the sampling conditions are determined. This includes sampling time and a volume flow for active sampling and determined with appropriate sampling pumps in accordance with ISO 13137.

As for the analytical methods, several measurement quantities are determined such as the limit of quantification, recovery, precision and reproducibility. It is necessary to take into account that the range of calibration does not have to match the measuring range, if samples can be diluted. This range of calibration is then used for all further samples.

The method is checked for either interferences with the sampling or analytical process, or both. Interferences that cannot be eliminated are considered in the sample's evaluation.

After the validation process, the expanded uncertainty of measurement needs to be determined. The uncertainty of results includes two main steps, the estimation of the uncertainty components of sampling and analysis. For the estimation of sampling uncertainty components, the uncertainty can be determined in relation to the sample air volume and sampling efficiency according to ISO 22065:2020, Annex C, ISO 23320, ISO 21832 and ISO 23861 depending on the hazardous substance present at the workplace. The combination of the random and non-random uncertainty components for sampling represent the major part in the measurement uncertainty.

The uncertainty components of the analysis cover the entire analytical preparation including sample preparation, if applicable dilution, calibration, recovery and precision. The concentration-dependent uncertainties of analysis according to this Annex are based on the ISO/IEC Guide 98-3.

The combination of all uncertainty contributions leads to combined measurement uncertainties of the expanded procedure. Examples for the calculation of the expanded uncertainty are given in Annexes of the specific International Standard. The relative expanded uncertainty has to meet the requirements stated in ISO 20581.

The measuring procedure is documented in accordance with ISO 20581:2016, Annex A, as a method description.

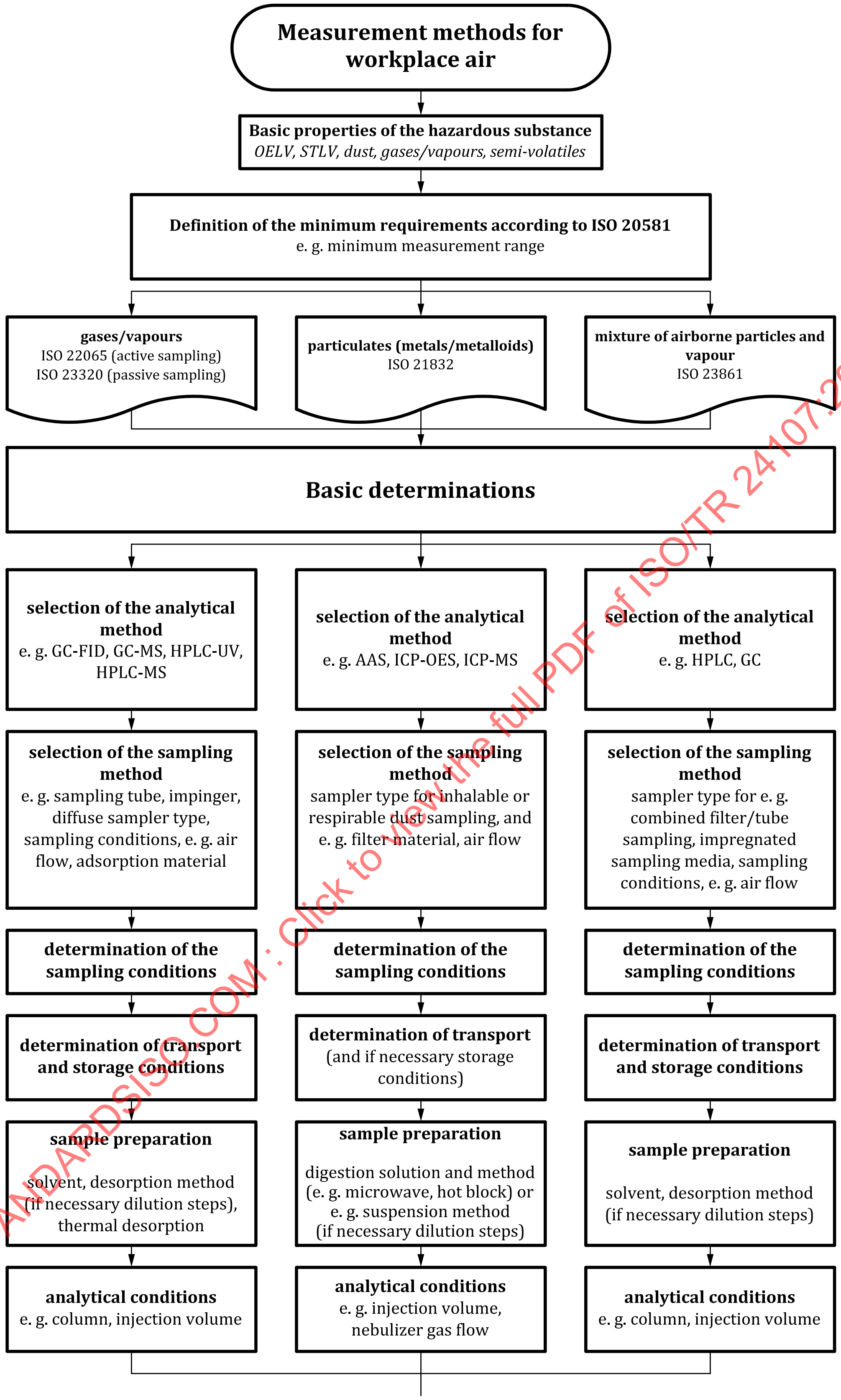
ISO 20581 is based on EN 482 and provides general requirements for the performance of procedures for the measurement of chemical agents. ISO 20581 includes clauses on the following topics:

- method classification (e.g. screening methods versus measurements for compliance with occupational exposure limit values);
- performance requirements (for comparison with occupational exposure limit values, these can include selectivity, measuring range, and acceptable expanded uncertainty, and dimension of result);
- test method;
- validation report;
- annexes on structure of a method description and calculation of measurement uncertainty.

