Performance standard for laboratories carrying out testing of samples from stack emissions monitoring

Environment Agency
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Version 3

mCERTS
THE ENVIRONMENT AGENCY'S MONITORING CERTIFICATION SCHEME

Record of amendments

Version 1 January 2017

Version 2 September 2017

- Amended some performance targets in Annex A
- Minor corrections to text
- Rewrite of clause 5.4.5.2 and 5.4.5.3 to add clarity

Version 3 November 2018

- Document reformatted and reordered to comply with changes to ISO 17025

Status of this document

This standard may be subject to review and amendment following publication. The most recent version is available on our website at:www.mcerts.net

Foreword

We set up our Monitoring Certification Scheme (MCERTS) to ensure good quality environmental measurements. The scheme is based on international standards and provides for the product certification of instruments, the competency certification of personnel and the accreditation of laboratories.

This document focuses on what you must do if you want to get accreditation to MCERTS to analyse samples that have been taken to monitor pollution released from chimney stacks.

Under MCERTS, laboratories must be accredited by the United Kingdom Accreditation Service (UKAS) to show they have reached the standard set out in this document. The standard focuses on how you should carry out and report analytical results for the stack emissions samples that you analyse.

Skilled people must carry out the work using internationally recognised methods.

You must report on the work you have done, using the format we ask you to.

The benefits of this MCERTS standard are:

- It makes sure that information on pollution released from chimney stacks is reliable.
- Everybody in performing testing of samples taken for monitoring pollution from chimney stacks will be working towards the same standard.
- It sends a message that performing chemical testing of samples taken for measuring pollution from chimney stacks is an important part of producing reliable information for regulatory purposes.
- By setting quality standards, which everybody must work towards, the standard promotes and raises the professional reputation of people and organisations involved in performing chemical testing of samples taken for monitoring pollution from chimney stacks.

If you have any questions regarding the accreditation process, or would like further information on how to apply, please contact:

UKAS
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TW18 3HR

Telephone: 01784 429000

Email: info@ukas.com

You can get more information on MCERTS, including the standards related to monitoring pollution from chimney stacks, from our website at www.mcerts.net.

If you have any general questions about MCERTS, please contact our National Customer Contact Centre: enquiries@environment-agency.gov.uk

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Introduction

Manual stack emission monitoring for regulatory purposes includes measurements for:

- determining compliance with numerical limits in permits
- calibration of continuous emission monitoring systems (CEMs)
- field testing of CEMs for type approval
- acceptance trials on new pollution abatement plant or alternative fuel applications
- determining emission factors for use in emissions trading and inventory reporting

Note 1: Stack emission monitoring is a general term used to describe the preparation work prior to a measurement campaign, undertaking the site work, calculating the monitoring results and producing the final report for the client. In most cases the client is a process operator.

The extension of MCERTS to include testing of samples taken from manual stack emission monitoring is built on proven international standards to ensure good quality monitoring data. The scheme requires accreditation of laboratories to this MCERTS performance standard.

Note 2: Testing can include the chemical analysis of determinands in solutions, solid absorbents and in particulate form. It also includes the gravimetric analysis of particulates.

The general requirements for the competence of testing laboratories are described in the International Standard EN ISO/IEC 17025. This contains all the requirements laboratories have to meet if they wish to demonstrate that they operate a suitable quality system, are technically competent, and are able to generate technically valid results.

This MCERTS performance standard provides criteria for the application of EN ISO/IEC 17025 in the specific field of performing testing of samples taken from monitoring of emissions from stationary sources (for example, chimney stacks).

The structure of this document follows that of EN ISO/IEC 17025. This standard does not re-state the provisions of EN ISO/IEC 17025. Laboratories are reminded of the need to comply with all the relevant criteria detailed in EN ISO/IEC 17025.

1 Scope

The manual monitoring of stack emissions can involve taking samples for laboratory analysis. Its primary use is for regulatory purposes, including measurements for determining compliance with authorised numerical limits, calibrating continuous emission monitoring systems and acceptance trials on new pollution abatement plant.

Note: This document applies to laboratory analysis. Generally, a separate organisation to the analytical laboratory will perform the sampling, which means organisations may have accreditation for either sampling or analysis. However, some organisations may have accreditation for both.

The monitoring of emissions from stationary sources is undertaken for a wide range of substances using various methods. Technical Guidance Note M2 provides details of methods and specific analytical requirements.

Accreditation of laboratories to this performance standard will demonstrate that they meet our MCERTS requirements for performing analysis of samples taken by stack emissions monitoring organisations.

The Environment Agency has an agreement with UKAS regarding the operation of MCERTS for performing analysis for samples taken from manual stack emissions monitoring. This agreement allows us to use information supplied by UKAS, as part of our regulatory duties.

The Environment Agency may carry out its own inspections and investigations and act upon their findings for laboratories accredited to ISO/IEC17025 for this MCERTS performance standard.

2 References

EN ISO/IEC 17025 “General requirements for the competence of testing and calibration laboratories”

Technical Guidance Note M2, Monitoring of stack emissions to air, Environment Agency

“A Manual on Analytical Quality Control for the Water Industry”, R V Cheeseman and A L Wilson, revised by M J Gardner, NS 30, Water Research Centre, 1989. ISBN 0-902156-85-3

International vocabulary of metrology – Basic and general concepts and associated terms (VIM 2012) 3rd edition

3 Terms and definitions

Batch – A number of samples prepared for a discrete analytical run.

Bias – Bias, which may be positive or negative is the difference (expressed as a percentage) between the mean of a number of determinations obtained under repeatability conditions and the true or accepted concentration.

$$\%\text{Bias} = \frac{(\text{mean of determinations} - \text{true or accepted value}) \times 100}{\text{True or accepted value}}$$

Bias can be estimated where appropriate certified reference materials are available and a stated (certified) concentration has been quoted. Recovery data can be used to estimate bias via spiking experiments.

Certified Reference Material (CRM) – Reference material, accompanied by a certificate, one or more of whose property values are certified by a procedure, which establishes its traceability to an accurate realisation of the unit in which the property values are expressed, and for which each certified value is accompanied by an uncertainty at a stated level of confidence. [ISO/IEC-Guide 30]

Competent authority – The organisation responsible for implementing environmental legislation, for example, the Environment Agency in England.

Concentration – Concentration is usually expressed as mass per sample, for example mass per volume (µg/l).

Critical level of interest – The concentration value around which a decision is often required, for example is the concentration above or below a certain value. A method is usually deemed acceptable if, when used properly, it is capable of establishing within defined limits of bias and precision, whether a concentration is above or below the critical level of interest. This is generally the Emission Limit Value for the pollutant.

Determinand – Within the sample, this is the measurand, analyte, substance, or group of substances, the concentration of which needs to be determined. It shall be clearly and unambiguously defined.

Laboratory – A laboratory, or sub-contracted laboratory, that undertakes the analysis of samples.

Limit of detection (LOD) – Measured quantity value, obtained by a given measurement procedure, for which the probability of falsely claiming the absence of a component in a material is β, given a probability α of falsely claiming its presence [VIM 2012].

