MCERTS standard for laboratories undertaking chemical testing of soil

October 2023

LIT 6625

We are the Environment Agency. We protect and improve the environment.

We help people and wildlife adapt to climate change and reduce its impacts, including flooding, drought, sea level rise and coastal erosion.

We improve the quality of our water, land and air by tackling pollution. We work with businesses to help them comply with environmental regulations. A healthy and diverse environment enhances people's lives and contributes to economic growth.

We can't do this alone. We work as part of the Defra group (Department for Environment, Food & Rural Affairs), with the rest of government, local councils, businesses, civil society groups and local communities to create a better place for people and wildlife.

Published by:

Environment Agency
Horizon House, Deanery Road,
Bristol BS1 5AH

www.gov.uk/environment-agency

Further copies of this report are available from our publications catalogue: www.gov.uk/government/publications or our National Customer Contact Centre: 03708 506 506

Email: enquiries@environment-agency.gov.uk

Contents

Introduction

The European and international standard EN ISO/IEC 17025 describes the general requirements for the competence of testing and calibration laboratories. Where you submit data for the chemical testing of soils to the Environment Agency for regulatory purposes, those data shall be generated using methods accredited to EN ISO/IEC 17025 and this MCERTS performance standard.

Accreditation is undertaken by an appropriate national organisation. In the United Kingdom this is the United Kingdom Accreditation Service (UKAS).

This MCERTS performance standard contains requirements that a laboratory must meet if it wishes to be considered as a laboratory registered under the MCERTS performance standard for the chemical testing of soil. There are also requirements for anyone who uses analytical services accredited to MCERTS (see Using MCERTS for the chemical testing of soils).

Some of the requirements of the performance standard are described in general terms. This allows flexibility for a laboratory to take advantage of technological developments. This means, a laboratory is not excluded because, for example, it lacks specific equipment. Along with this flexibility is the need for the provision of appropriate information. For example, if you generate test data for a specific site over an extended period you must make consistent and meaningful comparisons. Where we assess data for regulatory purposes, you must record all relevant information and it be available to us, if requested.

We recognise that variations due to sampling can be greater than those introduced by analysis; but this performance standard does not specifically cover sampling or the competency of personnel in relation to sampling procedures and strategies.

The MCERTS performance standard does not restate all the provisions of EN ISO/IEC 17025 which must be fully complied with. It only states the additional requirements which laboratories must comply with to become registered under MCERTS for the chemical testing of soil.

The clause numbers in this document align with those of EN ISO/IEC 17025:2017 and will not be the same as those in other dated versions of EN ISO/IEC 17025.

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

UKAS
2 Pine Trees
Chertsey Lane
Staines-upon-Thames
TW18 3HR

Telephone: 01784 429000

Email: info@ukas.com

For more information on MCERTS and for copies of the performance standards and further guidance, see our website at: www.mcerts.net

Contact us

You can contact the Environment Agency if you need any help.

General enquiries
National Customer Contact Centre
PO Box 544
Rotherham
S60 1BY

Email enquiries@environment-agency.gov.uk

Telephone 03708 506 506

Monday to Friday, 8am to 6pm.

1 Scope

The chemical testing of soil can be undertaken for a wide range of parameters using a wide range of methods. The methods that a laboratory uses to generate data that are submitted to the Environment Agency for regulatory purposes shall be accredited to EN ISO/IEC 17025 and this MCERTS performance standard. Laboratories shall define these methods in their scope of activities.

This performance standard applies to all laboratories and users of analytical services where results, generated for the chemical testing of soil, are submitted to the Environment Agency for regulatory purposes.

Most of the requirements of this performance standard are laboratory activities. But users of analytical services must make sure that the requirements are satisfied and that the appropriate information is provided to us, or the laboratory, if requested.

When a laboratory meets all the appropriate requirements of this performance standard, that laboratory will have shown that it meets the Environment Agency's MCERTS requirements for the chemical testing of soil. It will show its competence to undertake the chemical testing of soil to the Environment Agency's requirements. The scope of its accredited activities shall be published on the UKAS website.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document.

EN ISO/IEC 17025 - General requirements for the competence of testing and calibration laboratories.

3 Terms and definitions

In the context of this performance standard, the following terms and definitions apply: It is recognised that some terms used in this document may have slightly different meanings to those used in other publications.

Air-dried sample – A sample dried at ambient temperatures not exceeding 30°C.

Analytical quality control (AQC) – The overall process of making sure that the application of an analytical method is controlled within specified tolerances.

Assisted-dried sample – A sample that has undergone a specified accelerated drying process. This may involve oven-assisted drying at a specified temperature, freeze-drying or some other process.

As submitted basis – The laboratory receives a sample for direct analysis of either the entire sample, or of a representative sub-sample, that is, without further sample pre-treatment.

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 by 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]

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', a regulatory limit, or some other concentration of importance. A method is usually deemed acceptable if, when used properly, it can establish within defined limits of bias and precision, whether a concentration is above or below the critical level of interest.

Laboratory – A laboratory, or sub-contracting laboratory, that undertakes the chemical testing of soil.

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 (LOD) that you need to estimate before using a method routinely.

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

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

Where SD = total standard deviation, M is the mean of results, both as indicated in section 7.2.2.3.

Repeatability conditions – Those conditions where analyses are carried out in one laboratory by one or more analysts, using the same equipment and reagents, within a short period of time.

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

Spiking recovery – The addition of a known quantity of a parameter to a sub-sample, followed by analysis to establish that fraction or percentage recovered using a defined method.

$$\%Recovery = \frac{(D - P) \times 100}{A}$$

Where:

D = the measured amount of parameter in sub-sample following addition of known amount of parameter

P = the measured amount of parameter in sub-sample prior to addition of known amount of parameter

A = amount of parameter added to sub-sample

This technique is often used as the only viable option for the analyst when appropriate certified reference materials are not available, and you cannot determine bias directly. When this is so, calculate bias from:

%Bias = %Recovery - 100

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

Sub-sample – A representative or homogenised portion of the sample. This portion is used in the analysis.