This includes the following considerations:

- carry out measurements at the lower and upper ends of the measuring range, and for at least one intermediate concentration;
- prepare at least six replicate samples for each set of tests and analyse the samples under repeatability conditions;
- calculate the expanded uncertainty;
- carry out further tests, as appropriate, to investigate the influence of interferences and environmental parameters;
- for a measuring procedure consisting of several independent steps, e.g. preparation of equipment, sampling, transport and storage, sample preparation and analysis, each step of the measuring procedure can be tested individually as an alternative to testing the procedure as a whole;
- validation report contains, at a minimum, the test conditions, the results obtained and the extent to which the measuring procedure complies with the requirements of this document (i.e. ISO 20581) and other relevant International Standards or European standards.

A systematic scheme of the validation process for gases and vapours, metals and metalloids and mixture of airborne particles and vapour are given in Figure B.1. Further information for the different types of hazardous substances are given in ISO 23320, ISO 21832:2018 and ISO 23861:2022.


Measurement methods for workplace air
Basic properties of the hazardous substance
OELV, STLV, dust, gases/vapours, semi-volatiles
Definition of the minimum requirements according to ISO 20581
e. g. minimum measurement range
gases/vapours
ISO 22065 (active sampling)
ISO 23320 (passive sampling)
particulates (metals/metalloids)
ISO 21832
mixture of airborne particles and vapour
ISO 23861
Basic determinations
selection of the analytical method
e. g. GC-FID, GC-MS, HPLC-UV, HPLC-MS
selection of the analytical method
e. g. AAS, ICP-OES, ICP-MS
selection of the analytical method
e. g. HPLC, GC
selection of the sampling method
e. g. sampling tube, impinger, diffuse sampler type, sampling conditions, e. g. air flow, adsorption material
selection of the sampling method
sampler type for inhalable or respirable dust sampling, and e. g. filter material, air flow
selection of the sampling method
sampler type for e. g. combined filter/tube sampling, impregnated sampling media, sampling conditions, e. g. air flow
determination of the sampling conditions
determination of the sampling conditions
determination of the sampling conditions
determination of transport and storage conditions
determination of transport (and if necessary storage conditions)
determination of transport and storage conditions
sample preparation
solvent, desorption method (if necessary dilution steps), thermal desorption
sample preparation
digestion solution and method (e. g. microwave, hot block) or e. g. suspension method (if necessary dilution steps)
sample preparation
solvent, desorption method (if necessary dilution steps)
analytical conditions
e. g. column, injection volume
analytical conditions
e. g. injection volume, nebulizer gas flow
analytical conditions
e. g. column, injection volume