Method Implementation Document – Document published by the Environment Agency outlining its interpretation of a method.

Performance characteristics – Those performance values, such as precision, bias (or recovery, as appropriate) and limit of detection that need to be estimated before a method is used routinely.

Periodic measurement (manual measurement) – Measurement of a determinand at specified time intervals. The specified time intervals can be regular (for example, once every month) or irregular. Determinands can include the amount, quantity or physical property of an emission. Measurements are usually made using portable equipment for typically less than 24 hours.

Precision – This is the distribution of a number of repeated determinations, expressed in this document as the percentage relative standard deviation (RSD).

$$\%RSD = \frac{S \times 100}{M}$$

Where S = total standard deviation, M is the mean of results

Reference method – Measurement method taken as a reference by convention, which gives, or is presumed to give, the accepted reference value of the determinand. These methods are listed in TGN M2.

Note: The method is a standard reference method if it is prescribed by European legislation.

Sample – That (uniquely identified) material removed from a site and submitted to the laboratory for analysis.

Stack – Structure through which waste gas is released to atmosphere. Stacks are intended to be of sufficient height to adequately disperse emissions in the atmosphere. Measurement of emissions may be carried out in ducts and stacks.

Stack emission monitoring organisations – Organisations that undertake the measurement of emissions to air from stationary sources. This can include work undertaken at the laboratory's permanent facilities, at sites away from their permanent facilities and in temporary or mobile laboratories.

Standard reference method – see reference method.

Statistical control – When the result or results of quality control samples are shown to be within defined limits of recognised acceptability, a method is said to be in statistical control. When these limits are breached, the method is considered out of control.

Technical procedure (operating procedure) – The organisation's detailed written procedures on how to perform a method in line with its quality system.

Testing laboratory – A laboratory that performs tests. A testing laboratory may undertake work at permanent facilities, at sites away from their permanent facilities and in temporary or mobile laboratories. The sampling and analysis stages may occur at different locations.

UKAS – The United Kingdom Accreditation Service, the body appointed by the Government to assess and accredit organisations that provide testing services to international standards, for example EN ISO/IEC 17025.

4 General requirements

4.1 Impartiality

4.1.1 No additional requirements to EN ISO/IEC 17025.

4.1.2 No additional requirements to EN ISO/IEC 17025.

4.1.3 Performing analysis of samples taken from stack emissions monitoring shall be carried out by a laboratory that is free from any commercial, financial and other pressures that might influence their technical judgement.

Process operators using in-house analysis shall have management structures that ensure this requirement is met.

4.1.4 – 4.1.5 No additional requirements to EN ISO/IEC 17025.

4.2 Confidentiality

No additional requirements to EN ISO/IEC 17025.

5 Structural requirements

Accreditation is through a programme of assessments carried out by UKAS.

Note UKAS assessments may be complemented by a programme of Environment Agency audits.

Some audits and assessments are carried out on an ’unannounced` basis. Laboratories shall co-operate with these events.

5.1 – 5.3 No additional requirements to EN ISO/IEC 17025.

5.4 For data to be submitted to the Environment Agency for regulatory purposes, the organisation shall carry out its sampling and testing activities in such a way as to meet the requirements of this performance standard.

5.5 – 5.7 No additional requirements to EN ISO/IEC 17025.

6 Resource requirements

6.1 General

No additional requirements to EN ISO/IEC 17025.

6.2 Personnel

No additional requirements to EN ISO/IEC 17025.

6.3 Facilities and environmental conditions

6.3.1 Equipment, reagents and samples shall be protected from damage or degradation, during collection, transportation and subsequent storage, as appropriate.

Note: There may be methods specifying the procedures necessary for protecting the integrity of samples and reagents during transportation and storage, such as collection into suitable containers and storage out of direct sunlight at specified temperatures.

The laboratory shall have procedures in place and use appropriate practices to ensure that conditions do not adversely affect the measurement result.

The laboratory shall ensure that requirements for monitoring, controlling and recording environmental conditions pertaining to the specific requirements in reference standard methods are met.

6.3.2 – 6.3.5 No additional requirements to EN ISO/IEC 17025.

6.4 Equipment

6.4.1 – 6.4.5 No additional requirements to EN ISO/IEC 17025.

6.4.6 Equipment shall be calibrated, and if appropriate with each batch of samples, using measurement standards that are traceable to national or international standards, except where they have been derived from natural physical constants, or where this degree of traceability is not possible.

6.4.7 For instrumental methods, calibration solutions may be taken through the entire method or be prepared solely for the determination stage. In either case, solutions shall be matched to the sample extract solution to be determined, both in terms of acid strength and content or solvent composition. In addition, the calibration shall cover the range of interest for the samples being analysed, and should, ideally, be linear over that range. At least 3 calibration points (not including the calibration blank) are required, but more shall be necessary for a non-linear calibration.

At least one blank sample shall be taken through the entire analytical system with each batch of samples. Laboratories shall demonstrate, according to written procedures, how the results obtained from blank samples are utilised. Blank sample results that show evidence of contamination shall be investigated and may require the analysis of the entire batch of samples to be repeated. This may not be appropriate for some determinations.

6.4.8 No additional requirements to EN ISO/IEC 17025.

6.4.9 The response of instruments may fall due to, for example, deterioration in a detector. This may not be immediately obvious from internal quality control sample results but might coincide with deterioration in both precision and limit of detection of the analytical system. The initial calibration shall, therefore, meet with appropriate predefined system suitability limits. Examples include the use of peak area or signal to noise ratio and for chromatographic methods criteria for acceptable peak shape and peak resolution for closely eluting peaks.

6.4.10 Confirmation of the continuing validity of calibration shall be achieved by analysis of calibration check standards regularly throughout the analytical batch according to a defined procedure. The instrument shall not be recalibrated using the check standard. If a check standard fails to meet appropriate predefined limits the cause shall be investigated and if necessary the instrument shall be fully recalibrated and affected samples reanalysed.

System suitability checks shall be carried out as quality control measures to ensure acceptable performance of an analytical system. Where appropriate the results of these checks shall be recorded and monitored. Laboratories shall have fully documented procedures of actions to be taken when system suitability checks fail assigned control limits, measures may include recalibration of the analytical instrument. Procedures should be in place to

assess trends, and take action where appropriate. Examples are: desorption efficiency checks and calibration drift standards.

All quality control requirements and quality assurance criteria prescribed in standard methods shall be undertaken

6.4.11 – 6.4.13 No additional requirements to EN ISO/IEC 17025.

6.5 Metrological traceability

No additional requirements to EN ISO/IEC 17025.

6.6 Externally provided products and services

No additional requirements to EN ISO/IEC 17025.

7 Process requirements

7.1 Review of requests, tenders and contracts

7.1.1 The requirements of the methods to be used shall be clearly and unambiguously defined and documented. The laboratory shall demonstrate that the requirements of the methods to be used shall be understood by those who undertake the analysis.

Note: The laboratory may or may not be aware that the data it generates will be submitted to the Environment Agency for regulatory purposes. However, the laboratory's customer or procurer of the analytical service should be aware that if it wishes to submit the data for regulatory purposes, then the requirements of this performance standard need to be satisfied.