Wet-weight basis – The sample as it is received at the laboratory for direct analysis either of the whole sample or of a representative sub-sample, that is, without further sample pre-treatment.

4 General requirements

4.1 Impartiality

No additional requirements to EN ISO/IEC 17025.

4.2 Confidentiality

No additional requirements to EN ISO/IEC 17025.

5 Structural requirements

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

5.5 to 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 The laboratory shall protect equipment, reagents and samples 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.

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

6.4 Equipment

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

6.4.6 The laboratory shall calibrate equipment, and if appropriate with each batch of samples. Use measurement standards that are traceable to national or international standards except where 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 just the determination stage. In either case, solutions shall match the sample extract solutions, both in terms of acid strength and content or solvent composition. The calibration shall cover the range of interest for the samples, and should, ideally, be linear over that range. Use at least 3 calibration points (not including the calibration blank), but more shall be necessary for a non-linear calibration. Laboratories should prepare calibration solutions, and standard solutions used for quality control purposes, where possible, using different analysts and from different lots or sources of materials.

When calibrating pH instruments, you may use the procedure in EN ISO 10523 Water quality. Determination of pH. This requires using 2 appropriate calibration standards, and a third to check linearity. Recalibrate if the third standard is outside limits. Full details are in the standard.

Laboratories shall take at least 1 blank sample, containing negligible amounts of the parameters of interest, through the entire analytical system (including sample preparation if appropriate) with each batch of samples. Laboratories shall demonstrate, according to written procedures, how they utilise blank samples. Laboratories shall investigate blank sample results that show evidence of contamination and may have to repeat the analysis of the entire batch of samples. This may not be appropriate for some determinations, for example pH.

6.4.8 No additional requirements to EN ISO/IEC 17025.

6.4.9 The response of instruments may fall. For example, due to 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 should, 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 The laboratory shall confirm the continuing validity of calibrations by regular analysis of calibration check standards throughout the analytical batch according to a defined procedure. The instrument shall not be re-calibrated using the check standard. If a check standard fails to meet appropriate predefined limits the laboratory shall recalibrate and reanalyse affected samples, unless they can demonstrate that the results are not affected. Where appropriate, procedures shall be in place to ensure calibration is valid through to the end of an analytical run.

6.4.11 to 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 For data to be submitted to the Environment Agency for regulatory purposes, the requirements of the methods used shall be clearly and unambiguously defined and documented. The laboratory shall demonstrate that those who undertake the analysis understand the requirements of the methods used.

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 user of the analytical service should be aware that if it wishes to submit the data to the Environment Agency for regulatory purposes, then the requirements of this performance standard need to be satisfied.

To submit data to the Environment Agency for regulatory purposes, the laboratory shall select the appropriate test and calibration methods that satisfy the requirements of this performance standard.

A laboratory may sub-contract the chemical testing of soil 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 terms of this clause do not apply to samples sent to a laboratory by an external quality control or inter-laboratory proficiency-testing scheme organiser.

7.1.2 to 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 they use suitable methods (including sample pre-treatment and preparation) for the analysis of a particular matrix and parameter. They shall also show that it is appropriate for 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. The laboratory shall make full details of the method and method validation procedures available to the Environment Agency, if requested.

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

7.2.1.4 The Environment Agency will not prescribe those analytical methods that an organisation should use, but the method used shall be appropriate for the matrix

and parameter at the level of concentration being analysed. Where results are submitted to the Environment Agency for regulatory purposes, the laboratory shall provide a clear and unambiguous description of the method used to generate the results, if requested. This description does not need to be fully comprehensive. However, it should comprise more than the title of the method and shall clearly indicate the parameter, scope, principle and matrix or matrices for which the method is applicable.

You shall describe the method, parameter, and matrix in enough detail to allow direct comparisons with similar methods, parameters, and matrices that other analysts or laboratories may use.

For example, if the laboratory uses an extraction technique to isolate or concentrate a particular parameter, they shall report:

- the name of the solvent or full details of the composition of the solvent mixture
- the amount of soil taken for analysis and the amount of solvent used in the extraction
- where the analytical determination of an extract is undertaken and, for example, that involves the use of a specific wavelength or mass number, then details shall also be given

The term ‘contaminated land’ will not be sufficient to describe the matrix, which shall include reference to the major constituents and components.

Here are examples of the description of the sample matrix:

- “an organic-rich (predominantly loam) soil visibly contaminated with hydrocarbons”
- “an industrial soil of mostly clay and sand (containing brick debris) from a former manufacturing site” possibly with a statement of the manufactured product

A fully documented method shall be made available to the Environment Agency, if requested.

7.2.1.5 to 7.2.1.7 No additional requirements to EN ISO/IEC 17025.

7.2.2 Validation of methods

7.2.2.1 Laboratories shall validate each method for a particular matrix and parameter and shall accredit each method to EN ISO/IEC 17025 for this performance standard. The process of full validation provides confidence that the established performance characteristics are robust experimental determinations and are statistically sound.

Validation procedures include a number of operations. Where available and appropriate these shall include the analyses of, matrix certified reference materials relevant to the matrices, parameters, and range of parameter concentrations under

investigation. The laboratory shall validate the method for each parameter analysed on matrices they are likely to analyse. This validation shall include at least three different soil matrices.

Laboratories shall consider sample pre-treatment and preparation as an important part in the validation process. Certified reference materials may not need any pre-treatment. In these cases, a separate exercise to determine the effects of sample pre-treatment and preparation shall be undertaken.