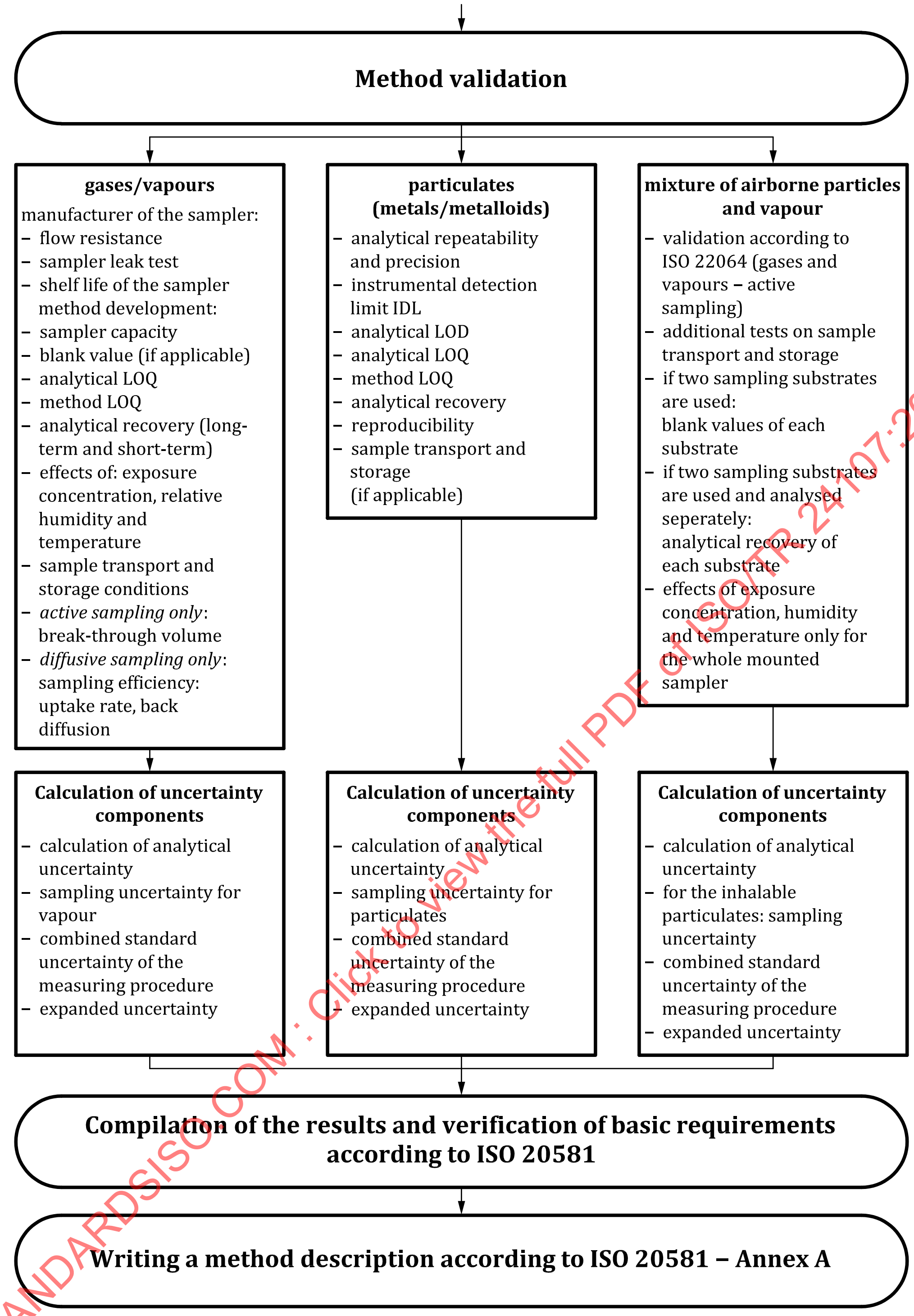


Figure B.1 — Validation scheme for measurement methods for workplace air

The following documents from ISO/TC 146/SC 2 provide additional information:

- ISO 22065 provides requirements evaluation of measuring procedures for gases and vapours using pumped samplers;
- ISO 23320 specifies measuring procedures for gases and vapours using diffusive samplers.

B.3 Validation of a measurement method for metals and metalloids – Description

B.3.1 General

Table B.1 gives an example how to perform experiments for method validation of both sampling and analytical methods for metals and metalloids in workplace air.

Table B.1 — Method validation example (ISO 21832:2018, Annex B)

Objective	Analytes[a]	Determination	Number of samples	Requirements
Analytical repeatability	filter spiked with 0,1; 0,5; 2 OELV 0,5; 2 ST-OELV	standard deviation	6	coefficient of variation less than 5 %
Instrumental detection limit	blank solutions	three times standard deviation (blank calibration standard)	≥ 10	total mass of analyte less than 0,03 OELV
Limit of detection, limit of quantification	blank sample solution with filter	three times (for LOD) and ten times (for LOQ) standard deviation (blank samples or spiked samples at the estimated LOQ)	≥ 10	LOQ less or equal than 0,1 OELV
Analytical recovery (including particle digestion)	filter spiked with 0,1; 0,5; 2 OELV 0,5; 2 ST-OELV	pure compounds	≥ 6	more than 90 %
Reproducibility (including particle digestion)	filter spiked with 0,1 OELV to 2 OELV	a) certified reference material (preferred) b) reference air samples	≥ 6	coefficient of variation less than 5 %
Sample storage[b]	filter spiked with 0,1; 2 OELV	storage test at least for four weeks	≥ 3/day	recovery more than 90 %

[a] OELV 8 h: 0,1; 0,5; 2 OELV for 0,1 OELV × 30 min, 0,5 OELV × 120 min, 2 OELV × 480 min, respectively; ST-OELV: 0,5; 2 ST-OELV for 0,5 ST-OELV × 15 min, 2 ST-OELV × 15 min, respectively.

[b] If necessary, the storage test can be shortened (e.g. for As_2O_3, Cr^{VI}).

B.3.2 Validation according to ISO 21832

The minimum requirements and testing for the determination of metals and metalloids in airborne particles are described in ISO 21832. An example on validation according to ISO 21832 is e. g. described in B.6 for determination of metals and metalloids in airborne particulate matter by inductively coupled plasma atomic emission spectrometry. This validation is described in ISO 15202-3:2004, Clause 10, and applies similarly to other analytical methods for the determination of metals and metalloids, such as atomic absorption spectrometry or inductively coupled plasma mass spectrometry. ISO 15202-2 describes the part sample preparation in detail. ISO 30011 describes in detail the determination of metals and metalloids in airborne particulate matter by inductively coupled plasma mass spectrometry.

Additional documents have been developed by ISO/TC 146/SC 2 for evaluation of measurement methods for workplace air quality.

B.3.3 Detection limits and quantification limits

Factors that can influence LOD and LOQ for metal analysis include the following:

- sampling matrix, e. g. filter, foam or wipe (due to the unknown content of workplace atmospheres, the LOQ can differ for the analysis of real workplace samples);
- sampling volume;

— sample preparation method, e. g. digestion media and volume:
  - analytical wavelength(s) selected (AAS);
  - analytical wavelength(s) selected and, if necessary, adjustments like inter element correction or multi spectral fitting (ICP-AES);
  - analytical mass selected and, if necessary, adjustments like numerical corrections or measurements in kinetic energy discrimination or dynamic reaction cell mode (ICP-MS).

