Manual stack emissions monitoring Performance Standard for laboratories carrying out analysis of samples

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mCERTS
THE ENVIRONMENT AGENCY'S MONITORING CERTIFICATION SCHEME

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

Implementation date

It is expected that laboratories, who carry out analysis of stack emission monitoring samples, will have met the requirements of this document by 1 October 2014.

Feedback

If you have any comments on this document please contact Rupert Standring at rupert.standring@environment-agency.gov.uk

Foreword

We set up our Monitoring Certification Scheme (MCERTS) to provide a framework of standards you can use to monitor things that affect the environment.

The standard we focus on in this document sets out what you must do if you want to get accreditation to MCERTS to perform analysis on 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 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 standard

- The standard makes sure that information on pollution released from chimney stacks is reliable.
- Everybody in the competitive market of performing chemical analysis for samples taken from monitoring pollution from chimney stacks will be working towards the same standard.
- The standard sends a message that performing chemical analysis for samples taken from 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 analysis for samples taken from monitoring pollution from chimney stacks.

If you have any questions about what you need to get an accreditation, please contact:

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

Contents

MCERTS Performance Standard for laboratories carrying out analysis of samples from stack emissions monitoring

Introduction

Manual stack emission monitoring for regulatory purposes includes measurements for:

- determining compliance with numerical limits in permits;
- the 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; and
- 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 performing analysis for samples taken from manual stack emission monitoring is built on proven international standards to ensure good quality monitoring data. The scheme is built on the accreditation of laboratories to this MCERTS performance standard.

Note 2: Analysis 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 quality system, are technically competent, and are able to generate technically valid results.

EN ISO/IEC 17025 recognises at paragraph 1.6 Note 1 that it might be necessary to explain or interpret certain requirements in this International Standard to ensure that the requirements are applied consistently.

This MCERTS performance standard provides criteria for the application of EN ISO/IEC 17025 in the specific field of performing analysis of samples taken from monitoring of emissions from stationary sources (for example, chimney stacks). In producing this MCERTS standard, the guidance for establishing applications for specific fields given in Annex B of EN ISO/IEC 17025 has been followed.

The structure of this document follows the structure 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 measurement 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 can be undertaken for a wide range of substances using various methods. Details of methods and specific analytical requirements are provided in our Technical Guidance Note M2.

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.

We have 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.

We may carry out our own inspections and investigations and act upon their findings for laboratories accredited to ISO/IEC17025 for the MCERTS performance standard.

2. References

a) EN ISO/IEC 17025 General requirements for the competence of testing and calibration laboratories

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

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 (see spiking recovery).

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 realization 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 – organisation responsible for implementing environmental legislation (for example, in England the Environment Agency).

Concentration - Concentration is usually expressed as mass per unit mass, for example mg kg-1. It may be quoted on an “as submitted” basis, a “wet weight” basis, or on a “dry weight” basis. (In certain circumstances the term concentration is not appropriate, for example in the determination of pH values).

Critical level of interest - This is the concentration value around which a decision is often required, for example is the concentration above or below a certain value. It may be for example a “soil guideline value” (which may be found for certain parameters on the Environment Agency website), a regulatory limit, or some other concentration of importance. 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.

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

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

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

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) - determination of a measureand at specified time intervals. The specified time intervals can be regular (e. g. once every month) or irregular. Measurands 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 % 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 measurand. These methods are listed in 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 - 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. Management requirements

4.1 Organisation

4.1.1

a) Ethical requirements

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.

b) Auditing

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

Note: UKAS audits will be complemented by a programme of Environment Agency audits.

Some audits will be carried out on an "unannounced" basis. Laboratories shall co-operate, when required, in planning these audits.

4.1.2 The laboratory shall carry out its testing and calibration activities in such a way as to meet the requirements of this performance standard.

4.1.3 - 4.3.3.4 No additional requirements to ISO/IEC 17025.

4.4 Review of requests, tenders and contracts

4.4.1 No additional requirements to ISO/IEC 17025.

4.4.1(a) 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 us 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 to us for regulatory purposes, then the requirements of this performance standard need to be satisfied.

4.4.1(b) No additional requirements to ISO/IEC 17025.

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

4.4.2 - 4.4.5 No additional requirements to ISO/IEC 17025.