Note: It is not acceptable to use a single validated method established for one particular matrix for all matrices.

When suitable CRMs are not available, recovery estimates relevant to the matrix and parameter under investigation shall be determined using spiking experiments. Where possible these experiments shall cover the entire method (including pre-treatment, extraction, and determination). The addition of a parameter to a sub-sample followed by immediate extraction is not a satisfactory test for estimating spiking recovery. Enough time must elapse to allow possible matrix-parameter interactions to occur. The laboratory shall demonstrate that its use of spiking experiments and the spiking procedures employed is appropriate.

If recovery estimates are made using spiking experiments, a suitable CRM may become available at a later date. The laboratory shall use the new CRM to check that bias is satisfactory. You can estimate the number of replicate determinations required to detect a bias at a target level (for example MCERTS performance targets) if you know the precision of the measurement.

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. The laboratory shall obtain recovery estimates using two significantly different but appropriate concentration levels, for example, at 20 % and 80 % of the expected range. All solutions shall be taken from bulk stock solutions that are stable over the entire period of testing. Alternatively, if solutions are not stable over the entire period of testing, they can be prepared immediately before the analysis of each validation batch. The laboratory shall establish traceability of these solutions.

When using Isotope Dilution Mass Spectrometry (IDMS), the recovery corrected values of spiked samples and CRMs shall be used to estimate bias against the CRM and added spike if:

- appropriate labelled analogues of the parameters are spiked into all samples (including calibration standards and matrix AQC standards)
- samples are equilibrated appropriately before sample preparation is undertaken

The recovery corrected values of spiked samples and CRMs obtained in this manner shall be used to estimate bias against the CRM and added spike.

7.2.2.2 Revalidation

After validation and accreditation of an analytical method, it is inevitable that in time some modification of procedures will take place. Any modifications to a method used within a laboratory may affect the resulting performance. Laboratories shall notify UKAS of any changes made to a method already accredited against the MCERTS requirements. 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 laboratories shall take care to make sure the cumulative effects of several changes do not affect system performance. For example, by closely monitoring internal and external AQC, 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 only need to demonstrate that the new instrument performs as well as the old instrument. Laboratories can achieve this by analysing several replicates of a representative matrix such as a spiked soil, a CRM or a soil AQC sample.

If you make a fundamental change to the analytical procedure or the equipment used, then a full validation on a minimum of 3 matrices is required in accordance with this performance standard. These changes may include, for example, replacing Inductively coupled plasma optical emission spectrometry (ICPOES) with inductively coupled plasma mass spectrometry (ICPMS) or using a new extraction technique.

Laboratories should carry out an intermediate degree of validation if significant changes are made to a method that are not considered fundamental to performance. They shall perform a partial validation (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 the method needs this level of validation, then it shall notify and gain the approval of UKAS. Laboratories shall make sure that they include amendments to the analytical system and any procedures that they may affect, in the revalidation.

7.2.2.3 Validation procedures

For the method, parameter and matrix, the laboratory shall determine performance characteristics with a minimum of ten degrees of freedom. The laboratory shall carry this out by analysing each certified reference material or spiked sample in duplicate in different analytical batches.

Ideally, laboratories should analyse each analytical batch with a new calibration, to make sure you fully reflect between batch variations. If you apply a fixed calibration or infrequent calibration in routine operation of a method and can demonstrate it is

appropriate for the method under test, you may need fewer calibrations. The laboratory shall agree the amended validation procedure with UKAS and the Environment Agency.

Eleven batches of duplicates will guarantee a minimum of 10 degrees of freedom, but you may achieve 10 degrees of freedom in less than 11 batches. You can check this after each batch of results, appropriate procedures are given in:

- 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
- ISO TR 13530:1997 Water Quality - A Guide to Analytical Quality Control for Water Analysis

The period of validation must be between 6 days and 3 months. If a method is routinely calibrated, for example monthly, laboratories shall spread the analytical batches used for validation over the 3-month period.

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

When you have collected the data, estimate precision using analysis of variance (ANOVA). From this you can estimate different sources of error (for example within batch and between batch random errors) and combined them to give a total error as a standard deviation. Details of the statistical procedures for ANOVA and recovery (bias) estimation are given in Annex B, and these references:

- ‘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
- ISO TR 13530:1997 ‘Water Quality - A Guide to Analytical Quality Control for Water Analysis’
- NORDTEST Handbook of Internal Quality Control NT TR 569

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

The laboratory shall demonstrate that the certified reference material for the matrix, methodology, parameter, and concentration of parameter being analysed is appropriate.

After validation of a method, its stated performance shall reflect the routine capability of the method. So, when the laboratory uses the method routinely, its day-to-day performance shall be typical of and maintained at the level of the stated validation performance.

The LOD 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 LOD shall be fit for the intended purpose and appropriate to the concentration level of interest required of the analysis. Laboratories shall calculate the LOD as described in Annex B1. Never use the limit of detection in isolation of other method validation data to judge the appropriateness of a method.

Note 3: 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.

Performance criteria

The Environment Agency has specified that the following performance characteristics are acceptable for the validation of methods for the chemical testing of soil. You should bear 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 entire method shall not be significantly greater than the figure indicated in Annex A (Tables 1 to 4) expressed as a percentage. Laboratories shall use the certified reference value of the certified reference material as the true or accepted value when calculating bias for a known critical level of interest, you can use one-twentieth of the critical level of interest as the target bias, rather than the value in Annex A. You can use the greater of the 2 values. Laboratories shall demonstrate that the bias satisfies the stated requirement at the critical level of interest.