The appropriate test method shall be selected and shall satisfy the requirements of this performance standard.

An important requirement of the contract review process is liaison with the sampling team to confirm the fitness for purpose of the analytical laboratory's method for any given determinand in terms of LOD and performance at the critical level of interest. This will include an understanding of the likely sample volume to be taken and any details related to the process to be monitored that may affect the measurement.

A laboratory may sub-contract testing of stack emissions monitoring samples to another laboratory. It is the responsibility of the laboratory to ensure that the sub-contracted laboratory is registered under MCERTS for the scope of work sub-contracted. The provisions of this clause do not apply to samples submitted to a laboratory by an external quality control or inter-laboratory proficiency-testing scheme organiser.

7.1.2 – 7.1.8 No additional requirements to EN ISO/IEC 17025.

7.2 Selection, verification and validation of methods

7.2.1 Selection and verification of methods

7.2.1.1 The laboratory shall demonstrate and provide justification that suitable methodology (including sample pre-treatment and preparation) has been used in the analysis of a particular matrix and determinand that it is appropriate with

respect to the concentration of the determinand in the sample. The laboratory shall demonstrate and provide justification that method validation procedures have been undertaken in such a manner as is appropriate to the sample matrix undergoing analysis. Full details of the method and method validation procedures shall be made available to the Environment Agency if requested.

7.2.1.2 – 7.2.1.3 No additional requirements to EN ISO/IEC 17025.

7.2.1.4 A list of acceptable analytical methods is given in TGN M2. Method Implementation Documents (MIDs), where provided, give details on how these methods shall be used for regulatory monitoring and subsequent analysis.

Note: MIDs are produced, where necessary, by the Environment Agency.

If the laboratory uses a method that is not listed within TGN M2, then the laboratory shall justify the use of the alternative. Any alternative methods shall be within the laboratory's scope of accreditation, whilst the alternative method shall have an acceptable uncertainty.

The laboratory shall use written technical procedures addressing the procedural operation of the method. The technical procedures shall meet the requirements of the method and the MID, where available.

The laboratory shall obtain accreditation for each method and each determinand they wish to measure.

The methods laboratories are accredited to use shall be defined in the laboratory's schedule of activities.

Laboratories may use alternative analytical techniques to those specified in standards. Procedures prescribed in EN 14793 shall be carried out where a reference method is available to compare against. If reference methods are not available then clause 7.2.2.1 shall be followed.

Note: An example of an alternative technique is the use of ion chromatography, instead of an ion selective electrode, to measure HF according to ISO 15713.

As a minimum, the alternative technique shall:

- be applicable to stack emissions monitoring samples
- have equal or better performance characteristics than the analytical method in the standard
- take account of information provided in MIDs, where available

Due to the complexity of analysing metals, dioxins and furans, dioxin like PCBs, particulates (dust) and PAHs, the analytical laboratory shall use the analytical methods specified in the relevant standard methods prescribed in TGN M2 and MIDs.

Any deviations from the method shall be reported in the analytical report, indicating how the deviations affect measurement uncertainty.

7.2.1.5 Where a method, published by CEN /ISO has been fully validated and performance characteristics are known, it shall be verified by laboratories, to demonstrate that the method can be reproduced in-house to meet the published performance characteristics. Laboratories shall demonstrate that the method they wish to employ is adequately validated by reference to published

performance data. Where the method validation of the published method does not adequately cover analytical performance, clause 7.2.2.1 shall be followed.

Note: An interlaboratory collaborative study should have been carried out for a standard method

To demonstrate verification of a suitable standard method, the following information shall be provided:

Laboratories shall ensure that the matrix to be analysed has been validated.

Demonstrate that the precision and bias targets of the method are met. If appropriate targets are not available, use those in Annex A.

Confirm calibration linearity using 4 standards in duplicate, unless specified differently in the standard method.

Limit of detection shall be estimated using the procedures in Annex B, the exception being EN 1948, where the method prescribed in the standard shall be used.

A CRM or a matrix sample with a concentration at the low end of the concentration range shall be used (for example low spike) for the verification of performance.

Acceptable performance in appropriate external quality control (inter-laboratory proficiency-testing) scheme (where available).

For all other methods listed in TGN M2, a full validation as described in clause 7.2.2.1 is required, unless the laboratory can demonstrate that the method used is an appropriately validated standard.

7.2.1.6 – 7.2.1.7 No additional requirements to EN ISO/IEC 17025.

7.2.2 Validation of methods

7.2.2.1 Where an appropriate standard method (CEN or ISO) is not available, or another method is employed without adequate validation, the performance characteristics of the method employed shall be determined with a minimum of 10 degrees of freedom. This shall be carried out by analysing certified reference material or matrix spiked samples in duplicate in different analytical batches. Eleven batches of duplicates will guarantee a minimum of 10 degrees of freedom. However, it may be that 10 degrees of freedom will be achieved in less than 11 batches. This can be checked after each batch of results (see reference c for appropriate procedures). Validation should normally be undertaken in a period not less than 6 days and no more than 6 months. This may be extended for methods carried out infrequently.

Note 1: This procedure is often termed an 11 x 2 test, as 11 batches containing 2 replicates of each test material are analysed.

Some methods prescribed in TGN M2, including national methods and those derived from ambient air methods, have insufficient performance data published, and may need validating for appropriate matrices. They therefore do not meet the criteria set out in 7.2.1.4 and require a full validation.

Precision should then be estimated using analysis of variance (ANOVA), from which different sources of error (for example within batch and between batch random errors) can be estimated and combined to give a total error as a

standard deviation. Details of the statistical procedures for ANOVA and recovery (bias) estimation are given in reference c); see also Annex C of this performance standard.

Note 2: The use of a validated method for one particular matrix may not be suitable for the analysis of a different matrix. This may also be the case when analysing samples of the same matrix containing significantly different concentrations of the same parameter.

The laboratory shall demonstrate that the certified reference material (where available) for the matrix, methodology, determinand and concentration of determinand being analysed is appropriate.

Where a suitable certified reference material is initially not available, but then, after recovery estimates have been undertaken becomes available, then the newly available certified reference material shall be used to check the bias is satisfactory.

For spiking experiments, the concentrations of the solutions used in the validation procedures shall be appropriate to the concentrations found in samples being routinely analysed. Recovery estimates shall be obtained using two significantly different but appropriate concentration levels, for example, at 20% and 80% of the expected range.

Impinger solutions that have been through the sampling process can be combined to provide a suitable solution for validation studies.

Where it is not possible to validate the whole analytical system directly, for example where fresh impinger solutions are spiked, selectivity and cross sensitivity against matrix interference shall be assessed.

Note 3: This can be achieved by analysing test samples containing suspected interferences and a known amount of the determinand of interest.

When a method has been validated, its stated performance shall reflect the routine capability of the method. That is, when the method is used routinely, its day-to-day performance shall be typical of and maintained at the level of the stated validation performance.