Other parameters based on the instrumentation used, e. g. injection volume for AAS methods or type of spray chamber, nebulizer and flow rates for ICP techniques.

B.3.4 Expanded uncertainty of sampling and analysis methods

It is best if each sampler airborne particle collection stage follows a sampling convention for one of the health-related fractions for the airborne particles, as described in ISO 7708. Aerosol sampling methods have random and non-random uncertainty components that result from how closely the samplers used comply the required sampling convention(s). ISO 21832:2018, Annex C, provides the expanded measurement uncertainty for selected inhalable and respirable samplers as well as estimates for the general use.

A detailed example for estimation of the expanded uncertainty is given in ISO 21832:2018, Annex E.

B.4 Validation of a measurement method for gases/vapours – Description

B.4.1 General

Table B.2 gives an example how to perform experiments for method validation of both sampling and analytical methods for gases and vapours in workplace air.

Table B.2 — Method validation example (ISO 22065:2019, Annex B)

Test	ρLV	t_s in h	v_a	RH in %	ϑ_{at} in °C	n	Requirements
Sampler capacity	2 LV	long-term: reference period + ≥1 h short-term: 2x reference period	recom-mended flow rate	(80 ± 5)	(20 ± 2)	≥3	with two subsequent samplers amount of analyte on back-up sampler ≤ 5 % of total recovered amount
Break-through volume	2 LV	not specified	according to sampler type	(80 ± 5)	(20 ± 2)	≥3	measurement until analyte is detected behind the sampler
Storage conditions	0,1 LV and 2 LV	recom-mended sampling time	recom-mended flow rate	(80 ± 5)	(20 ± 2)	≥6	recovery difference before and after storage less than 10 %.
Analytical quantification limit	[a]	not applicable				10	≤ 0,1 LV for long-term LV ≤ 0,5 LV for short-term LV

[a] Spiked samples near estimated LOQ.

[b] The effect of exposure concentration can typically be calculated from the results of replicate samples taken from a test gas atmosphere (see ISO 22065;2020, 8.3.3.2). The method bias can be calculated as described in ISO 22065;2020, C.5.3.

[c] At least three concentration of measuring range (upper, lower end and intermediate).

Table B.2 *(continued)*

Test	ρLV	t_s in h	ν_a	RH in %	ϑ_{at} in °C	n	Requirements
Analytical recovery (long-term)[b]	0,1 LV up to 2 LV	recommended sampling time	recommended flow rate	not specified		[c]	Type A samplers: *Ran* ≥ 75 % with *Kv* ≤ 10 %
Analytical recovery (short-term)[b]	0,5 LV up to 2 LV	reference period					Type B samplers: *Ran* ≥ 95 % with *Kv* ≤ 10 %
Blank value	unused samplers	not applicable				≥6	see 6.3.2.3
Effect of exposure concentration	0,1 LV; 0,5 LV and 2 LV	recommended sampling time	recommended flow rate	(50 ± 5)	(20 ± 2)	≥6	no specific requirement
Effect of relative humidity	0,1 LV and 2 LV			(20 ± 5) and (80 ± 5)	(20 ± 2)	≥6	no specific requirement
Effect of temperature	2 LV			(50 ± 5)	(10 ± 2) and (40 ± 2)	≥6	no specific requirement

[a] Spiked samples near estimated LOQ.

[b] The effect of exposure concentration can typically be calculated from the results of replicate samples taken from a test gas atmosphere (see ISO 22065;2020, 8.3.3.2). The method bias can be calculated as described in ISO 22065;2020, C.5.3.

[c] At least three concentration of measuring range (upper, lower end and intermediate).

B.4.2 Validation according to ISO 22065

The minimum requirements and testing for the determination of gases and are described in B.2. The validation of gases and vapours is described in Table B.2.

Additional documents have been developed by ISO/TC 146/SC 2 for evaluation of measurement methods for workplace air quality.

B.4.3 Quantification limits

Factors that can influence LOQ for gases and vapours analysis include the following:

- sampling matrix (e.g. activated carbon tube, silica gel tubes, impregnated filters);
- sampling volume;
- sample preparation method, e. g. extraction volume;
- analytical instruments and detectors (e.g. flame ionisation detector (FID), mass selective detector [MSD]).

B.4.4 Expanded uncertainty of sampling and analysis methods

In addition to the components stated in B.2, the uncertainty associated with the influence of the relative humidity and temperature is essential to consider. For pumped samplers the sampling efficiency is assumed to be 100 % if the sample volume is kept below the break-through volume, and therefore the uncertainty of the sampling efficiency is not taken into account.

B.5 Validation of a measurement method for mixtures of airborne particles and vapours (mixed phase aerosols) — Description

B.5.1 General

Table B.3 (taken from ISO 23861) gives an example how to perform experiments for method validation of both sampling and analytical methods for gases and vapours in workplace air.