The precision, as expressed as the percent RSD, of individual results determined for the entire method shall not be significantly greater than the figure indicated in Annex A (Tables 1 to 4). Laboratories shall estimate precision using ANOVA to determine total standard deviation. For a known critical level of interest, you can use one-fortieth of the critical level of interest as the target precision, rather than the value in Annex A. You can use the greater of the 2 values. Laboratories shall demonstrate that the precision satisfies the stated requirement at the critical level of interest. Laboratories shall carry out testing for significance as described in Annex B2. If, for a particular parameter, testing shows a significant difference exists, then the laboratory may need to carry out further method development or refinement or use a different analytical method.

Annex A (Tables 1 to 4) specifies the performance characteristics for a selection of parameters (which is not exhaustive).

Note 4: In the context of soil analysis, bias and recovery can both be used to estimate systematic error. Where possible, laboratories should use certified reference materials in preference to spiked soils. If appropriate certified reference materials are not available (either for the matrix, parameter, or parameter concentration under investigation) then spiking experiments may offer the only suitable means of estimating recovery. Where the analysis

involves preparation and steps (for example drying and grinding) that are not required for the certified reference material, then you may need to use a combination of CRM analyses and spiked soil analyses.

When a laboratory requests accreditation of additional parameters not listed in Annex A of this standard, the performance requirements laboratories shall use are:

- metals – 7.5% precision and 10% bias
- organometallics – 15% precision and 30% bias
- inorganics – 10% precision and 20% bias
- organics – 15% precision and 30% bias

If a laboratory is unable to meet these requirements due to matrix effects or fitness for purpose issues it shall propose alternative performance characteristics and submit them to the Environment Agency through UKAS for assessment.

Unvalidated matrices

If a laboratory receives soils of a different matrix to those on which they have carried out full validation, then for each sample type/matrix the laboratory shall undertake replicate analyses and carry out spike recovery tests with batches of samples as they are received. They should include spikes and replicates at random, each at a minimum frequency 1 per 20 samples. If the batch size is less than twenty, then they shall still include one spike and one replicate sample.

Use the results from the spiked and unspiked samples to calculate the percentage recovery. Report the results of sample spikes and replicates.

For some parameters a high background concentration may make it difficult to assess spike recovery. The laboratory may need an alternative approach, such as pre-dilution of spiked samples before analysis.

An alternative to spiking and replicating samples for unvalidated matrices is the use of isotopically labelled surrogate compounds to establish the recovery of each parameter for each sample. The laboratory shall add a known amount of the isotopically labelled surrogate compound to every sample prior to sample analysis. The recovery of the surrogate compound shall fall within acceptable limits and should be reported with the associated sample results.

7.2.2.4 No additional requirements to EN ISO/IEC 17025.

7.3 Sampling

7.3.1 Laboratories shall analyse a sample using either all of the sample or a representative or homogenised sub-sample. If a parameter is unstable, or suspected of being unstable, or begins to degrade once sampled, then the analysis shall be carried out as soon as possible.

7.3.2 The analysis shall be undertaken on a sub-sample of the sample as removed from the site or preserved or stabilised on site. The results of this analysis shall then be converted to, and reported on, a dry-weight basis of the sample submitted to the laboratory. This means the sample shall be analysed on a ‘wet-weight’ or ‘as submitted’ basis, but results reported on a dry-weight basis, and this fact recorded. The laboratory shall define and report procedures used to establish the dry-weight basis, as well as the drying temperature.

7.3.3 No additional requirements to EN ISO/IEC 17025.

7.4 Handling of test or calibration items

7.4.1 When a sample undergoes stabilisation or preservation before analysis, then the laboratory shall record this fact when they report the results and also details of the stabilising or preserving agents used. 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.

When a laboratory dries a sample before analysing it, they shall provide sufficient information to establish the stability of the parameter analysed. This information provides justification for the analysis of the dried sample, rather than analysing the sample on a ‘wet-weight’ or ‘as submitted’ basis.

Note 1: This information may be in the form of a statement, or describe the work undertaken to justify the approach adopted.

The laboratory shall define and report the procedures used to prepare dried samples. This may include air-drying, assisted-drying or both. The drying temperature shall be appropriate, to make sure that the parameter does not undergo degradation or loss from the sample during drying. If a sample is to be described as air-dried the drying temperature shall not be more than 30 ^{0}C.

When a sample is removed from the site, it often contains a variety of substances and constituents other than the soil and contaminants under investigation. Once dried, the sample may need to be crushed, ground, or sieved, or certain constituents removed. If so, appropriate details of the sieve and any material remaining on the sieve, or any constituent parts removed, shall be recorded and reported. These details shall include, for example, the amount, type and nature of such materials.

Laboratories shall note whether any constituent parts removed or material not crushed, ground or sieved undergoes the same analysis as that carried out on material that undergoes crushing, grinding or sieving. Reports shall provide all relevant information (including details of the sieve) to establish whether the analysis of the sub-sample relates to all, or constituent parts, of the sample submitted to the laboratory.

Note 2: Different practices exist for sample preparation and pre-treatment and that these practices depend on the nature of the sample submitted, the site from where samples come from and the need for the analysis. It is of paramount importance that relevant information is reported.

7.4.2 to 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 minimum of 6 years. This period of time shall take into account the need of the customer (user of the analytical 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

No additional requirements to EN ISO/IEC 17025.

Note: You can find information about the estimation of measurement uncertainty in these references:

- S L R Ellison and A Williams (Eds). Eurachem/CITAC guide: Quantifying Uncertainty in Analytical Measurement, Third edition, (2012) ISBN 978-0-948926-30-3
- Handbook for Calculation of Measurement Uncertainty in Environmental Laboratories. Version 4, Nordtest Report TR 537

7.7 Ensuring the validity of results

7.7.1 Internal Quality Control

7.7.1.1 For internal quality control, the laboratory shall verify the performance of each analytical method for each batch of samples analysed. Laboratories shall analyse control samples within the analytical batch with which they prepare them.