4.5 Sub-contracting of tests and calibrations

4.5.1 A laboratory may sub-contract analysis 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.

4.5.2 - 4.13.1.4 No additional requirements to ISO/IEC 17025.

4.13.2 Technical records

4.13.2.1 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 analytical services) and the need to submit these records to us, if requested.

4.13.2.2 - 4.15.2 No additional requirements to ISO/IEC 17025.

5. Technical requirements

5.1 General

No additional requirements to EN ISO/IEC 17025.

5.2 Personnel

No additional requirements to EN ISO/IEC 17025.

5.3 Accommodation and environmental conditions

5.3.1 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 etc.

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

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

5.3.3-5.3.4 No additional requirements to EN ISO/IEC 17025.

5.4 Test methods and method validation

5.4.1 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 parameter and that it is appropriate with respect to the concentration of the parameter 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 us, if requested.

5.4.2 a) Selection of methods

MCERTS accreditation for stack emissions sampling and analysis is applicable to methods in TGN M2 only.

Note 1: Even though a determinand may not be listed specifically in TGN M2, it may fall under a general method, such as speciated VOCs. Under these circumstances MCERTS accreditation can be obtained because it falls under the procedural framework of a CEN standard.

Method Implementation Documents (MIDs) provide details on how the preferred methods shall be used for regulatory monitoring and subsequent analysis (as applicable).

Note: MIDs are produced, where necessary, by us.

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 they wish to use.

Note: UKAS will accredit laboratories for the technical procedures to ensure they follow the standard methods, MIDs and the requirements of EN ISO/IEC 17025.

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

b) Analytical methods

Laboratories are allowed to use an alternative analysis techniques to those specified in standards (exceptions to this are given below).

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 air samples
- have equal or better performance characteristics than the analytical method in the standard.

Due to the complexity of analysing metals, dioxins and furans, dioxin like PCBs and PAHs, the analytical laboratory shall use the analytical methods specified in the relevant standard methods.

5.4.3 – 5.4.4 No additional requirements to ISO/IEC 17025.

5.4.5 Validation of methods

5.4.5.1 – 5.4.5.2 No additional requirements to ISO/IEC 17025.

5.4.5.3 The limit of detection for the analytical methods shall be calculated as described in Annex A.

5.4.6 Estimation of Uncertainty of Measurement

5.4.6.1 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.

5.4.6.2 – 5.5.12 No additional requirements to ISO/IEC 17025.

5.6 Measurement traceability

5.6.1 - 5.6.2.1.2 No additional requirements to ISO/IEC 17025.

5.6.2.2 Testing

5.6.2.2.1 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.

5.6.2.2.2 – 5.6.3.4 No additional requirements to ISO/IEC 17025.

5.7 Sampling

5.7.1 A sample shall be analysed using either all of the sample or a representative or homogenised sub-sample. If a parameter is known to be unstable, or suspected of being unstable, or begins to degrade once the sample has been taken, then the analysis shall be carried out without undue delay.

When a sample is stabilised, or preserved and subsequently analysed, then this fact shall be recorded when the results are reported and details of the stabilising or preserving agent shall be recorded. Where a party independent of the analysing laboratory performs this activity (for example the provider of the samples), the laboratory should obtain this information and report it as above.

5.7.2 - 5.7.3 No additional requirements to ISO/IEC 17025.

5.8 Handling of test items

5.8.1 A chain of custody record shall be maintained from the collection of samples, to sample storage, to sample analysis. The record should detail the person who has possession of the samples and the location of the item.

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.

5.8.3 Where non-conforming samples or potentially non-conforming samples (deviating samples) are received at the laboratory or in the event of discovery a non-conforming (deviating) sample whilst in the custody of the laboratory the customer (that may be the sampling organisation) shall be notified immediately.

5.9 Assuring the quality of test results

5.9.1 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.

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.

Full details of the scheme, including the number of samples, parameters 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.

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

Internal Quality Control

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.

In each analytical batch, a minimum of 5% of samples shall be laboratory control samples. Laboratory control samples may be certified reference materials, reference materials, in-house reference materials or spiked samples or others. If the batch size is less than twenty, one laboratory control sample per batch is still required.

For analytical procedures that are carried out infrequently, it shall be necessary to employ a greater degree of quality control to ensure control is maintained.

Note 1: To be able to monitor trends in analytical performance using a Shewhart chart, a minimum of 30 points are required to be plotted in a 12 month cycle, spread evenly over the period.