Table B.3 — Spiking and transfer conditions in function of the required tests and the extraction mode

Tests	Joint extraction		Separate extraction	
	First collection substrate	Subsequent collection substrates	First collection substrate	Subsequent collection substrates
ISO 22065:2019, 8.3.1.2 Sampler capacity	spike & pumping air at (20 ± 2) °C and (80 ± 5) % RH		spike & pumping air at (20 ± 2) °C and (80 ± 5) % RH	
ISO 22065:2019, 8.3.1.6.1 Storage conditions	spike	spike & pumping air at (20 ± 2) °C and (80 ± 5) % RH	spike	spike & pumping air at (20 ± 2) °C and (80 ± 5) % RH
ISO 22065:2019, 8.3.2.1 Limit of quantification	spike & pumping air at (20 ± 2) °C and (50 ± 5) % RH		spike	spike & pumping air at (20 ± 2) °C and (50 ± 5) % RH
ISO 22065:2019, 8.3.2.2 Analytical recovery	spike	spike & pumping air at (20 ± 2) °C and (50 ± 5) % RH	spike	spike & pumping air at (20 ± 2) °C and (50 ± 5) % RH

B.5.2 Validation according to ISO 23861

The tests to be carried out are essentially based on the procedure for the development of measurement methods for gases and vapours according to ISO 22065. The minimum requirements and testing for the determination of gases and are described in ISO 22065.

However, since the substances are not exclusively present as vapour, but rather as a mixture of particles and vapour, the tests are modified accordingly. Possible approaches to sample mixtures of airborne particles and vapour are described in ISO 23861:2022, Annex B.

Since the ratio of vapour to particles is a dynamic equilibrium, the influence of temperature on sampling is taken into account. In the case of polar substances, the humidity can also have a very large influence on the distribution. Special attention is also paid to the behaviour of the semi-volatiles during transport and storage of the samples.

Additional documents have been developed by ISO/TC 146/SC 2 for evaluation of measurement methods for workplace air quality.

B.5.3 Quantification limits

Factors that can influence LOQ for semi-volatiles analysis are similar to the factors of gases and vapours given in B.4.3.

B.5.4 Expanded uncertainty of sampling and analysis methods

Additional to the components stated in B.2, the uncertainty associated with the influence of the relative humidity and temperature are considered. For the collection efficiency, in contrast to the collection of gases and vapours, the influences of the particle collector are also considered. Since particle-vapour mixtures are to be collected as an inhalable fraction, the uncertainty components are given in ISO 21832:2022, Annex C. For the sampling efficiency of the vapour part is assumed to be 100 % if the sample volume is kept below the break-through volume, and therefore the uncertainty of the sampling efficiency for the volatile part of the mixture does not need to be taken into account.

B.6 Example: Validation of ISO 15202-3

B.6.1 Description

This example is based on validation of the method described in ISO 15202-1, ISO 15202-2 and ISO 15202-3, for determination of metals and metalloids in airborne particulate matter by inductively coupled plasma atomic emission spectrometry. This validation is described in B.6.2 and in ISO 15202-3:2004, Clause 10.

Additional documents have been developed by ISO/TC 146/SC 2 for evaluation of measurement methods for workplace air quality.

B.6.2 Validation details

B.6.2.1 Method detection limits and quantification limits

Factors that can influence limit of detection (LOD) and limit of quantification (LOQ) for inductively coupled plasma atomic emission spectrometry (ICP-AES) include the following:

- sampling matrix (e.g. filter or wipe);
- sample preparation method (several options are provided in ISO 15202-2);
- analytical wavelength(s) selected;
- other parameters based on the instrumentation used.

The validation of ISO 15202 was based on mixed cellulose ester filters and a sampling flow rate of 2 l/min (ISO 15202-1) and the closed-vessel microwave procedure in ISO 15202-2. Ten blank test solutions were prepared from unused filters using the closed-vessel microwave procedure, and then analysed in accordance with ISO 15202-3. LOD and LOQ values were determined for 18 metals and metalloids.

B.6.2.2 Overall uncertainty of sampling and analysis methods

Method validation for ISO 15202 was performed by the U.K. Health and Safety Laboratory [94]. Laboratory experiments were performed, and uncertainty from the analytical measurements (using the draft of ISO 15202-3 available at the time) was combined with uncertainty from the sampling method (utilising ISO 15202-1:2000) and sample preparation (utilising ISO 15202-2:2001). The combined uncertainty was compared with requirements in EN 482 using the protocol for metals and metalloids found in EN 13890. For comparison with occupational exposure limit values (OELV), the upper limits of measurement uncertainty are 50 % for measurements between 0,1 and 0,5 times the OELV, and 30 % for measurements between 0,5 and 2,0 times the limit value.

The overall uncertainty data are depicted in Table B.4 and Table B.5 (taken from Reference [94]). Comparisons with the EH 40/2002 [95] short-term and long-term exposure limits are provided in these tables. The requirements of EN 482 were met for all measurements involving comparisons with short-term exposure limits (STEL), and in most cases involving comparison with OELV based on an 8 h time weighted average concentration (TWA) and a sampling period of 30 min. In a few cases, a sampling period of 2 h was required to meet the EN 482 criteria; these included arsenic, selenium and tellurium in comparison with U.K. EH 40/2002 limit values.