Note 1: Annex E contains the internal quality control requirements for hydrocarbon banding methods.

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 soils, in that order of preference. If the batch size is less than twenty, one laboratory control sample per batch is still required.

To monitor the variation of laboratory control samples, laboratories shall record or plot control sample results on quality control charts (see Annex C). Laboratories shall review the charts regularly and update the control limits as necessary (see Annex C). To demonstrate statistical control, plot a minimum of 30 points in a 12-month cycle, spread evenly over the period.

Note 2: When you update control limits, estimates of measurement uncertainty should also be updated.

If a laboratory carries out an analytical procedure infrequently, it shall be necessary to employ a greater degree of AQC to make sure you maintain statistical control of the method. The approach taken shall be fully justified.

Note 3: 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.

If laboratories use their own reference materials or spiked soils, the actual values used must conform to the traceability criteria as described in EN ISO/IEC 17025. The following types of control material may be suitable:

1. Certified Reference Material or Reference Material– a sample of the target matrix, the concentration of parameter being certified to a quoted uncertainty and preferably traceable to an international or national Standard.

Note 4: Where possible use reference materials from producers that meet ISO 17034. ISO Guide 33 provides guidance on the selection and use of reference materials.

2. In-house Reference Material – a sample produced by the laboratory. It is vital that the sample is fully homogenised so that variations in repeat analyses reflect the analytical method performance and not inhomogeneity of the sample. The amount of material should be large enough to provide consistent and stable samples for as long a period as possible. An advantage of using in-house reference materials is the ability to match the parameter concentration and matrix of the material to samples normally encountered in the laboratory.

Note 5: You can find guidance on the production of in-house reference materials in references:

- Guidelines for the In-House Production of Reference Materials – version 2, B Brookman, R Walker 1998 LGC/VAM/1998/040.
- Applications of Reference Materials in Analytical Chemistry - V. Barwick, S. Burke, R. Lawn, P. Roper and R. Walker Royal Society of Chemistry, Cambridge, 2001 ISBN 0-85404-448-5.
- ISO guide 80 Guidance for the in-house preparation of quality control materials (QCMs)

Note 6: You may achieve traceability for this material 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 Soil – A soil representative of the matrix being analysed, to which you add a known quantity of a parameter standard solution before analysis. A parameter that has been added to the soil may not be present in its 'natural' state or fully integrated with the sample matrix. However, this may be the only option available, for example when the parameter is unstable or volatile. Standards used for spiking the sample should be from a different source to that used for calibration. Suitable contact times between spiking and extraction should be determined to provide interaction between spike and sample and to ensure there is no degradation of the parameter.

Note 7: 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 – When you carry out a test infrequently consider duplicate analyses of individual samples as submitted to the laboratory, and 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 For the individual parameters listed in Annex A (Tables 1 to 4) laboratories shall plot quality control results on appropriate control charts. You can find instructions on how to prepare and interpret AQC charts in Annex C.

In multi-parameter organic methods, for example volatile organic compounds (VOCs) or semi-volatile organic compounds (SVOCs), laboratories shall plot all parameters on control charts. Laboratories shall use all parameters listed in Annex A and a minimum of 20% of parameters not listed for immediate laboratory quality control. Groups of parameters with similar properties shall have representative parameters selected for this. The selection of these parameters should include critical parameters, for example:

- those most likely to be laboratory contaminants
- for chromatographic methods, parameters that elute at the beginning and end of a chromatogram, or those whose peaks are poorly resolved.

Laboratories shall justify their approach. They shall record the other results and review them as part of regular AQC performance review. Precision and bias shall not statistically exceed 15% precision and 30% bias performance requirements.

7.7.1.3 Laboratories shall have documented procedures that define loss of statistical control and specify actions to take (control rules) when control samples breach control limits. They shall investigate all breaches, record the findings and actions, and make them available to the Environment Agency, if requested. Laboratories shall reanalyse samples in an analytical batch where laboratory control samples breach the defined control rules.

Laboratories shall include the following checks in their investigations, but may need to carry out other checks:

- changes in concentration of stock standard solutions and reagents, and that they do not exceed expiry date
- 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 (such as analysis repeated, or results reported – see Annex C3)

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 parameter concentrations analysed within the laboratory.

Note: The Environment Agency will encourage scheme organisers to provide appropriate samples (in terms of matrices, parameters, and concentrations of parameters) for distribution that reflect real-life situations and site investigations.

7.7.2.2 Where possible, the methods, used by the laboratory to generate analytical data for the chemical testing of soil 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, the laboratory should treat samples distributed by the proficiency-testing scheme organiser in the same manner as normal routine samples submitted for chemical testing of soils. 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, 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.

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

This review procedure should take into consideration the number of other laboratories participating in the scheme 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 of results

7.8.1 General

No additional requirements to EN ISO/IEC 17025.

7.8.2 Common requirements for reports (test, calibration or sampling)

No additional requirements to EN ISO/IEC 17025.

7.8.3 Specific requirements for test reports

7.8.3.1 For data submitted to the Environment Agency for regulatory purposes, the report shall include appropriate information that clearly identifies and locates the sample relating to the results. This information shall record all data necessary to allow a complete audit trail to be made. Relevant information includes:

- location of sample, including depth where necessary
- unique sample code or reference
- date/time sample taken
- name of laboratory
- name of any sub-contracting laboratories, if used
- date sample analysis completed
- parameter analysed, including any sample preservation or stabilisation at sampling site
- whether analysis carried out on dried, air-dried or ‘as submitted’ basis
- result of analysis on dry-weight basis
- other relevant comments, for example, visual characteristics of sample

Note: Some of this information may only be available from, or be able to be provided by, whoever commissions the analytical service or takes the samples and not the laboratory.