The limit of detection of a method used to analyse highly contaminated samples may be higher than the limit of detection of a method used to analyse slightly contaminated samples. The reported limit of detection shall be fit for the intended purpose and appropriate to the concentration level of interest required of the analysis. The limit of detection shall be calculated as described in Annex B. The limit of detection should never be used in isolation of other method validation data to judge the appropriateness of a method.

Note 4: The maximum value of the limit of detection usually regarded as being fit for purpose is 10% of the concentration regarded as the critical level of interest.

7.2.2.2 Revalidation

After an analytical method has been validated and accredited, it is inevitable that in time some modification of procedures will take place. Any modifications to a method routinely used within a laboratory may affect the resulting performance. Any changes made to a method already accredited against the

MCERTS requirements shall be notified to the national accreditation organisation. These changes could range from replacing a piece of equipment to a fundamental procedural modification, such as a different extraction procedure.

Minor changes to the analytical system may not require revalidation, but care should be taken to ensure the cumulative effects of several changes do not affect system performance. This can be achieved by, for example, closely monitoring internal and external quality control, and reanalysing CRMs used for validation.

If an instrument is being replaced by one of the same model, and performance is not expected to fundamentally change, laboratories need only demonstrate that the new instrument performs as well as the old instrument. This could be achieved, for example, by analysing several replicates of a representative matrix or a matrix matched quality control sample.

If a fundamental change is made to the analytical procedure or the equipment used, then a full validation is required in accordance with this performance standard. These changes may include, for example, replacing ICPOES with ICPMS, using a new extraction technique. Any modification of a standard method may need revalidation or reverification.

It is recognised that an intermediate degree of validation should be carried out if significant changes are made to a method that are not considered fundamental to performance. A partial validation shall be performed (for example analysis of 6 batches of duplicates), using only one spiked sample from the lower end of the calibration range, or preferably a CRM, for all appropriate matrices. If a laboratory judges that this level of validation is required, then it shall notify and gain the approval of UKAS. Laboratories shall ensure that the amendments to the analytical system and any procedures that may be affected are included in the revalidation.

7.2.2.3 Performance characteristics.

The Environment Agency has specified that the following performance characteristics are acceptable for the validation of methods for the chemical testing, bearing in mind the need to take meaningful decisions, current analytical capabilities and other likely sources of variation.

The bias (or systematic error) of individual results determined for the method shall not be significantly greater than the figure indicated in Annex A expressed as a percentage. If a CRM is used, the certified reference value shall be used as the true or accepted value when calculating bias. If a critical level of interest is known, the target bias value used can be taken as one-twentieth of the critical level of interest and either bias value used whichever is the greater. Laboratories shall demonstrate that the bias satisfies the stated requirement at the critical level of interest.

The precision, as expressed as the percentage relative standard deviation, of individual results determined for the method shall not be significantly greater than the figure indicated in Annex A. Precision shall be estimated using analysis of variance to determine total standard deviation. If a critical level of interest is known, the target precision value used can be taken as one-fortieth of the critical level of interest and either precision value used whichever is the

greater. Laboratories shall demonstrate that the precision satisfies the stated requirement at the critical level of interest.

Testing for significance shall be carried out as described in Annex C2. If, for a particular determinand, testing shows a significant difference exists, then further method development or refinement is required, or a different analytical method used.

Annex A specifies the performance characteristics for a selection of determinands (which are not to be regarded as exhaustive).

7.3 Sampling

7.3.1. – 7.3.3 No additional requirements to EN ISO/IEC 17025.

Note: the MCERTS performance standard for manual stack emissions monitoring provides information on sampling.

7.4 Handling of test or calibration items

7.4.1 If preservation of samples by refrigeration or other controlled environmental parameter is required, then during transportation (if provided by the laboratory) and subsequent storage of samples, including retention time, the sample storage environment shall maintain the controlled environmental parameter (such as temperature) as specified in the relevant Standard Reference Method. It is recognised that some time may be required to bring the sample temperature to within this range.

If non-standard methods are used, or stability and storage of samples are not specified adequately in the standard method employed, then the laboratory shall demonstrate that the maximum storage time between sampling and analysis, and preservation procedures being used are appropriate.

7.4.2 A chain of custody record shall be maintained from the collection of samples, to sample storage, to sample analysis.

7.4.3 - 7.4.4 No additional requirements to EN ISO/IEC 17025.

7.5 Technical records

7.5.1 The laboratory shall retain records for a defined period of time of not less than six years. This period of time shall take into account the need of the customer (procurer of the services) and the need to submit these records to the Environment Agency, if requested.

7.5.2 No additional requirements to EN ISO/IEC 17025.

7.6 Evaluation of measurement uncertainty

7.6.1 The laboratory shall have procedures in place for providing an estimate of the uncertainties relating to results, this information shall be made available to the sampling organisation for inclusion in their report.

7.6.2 to 7.6.3 No additional requirements to EN ISO/IEC 17025.

Note: Useful information regarding the estimation of measurement uncertainty is given in references g), j) and k).

7.7 Ensuring the validity of results

7.7.1 Internal Quality Control

7.7.1.1 For internal quality control, the performance of each analytical method shall be verified for each batch of samples analysed. Control samples shall be analysed within the analytical batch with which they have been prepared. The results obtained from the control samples shall be treated as in clause 7.7.1.

In each analytical batch, a minimum of 5% of samples shall be laboratory control samples. If the batch size is less than 20, one laboratory control sample per batch is still required.

These requirements do not replace quality assurance and control procedures recommended in standard and adapted methods, which shall also be carried out, including system suitability checks (see 6.4.10).

To be able to monitor trends in analytical performance using a control chart, a minimum of 30 points plotted in a 12-month cycle, spread evenly over the period is recommended. For analytical procedures that are carried out infrequently, the laboratory shall employ a greater degree of quality control to ensure control is maintained.

Note 1: Examples of greater degree of quality control include increasing the number of control samples in a batch, duplicates, use of the standard additions approach, and use of isotopically labelled surrogate compounds in organic analysis.

The following types of laboratory control sample may be suitable:

1. **Certified reference material or reference material**.– A sample of the target matrix, the concentration of determinand being certified to a quoted uncertainty and preferably traceable to an international/national Standard.

Note 2: It is recommended to use reference materials from producers that meet ISO 17034. ISO Guide 33 provides guidance on the selection and use of reference materials. ISO guide 80 provides guidance to produce in house quality control materials.

2. **In-house quality control material** – a sample produced by the laboratory, which may be synthetic, containing known concentrations of determinands of interest.

Note 3: It is vital that the sample is homogenised so that variations in repeat analyses reflect the analytical method performance and not any inhomogeneity of the sample. An advantage of using in-house reference materials is the ability to match the determinand concentration and matrix of the material to those of samples normally encountered in the laboratory.

Note 4: Traceability for this material may be achieved by characterisation against a certified reference material, for example during method validation or by comparison with the analysis of the material by accredited third-party laboratories.

3. **Spiked sample** – a sample representative of the matrix being analysed, to which a known quantity of a determinand standard solution is added before analysis.