Table B.4 — Overall uncertainty of measurements for comparison with EH 40/2002 short-term exposure limits[a]

Substance	Air concentration	Sample mass in µg	Analytical precision	Overall uncertainty for analytical bias		
				0 %	5 %	10 %
Cadmium oxide, fume	0,1 × OELV 0,5 × OELV	0,075 0,375	4,0 % 3,1 %	18,2 % 17,3 %	23,0 % 22,0 %	27,7 % 26,8 %
	0,5 × OELV 2 × OELV	0,375 1,5	2,8 % 2,6 %	17,0 % 16,7 %	21,7 % 21,5 %	26,5 % 26,2 %
Indium and compounds	0,1 × OELV 0,5 × OELV	0,9 4,5	6,7 % 4,2 %	22,0 % 18,5 %	26,7 % 23,2 %	31,5 % 28,0 %
	0,5 × OELV 2 × OELV	4,5 18	4,2 % 2,8 %	18,5 % 17,0 %	23,2 % 21,7 %	28,0 % 26,5 %
Iron oxide, fume	0,1 × OELV 0,5 × OELV	30 150	2,8 % 1,4 %	16,9 % 15,9 %	21,7 % 20,7 %	26,4 % 25,4 %
	0,5 × OELV 2 × OELV	150 600	1,4 % 0,8 %	15,9 % 15,7 %	20,7 % 20,4 %	25,4 % 25,2 %
Manganese, fume	0,1 × OELV 0,5 × OELV	9 45	1,2 % 0,6 %	15,8 % 15,6 %	20,5 % 20,4 %	25,3 % 25,1 %
	0,5 × OELV 2 × OELV	90 180	0,6 % 0,3 %	15,6 % 15,6 %	20,4 % 20,3 %	25,1 % 25,1 %
Tin compounds, inorganic	0,1 × OELV 0,5 × OELV	12 45	5,5 % 2,9 %	20,2 % 17,0 %	24,9 % 21,8 %	29,7 % 26,5 %
	0,5 × OELV 2 × OELV	60 240	2,9 % 1,7 %	17,0 % 16,1 %	21,8 % 20,8 %	26,5 % 25,6 %
Yttrium	0,1 × OELV 0,5 × OELV	9 45	2,0 % 1,5 %	16,3 % 16,0 %	21,1 % 20,7 %	25,8 % 25,5 %
	0,5 × OELV 2 × OELV	45 180	1,5 % 1,2 %	16,0 % 15,8 %	20,7 % 20,6 %	25,5 % 25,3 %
Zinc oxide, fume	0,1 × OELV 0,5 × OELV	30 150	2,0 % 0,8 %	16,3 % 15,7 %	21,0 % 20,4 %	25,8 % 25,2 %
	0,5 × OELV 2 × OELV	150 600	0,8 % 0,4 %	15,7 % 15,6 %	20,4 % 20,3 %	25,2 % 25,1 %

[a] Sampling time was 15 min.

Table B.5 — Overall uncertainty of measurements for comparison with EH 40/2002 long-term exposure limits