However laboratories determine results, they shall calculate and report all results on a dry-weight basis. The laboratory shall report the procedures used, how they define and determine air-dried and dry-weight results and the sample drying temperature.

Results that are submitted to the Environment Agency shall be accompanied with a statement indicating whether the results have been recovery corrected or not. If corrected you shall explain the criteria used, including the manner of calculation.

Whenever possible and where appropriate, individual compounds should be analysed, and individual results reported. Where a group of similar compounds is analysed and the combined concentrations of these compounds are expressed as the sum of individual concentrations, the laboratory shall record the number and identity of each compound analysed. This information shall be reported with the results. If this approach is not possible or appropriate, the laboratory shall define the analysis undertaken and the calculated result. This information shall be reported with the result.

7.8.3.2 No additional requirements to EN ISO/IEC 17025.

7.8.4 to 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

Table 1: Metals and organometallics

In the table, although no limit of detection has been specified, it shall be fit for purpose. Especially, for example, when compared to ‘soil guideline values’ or critical levels of interest.

Parameter	Precision (%RSD)	Bias (%)
Antimony	7.5	15
Arsenic	7.5	15
Barium	7.5	10
Beryllium	7.5	10
Boron (water soluble)	10	20
Cadmium	7.5	10
Cobalt	7.5	10
Copper	7.5	10
Chromium	7.5	10
Hexavalent chromium	7.5	10
Iron	7.5	10
Lead	7.5	10
Manganese	7.5	10
Mercury	7.5	15
Molybdenum	7.5	10
Nickel	7.5	10

Parameter	Precision (%RSD)	Bias (%)
Organolead compounds	15	30
Organotin compounds	15	30
Selenium	7.5	15
Thallium	7.5	10
Vanadium	7.5	10
Zinc	7.5	10

Table 2: Inorganics

In the table, although no limit of detection has been specified, it shall be fit for purpose. Especially, for example when compared to ‘soil guideline values’ or critical levels of interest.

Parameter	Precision (%RSD)	Bias (%)
Ammonia	10	20
Chloride	10	20
Easily liberatable cyanide	15	30
Complex cyanide	15	30
Total cyanide	15	30
Loss on ignition	7.5	15
pH	0.2	0.2
Sulfide	15	30
Sulfate	10	20
Sulfur	10	20
Thiocyanate	15	30

Table 3: Organics

In the table:

- although no limit of detection has been specified, it shall be fit for purpose, especially, for example when compared to 'soil guideline values' or critical levels of interest
- the data for 'explosive substances' covers explosive compounds listed as the "11 most common" in the R&D Technical Report P5-042/TR/03
- for petroleum hydrocarbons, the requirements for validation of hydrocarbon banding methods can be found in appendix E

Note 1: performance targets are for individual compounds within these groups. If a total (for example total PAH) result is requested, then each individual component should be determined and reported with the total.

Parameter	**Precision (%RSD)**	**Bias(%)**
Benzene	15	30
Benzo[*a*]pyrene	15	30
Chlorobenzene	15	30
Chloromethane	15	30
Chlorophenol	15	30
Chlorotoluene	15	30
Dichloroethane	15	30
1,2-dichloroethene	15	30
Dichloromethane	15	30
Dioxins	15	30
Explosive substances	15	30
Ethylbenzene	15	30
Furans	15	30
Hexachloro-1, 3-butadiene	15	30

Parameter	Precision (%RSD)	Bias(%)
Petroleum hydrocarbons	15	30
Nitroaromatics	15	30
Pentachlorophenol	15	30
Phenols	15	30
Phthalate esters	15	30
Polyaromatic hydrocarbons(PAH)	15	30
Polychlorinated biphenyls (PCB)	15	30
Tetrachloroethane	15	30
Tetrachloroethene	15	30
Tetrachloromethane (carbon tetrachloride)	15	30
Total organic carbon (soil organic matter estimation)	10	20
Toluene	15	30
Trichloroethane	15	30
Trichloroethene	15	30
Trichloromethane (chloroform)	15	30
Vinyl chloride	15	30
Xylene	15	30

Table 4: Additional parameters

In the table although no limit of detection has been specified, it shall be fit for purpose. Especially, for example. when compared to ‘soil guideline values’ or critical levels of interest.

Method or parameter	Precision (%RSD)	Bias (%)
Extractable phosphate content (Olsen)	10	15
Extraction of the exchangeable cations in soil: potassium	10	15
Extraction of the exchangeable cations in soil: magnesium	10	15
Extraction of the exchangeable cations in soil: sodium	10	15
Organic carbon content % modified Walkley Black	5	10
Determination of electrical conductivity	5	15
Metals by nitric acid extraction and microwave digestion	7.5	10
Total nitrogen	5	15
Determination of carbonate content – volumetric method	6	10
Fluoride	10	20

Annex B (normative): Statistical Analysis

B1 Limits of detection and reporting

B1.1 Introduction

We do not specify the limit of detection (LOD) in this performance standard. But a common approach to the estimation of LOD is, to allow a laboratory's performance to be evaluated in a consistent and comparable way. If data reported to the Environment Agency are to include results reported as less than values, the LOD shall be estimated using the following protocol.

For further guidance on estimation of LOD for hydrocarbon banding methods see Appendix E2.3

B1.2 Choice of sample and sample pre-treatment

The blank sample used to estimate LOD shall be a soil containing a small but measurable amount of parameter(s) of interest. If it can be demonstrated that a suitable soil cannot be obtained, then a sand containing a negligible amount of parameter of interest shall be used.

Note 1: The sample used for estimating LOD should be as similar as possible to the matrix being analysed. Using a single sample for the determination of LOD for a given method will not take into account different matrix effects.