Note 5: Standards used for spiking the sample should be from a different source or lot number to that used for calibration. Suitable contact times between spiking and extraction should be determined to provide adequate time for interaction between spike and sample while ensuring that there is no degradation of the determinand.

Note 6: Estimates of bias are often complicated with ‘recovery' terms, especially if the method involves an extraction stage. An estimate of precision is easily obtainable, but the apparent precision of the spike is a combination of the precision of the sample and that of the spiked sample.

4. **Other options** - duplicate analyses of individual samples as submitted to the laboratory should be considered when a test is carried out infrequently, as should the use of duplicate control charts; standard addition techniques may be appropriate; other alternative procedures or a combination of approaches may be necessary to demonstrate control of infrequently performed tests.

7.7.1.2 In order to monitor the variation of laboratory control samples, results shall be recorded or plotted on statistically based quality control charts. After initial validation procedures laboratories shall have sufficient data to construct statistically based quality control charts.

As further data are obtained, a new chart should be produced based on the latest 60 to100 results (depending on frequency of analysis), giving a new and more robust estimate of mean and standard deviation. If any of the data points have breached the control rules and a cause is assigned (for example use of wrong standard, air in flow-cell), then it should not be used. However, some results, which are part of the normal distribution, will breach the limits, and these should be used where no specific reason for the breach can be assigned.

A senior member of staff shall review analytical quality control performance regularly. The timescale will depend on frequency of analysis. All significant changes should be investigated. If a statistically significant change has occurred, then the new values are used in the control rules, and new control limits should established and drawn on the control chart.

A comparison of the last 60 data points with the previous 60 is recommended for routine analytical methods, although this will depend on the amount of data collected. If no significant changes are detected then the latest data may be incorporated into the calculation of control limits. Any decision made regarding updating of charts shall be justified and recorded.

7.7.1.3 Laboratories shall have documented procedures that define loss of statistical control and specify actions to be taken (control rules) when control limits are breached. All breaches shall be investigated, and the findings and actions recorded and made available to us, if requested. Samples in an analytical batch where laboratory control samples breach the defined control rules shall

be reanalysed, where possible. If this is not possible, then a comment should be added to the analysis report.

The investigation shall include but shall not be restricted to the following checks:

- changes in concentration of stock standard solutions and reagents and that expiry date has not been exceeded
- calibration of instruments used in the analytical process
- documented methods were strictly adhered to
- that system suitability check data meet requirements
- significant drift does not occur for automated determinations
- service/fault records
- recent proficiency testing scheme results

Records shall include:

- identification of control sample and all associated sample results
- control rules in force at time of breach and breach result
- investigation details, conclusions and actions taken
- action taken with respect to affected sample results (for example, analysis repeated or results reported)

7.7.2 Participation in interlaboratory comparison or proficiency-testing programmes

7.7.2.1 The laboratory shall participate in an appropriate external quality control or inter-laboratory proficiency-testing scheme. Where possible, samples from the scheme organiser should reflect typical matrices and determinand concentrations analysed within the laboratory.

7.7.2.2 As far as is possible, the methods, used by the laboratory to generate analytical data for the testing of stack emissions monitoring samples, which are submitted under MCERTS, shall be the same as those methods used by the laboratory for the analysis of samples distributed by the proficiency-testing scheme organiser. In addition, as far as is possible, samples distributed by the proficiency-testing scheme organiser should be treated by the laboratory in the same manner as normal routine samples submitted for testing of stack emissions monitoring samples. For example, procedures for registration, storage, analysis and the recording and reporting of results should be similar.

7.7.2.3 Full details of the scheme, including the number of samples, determinands and analyses to be undertaken by the laboratory and the types of matrices to be analysed, shall be made available. The reports of the results of all analyses submitted by the laboratory to the scheme organiser shall be made available.

7.7.2.4 The laboratory shall have a documented system in operation to review, investigate and address the results submitted to the proficiency scheme that are considered to be unsatisfactory by the scheme organiser, and to examine trends in performance. If a significant deterioration in method performance is detected and cannot be corrected within a reasonable period of time, then the method shall be re-validated.

This review procedure should take into consideration the relevance of the matrices and concentrations provided by the scheme, the number of other

laboratories participating and whether these laboratories use the same or similar analytical methods.

7.7.3 No additional requirements to EN ISO/IEC 17025.

7.8 Reporting the results

7.8.1 General

7.8.1.1 – 7.8.1.2 No additional requirements to EN ISO/IEC 17025.

7.8.1.3 A simplified reporting format may be used, however all information as required in EN ISO/IEC 17025 and the relevant Standard Reference Method and associated MID, where available, shall be made available to the sampling organisation for inclusion in their report when requested.

Information on reporting results for PAH analysis is provided in Annex D.

7.8.2 – 7.8.8 No additional requirements to EN ISO/IEC 17025.

7.9 Complaints

No additional requirements to EN ISO/IEC 17025.

7.10 Non conforming work

No additional requirements to EN ISO/IEC 17025.

7.11 Control of data – information management

No additional requirements to EN ISO/IEC 17025.

8 Management system requirements

No additional requirements to EN ISO/IEC 17025.

Annex A (normative): Performance characteristics for methods

Determinand	Test method	Precision (%RSD)	Bias (%)
Aldehydes (screening)GCMS	EN/TS 13649 + NIOSH 2539	10	20
Formaldehyde	EN/TS 13649 +NIOSH 2016/ NIOSH 2541 or EPA 316	15	30
Amines & Amides	EN/TS 13649 +NIOSH 2002 or NIOSH 2010	15	20
Ammonia	No method defined in M2 targets reported to be achievable for EPA CTM 027	5	5
Arsine	EN/TS 13649 +NIOSH 6001	6	7.5
Carbon disulfide	EN/TS 13649 + NIOSH 1600	5	5
Carboxylic acids (acetic only)	EN/TS 13649 + NIOSH 1603	5	5
Dioxins	EN 1948	Note 1	Note 1
Dioxin like PCBs	EN 1948-4	Note 1	Note 1
Fluoride (gaseous)	EN 15713	5	10
HCl	EN 1911	5	10
Halogens and Halides (HCl, HBr, HF, Cl_2, Br_2)	EPA 26 or EPA 26A	5	10
HF	ISO 15713	5	10
HCN	EPA OTM 29	5	10
hydrogen sulfide	EPA 11 EN 13649 + NIOSH 6013	10	20
Hexavalent chromium	EPA 0061	5 to10	10
Isocyanates	EPA CTM 36A	10	20
Mercaptans	NIOSH 2542	6	10
Mercury	EN 13211 by impinger	7.5	10
Mercury	EN 13211 by filter	7.5	10
Metals	EN 14385 by impinger	5	5
Metals	EN 14385 by filter	10	10
Methane	EN 25139	5	5
Methanol	EN/TS 13649 then NIOSH 2000 or OSHA 91	3	5
Nitric Acid vapour	EPA M7d	10	10
Oil Mist	EN 13284-1 then MDHS 84	5	15