Note 2: Examples of greater degree of quality control include increasing the number of control samples in a batch, use of the standard additions approach, and use of isotopically labelled surrogate compounds in organic analysis.

The following types of control sample may be suitable:

Certified 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.

Reference Material – A sample of the target matrix, the concentration of determinand being characterised to a quoted uncertainty.

In-house Reference Material – A sample produced by the laboratory, which may be synthetic, containing known concentrations of determinands of interest. 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 1: 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.

Spiked Sample – A sample representative of the matrix being analysed, to which a known quantity of a determinand standard solution is added before analysis. 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 2: 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.

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.

5.9.2 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 60-100 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 etc.), 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 AQC performance on a regular basis. The timescale will depend on frequency of analysis. All significant changes should be investigated, even if precision and bias are still within the MCERTS targets. 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. Comparison of the last 60 data points with the previous 60 is recommended for routine analytical methods, but again 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.

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.

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 (i.e. analysis repeated or results reported).

5.10 Reporting of results

5.10.1 A simplified reporting format may be used, however all information as required in ISO/IEC 17025 and the relevant Standard Reference Method and/or MID 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 B.

5.10.2 – 5.10.9 No additional requirements to EN ISO/IEC 17025.

Annex A - Limit of detection for laboratories who analyse stack emissions monitoring samples

C.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.

Also, 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 us includes results reported as less than values, the LOD shall be estimated using the following protocol.

C.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 parameter(s) of interest. The sample used to estimate the LOD shall consist of the matrix used for the specific test.

Ideally, analysis of the sample, used to estimate the LOD, will produce normally distributed results scattered around zero; i.e. 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 parameter to fulfil this requirement. However, this may not always be possible because in some analytical systems negative or low results cannot be obtained. In these cases the LOD sample should be spiked with a small amount of the parameter, sufficient to produce a small but significant response from the analytical system, i.e. close to the expected LOD. This concentration shall not exceed 5 times the 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 be put through the entire analytical process. Extraction and measurement based on reagent blanks only is not sufficient for estimating LODs for the purpose of 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.

C.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)
$\mathbf{s_w}$ is the within-batch standard deviation of results from samples ideally containing negligible concentration of the parameter 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 parameter being determined 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 $\mathbf{n_i}$ give a series of within-batch standard deviations $\mathbf{s_i}$:

The pooled value of $\mathbf{s_w}$ is given by:

$$\mathbf{s_w}\ \text{(pooled)} = \sqrt{\frac{\sum s_i^2.(n_i - 1)}{\sum (n_i - 1)}}$$

where:

$\mathbf{s_i}$ = individual batch standard deviation,
$\mathbf{n_i}$ = number of results in the batch.

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

$$\mathbf{s_w}\ \text{(pooled)} = \sqrt{\frac{\sum s_i^2}{m}}$$ with **m(n-1)** degrees of freedom

for example for 10 batches of 2 blanks:

$$\mathbf{s_w}\ \text{(pooled)} = \sqrt{\frac{\sum s_i^2}{10}}$$ with 10 degrees of freedom

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

Then LOD = $2\sqrt{2}.\mathbf{t}.\mathbf{s_w} = 5.13\mathbf{s_w}$

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.

As an ongoing check, an estimate of LOD can be obtained by analysing 11 LOD samples in the same batch, here $\mathbf{s_t}$ (total standard deviation) equates to $\mathbf{s_w}$, with 10 degrees of freedom.

C.4 Form of expression

For a multi-parameter 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 usually used for regulatory compliance purposes. The same statistical approach can be taken to estimate this LOD, using this overall calculated value.

Some Standards/methods contain definitions of limit of quantification (LOQ) as well as LOD. These usually involve multiplying the LOD by a factor to obtain the LOQ number.

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

C.5 Reporting limit

Typically, the reported LOD will be the LOD calculated as above. 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, i.e. if a sample is diluted 1:5, and the analytical result is <5, then <25 should be reported.

Annex B - Reporting PAH measurements for operators of waste incinerators subject to the requirements of the Industrial Emissions Directive

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 should be carried out using a method accredited to EN ISO 17025 and the requirements of this document.

D.4 Reporting

The monitoring organisations should 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. There is no requirement to calculate toxic equivalents for PAHs or for reporting them as a standardised mass, corrected to one specific PAH.