Ideally analysis of the blank sample will produce normally distributed results scattered around zero, that is, both negative and positive results will be seen. It is usually possible for the blank 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 blank sample should be spiked with a small amount of the parameter, sufficient to produce a small but significant response from the analytical system that is close to the expected LOD. This concentration shall not exceed 5 times the LOD.

The blank or spiked sample shall be put through the entire analytical process (including, as necessary, drying, grinding, extraction, clean-up, and measurement). The extraction and measurement of blank solutions based only on solvent or reagent blanks is not sufficient for estimating LODs for the purpose of satisfying MCERTS requirements. The blank samples or spikes shall be processed in the same way and using the same equipment and reagents as other samples in a batch.

Note 2: Soils may contain a significant amount of common substances such as iron, zinc, chloride and sulfate. If pure sand or silica blank is used to determine LOD an optimistic (lower concentration) estimate can be obtained. If an 'uncontaminated natural' soil is used and it contains a significant amount of these substances then a pessimistic (higher concentration) LOD will be obtained

Note 3: It is important that users of results should appreciate that the LOD for these common substances obtained by all MCERTS accredited laboratories should be adequate for all these commonly (naturally) occurring substances. However, it is unlikely that LOD will be an issue with these substances, as adequate precision and bias at the level of interest is more pertinent.

Note 4: For commonly occurring substances the variation in blank values should be consistent and within acceptable limits. Ideally all blank values for these substances should be less than 10% of the critical level of interest.

B1.3 Calculation

In this 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)

$\boldsymbol{S_w}$ 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 sample blanks shall be analysed in at least 10 different analytical runs or batches. Ideally these blanks 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 sample blanks shall not be used as a calibration blank, and if the analytical procedure requires samples to be blank corrected, then the sample blanks 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, 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 = 5.13S_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 blank samples in the same batch, here $\mathbf{S_t}$ (total standard deviation) equates to $\mathbf{S_w}$, with 10 degrees of freedom. This procedure should be used when a matrix is analysed by a method that has not been fully validated for that matrix.

B1.4 Form of expression

For a multi-parameter method such as PAH, each individual PAH will need to have its own LOD estimated.

For TPH and similar parameters, it would not be appropriate to estimate the LOD using just one of the hydrocarbons within the analytical range. Blank sample data shall be generated in the same way as normal sample data to obtain the results used in estimating LOD.

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.

B1.5 Reporting limit

For the purposes of this MCERTS performance standard the reporting limit will be the limit of detection calculated as above. However, a laboratory may use higher reporting limits than calculated LODs. For example, a laboratory calculated LOD for a method as <0.2 mg/kg but prefer to report <1 mg/kg due to issues with reporting software and customer requirements. This is considered wholly acceptable by the Agency, as long as LOD is calculated in the correct way.

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

B2 The use of statistical significance tests in the interpretation of method performance

B2.1 Introduction

Method validation aims to produce data on the precision of analysis and to provide an indication of any susceptibility to systematic error or bias.

Assuming that validation has been carried out as described in section 7.2.2 and that Analysis of Variance (ANOVA) has been applied to the results, there should be sufficient data to assess whether method performance complies with Annex A criteria (see section 7.2.2.3).

B2.2 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 three stages:

1. Determine the target standard deviation at the concentration of interest, in accordance with section 7.2.2.3..
2. If the measured standard deviation is less than the target standard deviation, the target has been achieved.
3. If 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.

B2.3 F-Test of standard deviation

The F-test or variance ratio test is a way of determining whether or not differences between 2 standard deviations are statistically significant (at a chosen probability level). The procedure is to calculate the F ratio as shown below:

$$F = S_t^2 / Z^2$$

where 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 S_t and Z.

Z is a target standard deviation and therefore has infinite degrees of freedom. In the case of 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:

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

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, that is, performance passes.

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

B2.4 Assessment of systematic error or bias

This assessment is only relevant and should 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 using reference materials or by spiking recovery experiments.

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

Significance is assessed by means of calculating the confidence interval about the mean and checking to see if this overlaps the limits of tolerable bias.

Overall Mean Recovery = $M = \Sigma R_i / m$

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

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

Where:

m = number of batches

R_i = %Recovery of the ***i***th batch

S_R = standard deviation of batch recoveries

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

If the calculated recovery range overlaps with the required target bias range the recovery is not significantly different to the MCERTS requirement and is regarded 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%.

Examples

Two examples are presented below to illustrate the application of the statistical tests mentioned above. The first considers a spiking exercise for cadmium, the second a CRM used to validate a method for benzo(b)fluoranthene.

Example 1: cadmium mg/kg in soil – spiked samples

Batch	Low sample replicate 1	Low sample replicate 2	Low sample batch mean values	Low sample batch mean % recovery	High sample Replicate 1	High sample Replicate 2	High sample batch mean values	High sample batch mean % recovery
1	3.60	3.81	3.705	92.625	47.0	48.5	47.75	119.38
2	3.96	3.83	3.895	97.375	42.6	43.1	42.85	107.13
3	4.10	4.02	4.06	101.5	47.5	49.3	48.4	121
4	4.30	4.12	4.21	105.25	44.0	46.1	45.05	112.63
5	3.84	4.05	3.945	98.625	47.02	46.37	46.695	116.74
6	3.91	3.70	3.805	95.125	40.12	40.69	40.405	101.01
7	3.34	3.44	3.39	84.75	41.93	41.32	41.625	104.06
8	3.83	3.68	3.755	93.875	43.4	44.87	44.135	110.34
9	3.80	3.85	3.825	95.625	42.19	42.95	42.57	106.42
10	3.32	3.52	3.42	85	43.46	43.0	43.23	108.08
11	3.90	4.02	3.96	99	43.81	44.34	44.075	110.09