Determinand	Test method	Precision (%RSD)	Bias (%)
PAH	ISO 11338-2	15 Note 1	15
Particulates (dust)	EN 13284-1 + MID	Note 2	Note 2
Phenols and cresols	EN/TS 13649 then OSHA 32 or NIOSH 2546	15	10
Phosphorus (and inorganic cmpds)	EN 14791 + NIOSH 6402	6.0	10
Phosphine	EN/TS 13649 then NIOSH 6002 or OSHA ID180	7.5	5
Siloxanes		5	10
Sulfuric acid (including mist and SO_3)	EPA 8	15	30
Sulfur dioxide	EN 14791	5	10
Tar and bitumen fume	MDHS 84	-	-
Total reduced sulfur compounds	EPA 15A, EPA 16A	5	5
VOCs (speciated)	EN/TS 13649	5	20

Note [1]: It may be difficult to meet this requirement for some PAHs, if this is consistently found for specific isomers precision will be raised to 20%

Note [2]: No additional performance targets required beyond those in the standard

Annex B (normative): Evaluating limit of detection

B.1 Introduction

Manual monitoring of stack emissions can involve taking samples for laboratory analysis. Stack emissions monitoring standards that require sampling and analysis, specify both sampling and analysis procedures. Unfortunately, the definition of limit of detection (LOD) is quite often vague and there is little consistency between standards.

In addition, the LOD is widely but inappropriately used as the primary performance measure of an analytical system. It does not indicate whether a method is fit for purpose. For example, a very low LOD value does not mean that the method is suitable for a particular purpose, as precision and bias could be unacceptable at the critical level of interest. The LOD is not specified in this performance standard. However, a common approach to the estimation of LOD is required in order to allow a laboratory's performance to be evaluated in a consistent and comparable way. If data reported to the Environment Agency includes results reported as less than values, the LOD shall be estimated using the following protocol.

B.2 Choice of sample and sample pre-treatment

The sample used to estimate LOD shall be a sample containing a small but measurable amount of the determinand of interest. The samples used to estimate the LOD shall consist wherever possible of a matrix as close as possible to those routinely analysed for the specific test (combined impinger solutions may be used).

Ideally, analysis of the sample, used to estimate the LOD, will produce normally distributed results scattered around zero; both negative and positive results will be generated. It is usually possible for the LOD sample to have a sufficiently small background concentration of the determinand to fulfil this requirement. However, in some analytical systems this may not always be possible because negative or low results cannot be obtained. In these cases, spike the LOD sample with a small amount of the determinand, sufficient to produce a small but significant response from the analytical system, close to the expected LOD.

Note: Determining the concentration of the spiked sample is based on judgement and potentially trial and error.

The sample, used to estimate the LOD, shall wherever possible be put through the entire analytical process. Extraction and measurement based only on reagent blanks is not sufficient for estimating LODs for satisfying the requirements of this document. The LOD sample shall be processed in the same manner and using the same equipment and reagents as other samples in a batch.

B.3 Calculation

For the purpose of this performance standard, LOD is defined by the equation:

$$\mathbf{LOD = 2\sqrt{2}.t_{(df,\alpha=0.05)}.}\ S_w$$

where:

df is the number of degrees of freedom (minimum 10)

t is the one-sided Student's t-test statistic (95% confidence level)

S_w is the within-batch standard deviation of results from samples ideally containing negligible concentration of the determinand of interest.

An estimate of the LOD can be made when initial validation studies are undertaken. Pairs of LOD samples shall be analysed in at least 10 different analytical runs or batches. Ideally these LOD samples should contain a negligible amount of the determinand being measured and should be consistent with and similar to the matrices of the samples being analysed. These LOD samples shall not be used as a calibration blank, and if the analytical procedure requires samples to be blank corrected, then the samples used to estimate LOD should also be blank corrected.

Results shall not be rounded before being used for the estimation of LOD.

In the most general case, where **m** batches of different numbers of replicates n_i give a series of within-batch standard deviations S_i:

The pooled value of S_w is given by:

$$S_w\,(pooled) = \sqrt{\frac{\sum {S_i}^2 \times (n_i - 1)}{\sum (n_i - 1)}}$$

where:

S_i = individual batch standard deviation,

n_i = number of results in the batch.

Where the batches all contain the same number of results, this equation simplifies to:

$$S_w\,(pooled) = \sqrt{\frac{\sum {S_i}^2}{m}}$$ with **m(n-1)** degrees of freedom

For example for 10 batches of 2 blanks:

$$S_w\,(pooled) = \sqrt{\frac{\sum {S_i}^2}{10}}$$ with 10 degrees of freedom

Since **t** $(\alpha = 0.05)$ for a one sided t-test with 10 degrees of freedom is 1.812

Then LOD = $2\sqrt{2}$.**t**. S_w = 5.13 S_w

If a different number of batches and replicates is used a minimum of 10 degrees of freedom shall be obtained. Where more than 10 batches of replicates are determined, all valid results shall be used in calculating the LOD.

B.4 Form of expression

For a multi-determinand method, such as dioxins and furans and polychlorinated biphenyls, each individual dioxin and furan will need to have its own LOD estimated. As upper bound results are included in the reports of these compounds, these upper bound values must include corrections for individual internal standard recoveries on a sample by sample basis. Otherwise an artificially low precision could be obtained where compounds are non-detect in blanks. Alternatively, the low spike approach should ensure that peaks are detected in every sample to allow a true assessment of performance to be obtained.

Where such multi-compound methods result in totals being calculated on a toxic equivalent basis, the overall LOD shall be determined. This is necessary because the combined result is the one that is usually used for regulatory compliance purposes. The same statistical approach can be taken to estimate this LOD, using this overall calculated value.

LOD values shall always be reported in the same units as the determinands they represent. The calculated value may be rounded up for convenience and ease of use.

B.5 Reporting limit

Typically, the reported LOD will be the LOD calculated (see B.3). However, a laboratory may use a higher reported LOD, than the calculated LOD. This is considered acceptable, as long as LOD is calculated in the correct way.

If samples are diluted before analysis then the LOD must be scaled up, so if a sample is diluted 1:5, and the analytical result is <5, then <25 should be reported.

Annex C (informative): Validation procedure

C1 A typical validation protocol

Performance tests to estimate precision, bias (recovery) and LOD shall only be carried out on a stable analytical system. The following samples are required, and should be put through the entire analytical procedure in a random order:

- field matrix blank or sample with determinand concentration close to the expected LOD
- samples of appropriate matrices
- internal quality control material
- CRMs and/or samples of appropriate matrices + spike at two concentrations if CRM not available

Each sample shall be analysed in duplicate, on 11 separate occasions (analytical batches) to guarantee at least 10 degrees of freedom. Treat validation samples as routine samples including the calculation of results.

Precision (within batch, between batch and total standard deviation) can be estimated using ANOVA (analysis of variance) procedures for each solution. Make an estimate of the number of degrees of freedom associated with each total standard deviation. Use the procedures described in reference c. Compare the total standard deviation with the appropriate precision targets listed in Annex A. If the value determined is greater than the target value, then it may be appropriate to ascertain if the difference is statistically significant using an F test at $\alpha = 0.05$ level. The target standard deviation will be the denominator with infinite degrees of freedom. Follow the procedure in Annex C2. If the difference is significant, then it may be likely that further method development or the use of an alternative analytical method is required.