Substance	Air concentration	Sampling time	Sample mass (µg)	Analytical precision	Overall uncertainty for analytical bias		
					0 %	5 %	10 %
Antimony and antimony compounds	0,1 × OELV	30 min	3	4,0 %	18,3 %	23,0 %	27,8 %
	0,5 × OELV	8 h	240	0,5 %	15,6 %	20,3 %	25,1 %
	0,5 × OELV	30 min	15	1,9 %	16,2 %	21,0 %	25,7 %
	2 × OELV	8 h	960	0,3 %	15,6 %	20,3 %	25,1 %
Arsenic and compounds	0,1 × OELV	30 min [a]	0,6	18,4 %	43,2 %	47,9 %	52,7 %
	0,1 × OELV	2 h	2,4	9,2 %	26,2 %	30,9 %	35,7 %
	0,5 × OELV	8 h	48	2,1 %	16,3 %	21,1 %	25,8 %
	0,5 × OELV	30 min [a]	3	8,2 %	24,5 %	29,3 %	34,0 %
	0,5 × LV	2 h	12	4,1 %	18,4 %	23,1 %	27,9 %
	2 × OELV	8 h	192	1,0 %	15,7 %	20,5 %	25,2 %
Beryllium and beryllium compounds	0,1 × OELV	30 min	0,012	4,9 %	19,4 %	24,2 %	28,9 %
	0,5 × OELV	8 h	0,96	3,2 %	17,3 %	22,1 %	26,8 %
	0,5 × OELV	30 min	0,06	4,2 %	18,5 %	23,2 %	28,0 %
	2 × OELV	8 h	3,84	2,8 %	16,9 %	21,7 %	26,4 %
Cadmium and compounds	0,1 × OELV	30 min	0,15	4,0 %	18,2 %	23,0 %	27,7 %
	0,5 × OELV	8 h	12	2,1 %	16,3 %	21,1 %	25,8 %
	0,5 × OELV	30 min	0,75	2,8 %	17,0 %	21,7 %	26,5 %
	2 × OELV	8 h	48	1,7 %	16,1 %	20,8 %	25,6 %
Chromium metal, Cr(II) and Cr(III) compounds	0,1 × OELV	30 min	3	3,1 %	17,2 %	21,9 %	26,7 %
	0,5 × OELV	8 h	240	0,7 %	15,6 %	20,4 %	25,1 %
	0,5 × OELV	30 min	15	1,7 %	16,1 %	20,9 %	25,6 %
	2 × OELV	8 h	960	0,4 %	15,6 %	20,3 %	25,1 %
Cobalt and cobalt compounds	0,1 × OELV	30 min	0,6	4,7 %	19,2 %	23,9 %	28,7 %
	0,5 × OELV	8 h	48	1,2 %	15,8 %	20,5 %	25,3 %
	0,5 × OELV	30 min	3	2,8 %	17,0 %	21,7 %	26,5 %
	2 × OELV	8 h	192	0,7 %	15,6 %	20,4 %	25,1 %
Copper, fume	0,1 × OELV	30 min	1,2	4,0 %	18,2 %	23,0 %	27,7 %
	0,5 × OELV	8 h	96	1,6 %	16,0 %	20,8 %	25,5 %
	0,5 × OELV	30 min	6	2,8 %	17,0 %	21,7 %	26,5 %
	2 × OELV	8 h	384	1,2 %	15,8 %	20,6 %	25,3 %
Indium and compounds	0,1 × OELV	30 min	0,6	7,5 %	23,3 %	28,1 %	32,8 %
	0,5 × OELV	8 h	48	2,1 %	16,4 %	21,1 %	25,9 %
	0,5 × OELV	30 min	3	4,7 %	19,2 %	23,9 %	28,7 %
	2 × OELV	8 h	192	1,4 %	15,9 %	20,7 %	25,4 %
Iron oxide, fume	0,1 × OELV	30 min	30	2,8 %	16,9 %	21,7 %	26,4 %
	0,5 × OELV	8 h	2400	0,4 %	15,6 %	20,3 %	25,1 %
	0,5 × OELV	30 min	150	1,4 %	15,9 %	20,7 %	25,4 %
	2 × OELV	8 h	9600	0,2 %	15,6 %	20,3 %	25,1 %
Lead and compounds (except lead alkyls)	0,1 × OELV	30 min	0,9	9,4 %	26,6 %	31,4 %	36,1 %
	0,5 × OELV	8 h	72	1,3 %	15,9 %	20,6 %	25,4 %
	0,5 × OELV	30 min	4,5	4,5 %	18,9 %	23,7 %	28,4 %
	2 × OELV	8 h	288	0,7 %	15,6 %	20,4 %	25,1 %
Manganese, fume	0,1 × OELV	30 min	6	1,4 %	15,9 %	20,7 %	25,4 %
	0,5 × OELV	8 h	480	0,2 %	15,6 %	20,3 %	25,1 %
	0,5 × OELV	30 min	30	0,7 %	15,6 %	20,4 %	25,1 %
	2 × OELV	8 h	1920	0,1 %	15,5 %	20,3 %	25,0 %

[a] EN 482 requirements not met (uncertainty ≤50 % for measurements between 0,1 and 0,5 times the OELV, and ≤30 % for measurements between 0,5 and 2,0 times the OELV).

Table B.5 *(continued)*

Substance	Air concentration	Sampling time	Sample mass (µg)	Analytical precision	Overall uncertainty for analytical bias		
					0 %	5 %	10 %
Nickel and insoluble compounds	0,1 × OELV	30 min	3	5,4 %	20,1 %	24,8 %	29,6 %
	0,5 × OELV	8 h	240	0,9 %	15,7 %	20,5 %	25,2 %
	0,5 × OELV	30 min	15	2,8 %	17,0 %	21,7 %	26,5 %
	2 × OELV	8 h	960	0,5 %	15,6 %	20,4 %	25,1 %
Selenium and compounds	0,1 × OELV	30 min[a]	0,6	16,9 %	40,4 %	45,1 %	49,9 %
	0,1 × OELV	2 h	2,4	8,6 %	25,2 %	30,0 %	34,7 %
	0,5 × OELV	8 h	48	2,0 %	16,3 %	21,0 %	25,8 %
	0,5 × OELV	30 min[a]	3	7,7 %	23,7 %	28,5 %	33,2 %
	0,5 × OELV	2 h	12	2,8 %	17,0 %	21,7 %	26,5 %
	2 × OELV	8 h	192	1,0 %	15,7 %	20,5 %	25,2 %
Tellurium and compounds	0,1 × OELV	30 min[a]	0,6	29,8 %	65,6 %	70,3 %	75,1 %
	0,1 × OELV	2 h	2,4	13,4 %	33,7 %	38,5 %	43,2 %
	0,5 × OELV	8 h	48	2,4 %	16,6 %	21,3 %	26,1 %
	0,5 × OELV	30 min[a]	3	11,8 %	30,8	35,5 %	40,3 %
	0,5 × OELV	2 h	12	5,3 %	19,9	24,7 %	29,4 %
	2 × OELV	8 h	192	1,1 %	15,8	20,5 %	25,3 %

[a] EN 482 requirements not met (uncertainty ≤50 % for measurements between 0,1 and 0,5 times the OELV, and ≤30 % for measurements between 0,5 and 2,0 times the OELV).

Annex C
(informative)

Ambient atmospheres

C.1 General

This annex provides information about aspects of the validation of ambient air measurement methods. Analysis of ambient air uses instrument-based measurements of compounds or electron microscopy methods involving the counting of inorganic fibres. These two groups of analyses have different criteria for validation as described in the following sections.

C.2 Example of an instrument-based method: ISO 13964

C.2.1 Repeatability

Studies have shown that for UV photometric ozone calibrations the repeatability can be as low as ±1 % or $\pm 1 \times 10^{-9}$ when expressed as a volume fraction, whichever is greater, if care is taken in operating the system. Even though there are some variabilities associated with the ambient analyser and calibration system, it is expected that the repeatability of the ozone analysis of ambient air can be within ±3,5 % [96].

C.2.2 Accuracy

The accuracy of the method is estimated to be better than ±4 % of the measured concentration.

The accuracy of the ambient ozone UV photometric method will be dependent on the accuracy of the procedure to which it is referenced. The accuracy of the UV photometer primary reference procedure will be limited by the accuracy of the coefficient of absorption (±1,5 %) and the measurements of the UV transmittance, pressure, temperature, ozone losses, etc. [97]. When a secondary reference procedure is used, additional inaccuracies inherent to the procedure will be introduced.

C.2.3 Continuing validation

The ozone absorption cross section in wide use, including in ISO 13964, was determined to be higher than the more recently determined value [98]. This newly published value, referred to as the CCQM.O3.2019 value, for the ozone absorption cross-section per molecule is $1{,}132\,9(35) \times 10^{-17}$ cm^2 and is recommended based on statistical analysis of the weighted data. This new cross-section value is 1,23 % lower and its uncertainty sixfold smaller than the uncertainty of the conventionally accepted reference value reported by Hearn, and currently referenced in International Standards. The CCQM.O3.2019 value has been adopted by the international metrology community, through CCQM recommendation 1 (2020), as the value for the ozone absorption cross-section per molecule at 253,65 nm (air) for use in ozone measurement standards maintained at the BIPM and for the calculation of the reference value for the BIPM.QM-K1 on-going comparison of surface ozone measurement standards, used to establish uniform measurements of surface ozone worldwide, ensuring SI traceability of these measurements highest accuracy achievable. ISO 13964 is being revised to replace the older ozone absorption cross-section per molecule with the newer value of $1{,}132\,9(35) \times 10^{-17}$ cm^2.

C.3 Electron microscopy methods

C.3.1 General

Most electron microscopy methods for ambient air measurements pertain to “asbestos”. These elongated mineral particles are referred to as “fibres” or “structures” in the ISO methods developed by ISO/TC 146/SC 3. “Fibers” and “structures” will be considered equivalent during discussions in this annex.

C.3.2 Validation challenges of electron microscopy methods

Several characteristics of electron microscopical analysis make rigorous validation difficult.

C.3.2.1 Statistical considerations for particle-counting results

Airborne particles deposited on filters are not usually uniformly distributed across the filter surface. Distribution generally follows a Poisson distribution and this is factored in when evaluating structure counts. At high structure counts, where there are adequate numbers of structures per grid opening to allow a sample estimate of the variance to be made, the distribution can be approximated to a Gaussian, with independent values for the mean and variance. Where the sample estimate of variance exceeds that implicit in the Poissonian assumption, use of Gaussian statistics with the variance defined by the actual data is the most conservative approach to calculation of confidence intervals (see ISO 10312:2019, Annex F).

An assumption is made that airborne fibres collected on a filter are an accurate representation of the particle population in the air at the time and place of sample collection. This has not been validated and can be an additional source of uncertainty when fibre counts per surface area are converted to fibre counts per volume of air.

Determining mass of asbestos typically adds variability to the fibre count because it relies on individual fibre dimensions. Small differences in fibre dimensions are amplified because the mass is a derived by multiplying three dimensions (length × width × width). Thus, a fibre with a length of 5 µm and a width of 0,5 µm will have a mass four times greater than a fibre that is only twice as big (5 µm × 1,0 µm). If the diameter distribution is narrow, such as that found in a dispersion of chrysotile fibrils, the mass concentration can be measured with approximately the same precision as that of the numerical concentration. If the diameter distribution is broad, mass concentration estimates derived from TEM examinations to determine numerical concentrations are statistically unreliable (see ISO 13794:2019, D.6).

C.3.2.2 Electron microscopy method bias

Microscope operating conditions such as resolution can affect the ability to correctly detect and identify fibres. This is usually controlled by microscope adjustments to standardized conditions and monitored by comparison between microscopes in the same laboratory and by interlaboratory studies.

C.3.2.3 Reference materials

Reference materials for asbestos analysis have typically been processed ore samples of commercial asbestos and have been most useful in validating the optical properties (polarized-light microscopy) and elemental and crystalline properties (electron microscopy) of the different asbestos types. These reference materials have also been used to synthesize bulk samples with known asbestos mass concentrations for use in quality-control validation and for interlaboratory proficiency testing [103]. ISO/TC 146/SC 3/WG 1 has determined that standard traceable reference materials previously available from national standards organizations (USA-NIST and UK-HSE) for microscopical asbestos analysis have been exhausted or are at very limited supply [100]. Other potential asbestos reference materials are available but most lack funding for proper standard reference characterization and distribution. There is a small program for the characterization of new asbestos reference materials on-going through the Research Triangle Institute in North Carolina, United States [101].

There are no reference materials that relate directly to concentrations of asbestos in the air. Thus, there is no accepted reference material suitable for determining the bias (accuracy) of an air test method for asbestos.