Assess recovery as follows:

Calculate recovery for each pair of results, using the equation:

$$\text{Recovery (spiked samples)} = \frac{C_m (V+W) - UV}{C_s W} \times 100\ \%$$

where:

U = measured conc. in unspiked sample

C_m = measured conc. in spiked sample

C_s = conc. of spiking solution

W = volume of spiking solution added

V = volume of sample to which spike is added

Then calculate the mean recovery of each analytical batch. Calculate the mean recovery of all analytical batches and its standard deviation (s) (the standard deviation of the 11 batch means).

The standard error (S) of this estimate of the mean recovery is now calculated from:

$S = \frac{s}{\sqrt{m}}$ where m is number of analytical batches, 11.

The true recovery should therefore lie in the range mean recovery ± $t_{(\alpha = 0.05)}$ S where $t_{(\alpha = 0.05)}$ = students t statistic at 95% probability with m-1 degrees of freedom.

LOD shall be calculated using the procedure outlined in Annex B.

Results of these validation tests can be presented with method documentation in a tabular format.

C2 The use of statistical significance tests in the interpretation of method performance

C2.1 Introduction

After the validation has been carried out as described in clause 5.4.5 and Analysis of Variance (ANOVA) has been applied to the results, there will be sufficient data to assess whether method performance complies with Annex A criteria.

C2.2 Assessment of precision

The convention in analysis has been to consider precision to be satisfactory if the measured standard deviation is found not to be statistically significantly larger than the target standard deviation.

This implies there is uncertainty about the measured standard deviation value, although this uncertainty is minimised by specifying its calculation with at least 10 degrees of freedom.

Assessment of precision is in 3 stages:

Determine the target standard deviation at the concentration of interest, in accordance with clause 7.2.1.

If the measured standard deviation is less than the target standard deviation, the target has been achieved.

If, however, the measured standard deviation is greater than the target it is still possible to comply with the requirements of this standard if it is not significantly greater. To assess this significance a statistical test is required.

C2.3 F-test of standard deviation.

The F-test or variance ratio test is a way of determining whether differences between 2 standard deviations are statistically significant (at a chosen probability level). The procedure is to calculate the F ratio as shown below:

$$F = \frac{{S_t}^2}{Z^2}$$

where $\boldsymbol{S_t}$ is the measured total standard deviation, estimated using between batch and within batch mean squares in ANOVA, and **Z** is the target standard deviation.

The calculated value of F is then compared with a reference value obtained from statistical tables. The reference value of F is obtained using the correct probability (5% for this performance standard) and using the relevant degrees of freedom for $\boldsymbol{S_t}$ and **Z**.

Z is a target standard deviation and therefore has infinite degrees of freedom. In the case of $\boldsymbol{S_t}$, the number of degrees of freedom is calculated during the analysis of

variance. If a complete 11x2 validation is performed, the equation can be simplified to:

$$df = \frac{\mathbf{110}[\boldsymbol{M_1} + \boldsymbol{M_0}]^2}{\mathbf{11}\boldsymbol{M_1}^2 + \mathbf{10}\boldsymbol{M_0}^2}$$

where M_1 ***and*** M_0 are the within batch and between batch mean squares respectively, each obtained from ANOVA.

If the F ratio is less than the tabulated reference F value then the measured standard deviation is not significantly greater than the target value so performance is satisfactory.

If the F ratio is greater than the tabulated reference F value then the measured standard deviation is significantly greater than the target value so performance is not satisfactory.

C2.4 Assessment of systematic error or bias

This assessment is only relevant and shall only be carried out if the assessment of precision is acceptable.

The assessment of bias depends on independent knowledge of a 'true' value with which to compare the average of measured data. This is accomplished by the use of reference materials or by spiking recovery experiments.

To assess bias and its associated uncertainty the procedure is to calculate the mean recovery for each batch and to use the batch mean recoveries to estimate the overall recovery and its standard deviation (strictly its standard error).

Assess significance by calculating the confidence interval about the mean and checking to see if this overlaps the limits of tolerable bias.

Overall Mean Recovery $M = \frac{\sum \boldsymbol{R_i}}{\boldsymbol{m}}$

Standard Error of Recovery $S_e = \frac{S_R}{\sqrt{m}}$

90% Confidence Interval of Recovery $= M \pm S_e \times t_{(0.05,m-1)}$

Where:

m = number of batches

$\boldsymbol{R_i}$ = %Recovery of the ***i***th batch

$\boldsymbol{S_R}$ = standard deviation of batch recoveries

$\boldsymbol{t_{(0.05,m-1)}}$ = single-sided Student's t value at 5% probability level and (**m-1)** degrees of freedom

If there is an overlap (one or both of the target recovery limits is within the confidence interval), the recovery is not significantly worse than required and shall be regarded as acceptable.

Note: When a bias is estimated it is either positive or negative, therefore a one sided t-test at the 95% confidence level is used to assess if observed bias is greater than permitted bias. However, by definition, a confidence interval is two sided,

therefore the significance test is at the 95% confidence level but the resulting confidence interval is 90%.

C3 Example

This example illustrates the application of the statistical tests mentioned above. It considers a spiking exercise for gaseous chlorides, using a low-level spike and a higher-level spike of an impinger solution. Spiking solution concentration was 5000 mg l^{-1} HCl; for the low-level sample 1 ml of this solution was made to 1 litre with impinger solution, for the high-level sample, 3 ml of the spiking solution was made to 1 litre with impinger solution.

Validation data: Gaseous Chlorides as HCl mg l^{-1} in solution – spiked samples

Batch	Replicate	Sample 1	Spiked sample 1	Recovery	Sample 2	Spiked sample 2	Recovery
1	1	0.327	5.073	4.746	5.333	18.25	12.917
1	2	0.450	5.311	4.861	5.55	19.13	13.580
	Mean.	0.3885	5.1920	4.80350	5.4415	18.69	13.2485
	Std.dev.	0.08697	0.16829	0.08132	0.15344	0.62225	0.46881
2	1	0.614	5.431	4.817	5.688	19.227	13.539
2	2	0.519	5.138	4.619	5.376	19.380	14.004
	Mean.	0.5665	5.2845	4.7180	5.532	19.3035	13.7715
	Std.dev.	0.06718	0.20718	0.14001	0.22062	0.10819	0.32880
3	1	0.281	5.427	5.146	5.560	19.637	14.077
3	2	0.416	5.394	4.978	5.417	20.336	14.919
	Mean.	0.3485	5.4105	5.062	5.4884	19.9865	14.498
	Std.dev.	0.09546	0.02333	0.11879	0.10112	0.49427	0.59538
4	1	0.430	5.872	5.442	5.770	17.871	12.101
4	2	0.557	6.086	5.529	5.564	18.039	12.475
	Mean.	0.4935	5.9790	5.48550	5.667	17.955	12.288
	Std.dev.	0.08980	0.15132	0.06152	0.14566	0.11879	0.26446
5	1	0.698	5.289	4.591	5.889	19.114	13.225
5	2	0.744	5.899	5.155	5.915	19.565	13.650
	Mean.	0.7210	5.5940	4.8730	5.902	19.3395	13.4375
	Std.dev.	0.03253	0.43134	0.39881	0.01838	0.31891	0.30052
6	1	0.495	5.395	4.900	6.255	19.389	13.134
6	2	0.415	5.845	5.435	5.920	18.773	12.853
	Mean.	0.4550	5.625	5.1675	6.0875	19.0810	12.9935
	Std.dev.	0.05657	0.32173	0.3783	0.23688	0.43558	0.1987
7	1	0.787	5.414	4.627	5.3388	18.304	12.965
7	2	0.570	5.735	5.165	5.678	19.836	14.158
	Mean.	0.6785	5.5745	4.896	5.50835	19.070	13.5615
	Std.dev.	0.15344	0.22698	0.38042	0.23971	1.08329	0.84358
8	1	0.940	5.391	4.451	5.971	19.437	13.466
8	2	0.647	5.201	4.554	6.013	19.736	13.723
	Mean.	0.7935	5.2960	4.5025	5.992	19.5865	13.5945
	Std.dev.	0.20718	0.13435	0.07283	0.0297	0.21142	0.18173
9	1	0.364	5.574	5.210	5.5014	18.513	13.012
9	2	0.490	4.934	4.444	5.149	19.835	14.686

	Mean.	0.4270	5.2540	4.827	5.325	19.1740	13.849
	Std.dev.	0.08910	0.45255	0.54164	0.2489	0.93480	0.61829
10	1	0.434	5.102	4.668	5.802	18.552	12.750
10	2	0.588	5.219	4.631	5.920	19.382	13.462
	Mean.	0.5110	5.1605	4.6495	5.8610	18.9670	13.106
	Std.dev.	0.10889	0.08273	0.02616	0.08344	0.58690	0.50346
11	1	0.516	5.249	4.733	5.72	18.952	13.232
11	2	0.468	5.047	4.579	5.608	18.642	13.034
	Mean.	0.4920	5.1480	4.656	5.664	18.797	13.133
	Std.dev.	0.03394	0.14284	0.10889	0.0792	0.21920	0.14001
Overall mean		0.534	5.411		5.679	19.086	
Overall mean recovery				4.876			13.4074

Precision test (From ANOVA)

	Sample 1	Spiked sample 1	Sample 2	Spiked sample 2
Mean	0.534	5.411	5.679	19.086
Within-Batch sd	0.104850	0.249703	0.163384	0.558675
Between-Batch sd	0.121030	0.186969	0.219837	0.339715
Total sd	0.160130	0.311944	0.273903	0.653853
elative sd %	29.98%	5.77%	4.82%	3.43%
Target sd:	0.125	0.27053	0.28395	0.95432
Tabulated F 0.05 value[1]	1.67	1.60	1.69	1.60
Calculated F-Value[2]	1.64	1.33	0.93	0.469
Estimate degrees freedom	15.17	18.01	14.19	19.07
Assessment	PASS	PASS	PASS	PASS

1 This is obtained from statistical tables for the estimated degrees of freedom at the 5% probability level (p=0.05)

2 This value is calculated as (total sd /target sd) ^{2}

In this example, the precision in terms of the observed relative standard deviation of sample 1 is much higher than the target value of 5%, so perform an F test. For this particular sample the critical level of interest is known to be 5 mgl^{-1} so the target standard deviation can be increased to one-fortieth of the critical level of interest (that is 0.125 mgl^{-1}). The 95% calculated F value (1.64) for sample 1 is less than the tabulated reference F value of 1.67, so the standard deviation of sample 1 is not significantly different from the target value, and therefore meets the MCERTS requirement. With spiked sample 1, the observed relative standard deviation (5.77%) is higher than the 5% target value of the mean (that is 0.2705). Following the F test calculation, the data for spiked sample 1 passes and therefore meets MCERTS requirements. Sample 2 and spiked sample 2 are within the 5% target value and the F test is not required.

The bias target value for gaseous HCl is 10%, so the tolerable range of recovery in this example is 90-110%. At 97.5% sample 1 is well within this range. In the case of sample 2, the overall mean recovery is lower than the tolerable range. However, the overlap of the confidence interval with the tolerable range means that although recovery is nominally outside this range it is not significantly so and is therefore statistically acceptable**. The precision must be acceptable before applying this test.**

Recovery

	Sample 1	Sample 2
Expected recovery concentration	4.9995	14.9823
Mean measured recovery	4.8764	13.4074
Overall mean recovery	97.54%	89.48%
sd of mean recovery	5.5261	3.771
Standard error of mean recovery	1.6662	1.137
90 % Confidence interval of recovery	3.02	2.06
Recovery range	94.52% - 100.56%	87.42% - 91.54%
Assessment	PASS	PASS

1 This value is the average of the mean recovery for each batch

2 This value is the relative sd of overall mean recovery divided by the square root of the number of batches

3 This value is the standard error of mean recovery multiplied by the Student's t value (p=0.05 single sided) for degrees of freedom equal to number of batches minus 1, (t=1.812 for 11 batches)

The concentration in the low-level sample is considered to be near the expected detection limit, so the data can also used to make an estimate of the detection limit.

LOD = $2\sqrt{2}.t.S_w$

S_w (within batch sd) = 0.105 and t (α = 0.05) for 11 batches = 1.796

therefore LOD estimate = 0.53 mg/l HCl

Annex D: Reporting PAHs for operators of waste incinerators subject to the requirements of the IED

D.1 Background

Some industrial operators subject to the requirements of the Industrial Emissions Directive (IED) are required to measure PAHs from stack gas emissions. The PAHs they must measure are given by Defra in “Guidance on: Directive 2000/76/EC on the incineration of waste Edition 2”.

D.2 List of PAHs provided in the Defra guidance

The following is the list of PAHs provided in the Defra guidance:

Anthanthrene
Benzo[a]anthracene
Benzo[b]fluoranthene
Benzo[k]fluoranthene
Benzo[b]naph(2,1-d)thiophene
Benzo[c]phenanthrene
Benzo[ghi]perylene
Benzo[a]pyrene
Cholanthrene
Chrysene
Cyclopenta[c,d]pyrene
Dibenzo[ah]anthracene
Dibenzo[a,i]pyrene
Fluoranthene
Indo[1,2,3-cd]pyrene
Napthalene

D.3 Analysis

The analysis of the individual PAHs listed above shall be carried out using a method accredited to EN ISO/IEC 17025 and the requirements of this document.

D.4 Reporting

The monitoring organisations shall report a result for each of the individual PAHs listed above.

The results for the individual PAHs should be included in Part 1 (Executive Summary) of an MCERTS accredited monitoring report.

It is not necessary to report the summed total of the PAHs measured. However, if this is asked for by the operator it should be done by simply adding each individual PAH together, including results at the LOD. There is no requirement to calculate toxic equivalents for PAHs or for reporting them as a standardised mass, corrected to one specific PAH.

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