Low sample overall mean (mean of low sample batch mean values) is 3.815 mg/l

Low sample overall mean recovery (mean of low sample batch mean % recovery values) is 95.39%

High sample overall mean (mean of high sample batch mean values) is 44.25 mg/l

High sample overall mean recovery (mean of high sample batch mean % recovery values) is 110.63%

Precision test (From ANOVA)

In the table:

- the tabulated $F_{0.05}$ value is obtained from statistical tables for the estimated degrees of freedom at the 5% probability level (p=0.05)
- the F-value is calculated as (total SD / target SD)^2

	Low sample	High sample
Mean	3.815	44.25
Within-Batch SD	0.112	0.812
Between-Batch SD	0.234	2.46
Total SD	0.26	2.58
Relative SD %	6.8%	5.9%
Target SD (5% of mean)	0.19	2.21
$F_{0.05}$ from tables	1.75	1.79
F-Value calculated	1.86	1.37
Estimate degrees freedom	12	11
Assessment	FAIL	PASS
Overall mean recovery	95.39%	110.63%

In this example the observed standard deviation of the low concentration sample is greater than the target standard deviation, so an F test is performed. F calculated is greater than the tabulated reference F value so the standard deviation of the low sample is significantly different than 5% and therefore fails to meet the MCERTS target. In the case of the high concentration sample the measured total SD is larger than target but the F test shows that this is not significantly larger – hence this is judged to meet MCERTS requirements.

Recovery for high sample

In the table:

- the mean measured value is the average of the mean recovery for each batch
- the standard error of mean recovery is the relative SD of overall mean recovery divided by the square root of the number of batches
- the 90% confidence interval of recovery 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)

Reference concentration	40
Mean measured value	44.25
Overall mean recovery	110.63%
SD of mean recovery	6.306
Standard error of mean recovery	1.901
90 % Confidence interval of recovery	+/-3.44
Recovery range	107.2% to 114.1%
Assessment	PASS

The bias target for cadmium is 10% so the tolerable range of recovery in this example is 90-110%. In the case of the high sample this overlap of confidence interval with the tolerable range means that although recovery is nominally outside this range it is not significantly so and is therefore acceptable**.** Note that the precision must be acceptable before this test can be applied, so it would not be appropriate to test the low sample.

Example 2: CRM for Benzo(b)fluoranthene

This CRM has a certified concentration of 26 μg/kg

Batch	Replicate 1	Replicate 2	Batch mean values	Batch mean % recovery
1	19.1	18.4	18.75	72.12
2	19.4	17.2	18.3	70.38
3	19.4	21.6	20.5	78.85
4	16.7	15.8	16.25	62.5
5	21.4	17.4	19.4	74.62
6	18.9	18.0	18.45	70.96
7	17.4	16.8	17.1	65.77
8	18.7	17.6	18.15	69.81
9	15.8	16.2	16.0	61.54
10	18.3	16.2	17.25	66.35
11	16.2	17.4	16.8	64.62

The overall mean of batch mean values is 19.91 mg/l.

The overall mean of batch mean % recoveries is 68.86%.

Precision test (From ANOVA)

Mean	17.91
Within-Batch SD	1.27
Between-Batch SD	1.04
Total SD	1.64
Relative SD %	9.16%
Target SD (15% of mean)	2.7
Assessment	PASS
Estimated Bias	-31.14%

In this example the requirements for precision have been met without the need for significance testing. However, the bias appears to be outside of the 30% target. As precision is acceptable the significance test for bias can be carried out.

Bias test (From ANOVA)

Reference concentration	26 µg/kg
Mean measured value	17.91
Overall mean recovery	68.9%
SD of mean recovery	5.2823
Standard error of mean recovery	1.5927
90% Confidence interval of recovery	+/-2.9
Recovery range	66.0% - 71.8%
Assessment	PASS

The calculated recovery range overlaps with the required range of 70-130% so the bias is not significantly different to the MCERTS requirement, at the 95% confidence level (p=0.05).

Annex C (normative): Production and use of Control Charts

C1 Introduction

The interpretation of results from the analysis of internal laboratory control samples is usually carried out using control charts. These charts compare current results against limits set after estimating the variability of an analytical system operating under statistical control. A method is in statistical control when the variability within the analytical system arises from stable sources of random analytical variability. Various forms of control chart may be appropriate for use, for example:

- Shewhart charts (individual result) the most common in use
- cusum (cumulated sum) charts – more sensitive to bias detection than Shewhart charts
- zone control chart (J-chart) – combines Shewhart and cusum charts capabilities

As a minimum use a Shewhart chart for each parameter, as described here. The use of other charts is described in these references:

- 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
- The J-chart: a simple plot that combines the capabilities of Shewhart and cusum charts, for use in analytical quality control". Analytical Methods Committee technical brief No.12, Royal Society of Chemistry 2003.
- Quality Control Charts in Routine Analysis, M J Gardner, WRc Report CO4239 1996.

C2 Setting up and updating Shewhart control charts

Control charts should be set up using estimates of mean (M) and standard deviation (SD) obtained from results of at least 20 control samples obtained when the analytical system is under statistical control. Laboratories shall obtain this data during method validation procedures.

The properties of the normal distribution allow the prediction that for on-going analysis, 95% of results will fall within M ± 2SD and that 99.7% of results will fall within M ± 3SD given no deterioration in method performance.

We have provided an example Shewhart chart. Construct the chart as follows:

- the y-axis is concentration, the x-axis time (that is date of analysis)
- the mean laboratory control standard value M is plotted as a line ('mean')
- two warning limits are plotted as lines at M ± 2SD
- two Action limits are plotted as lines at M ± 3SD

- the laboratory control standard nominal value may also be plotted as a line but is not shown in the example.

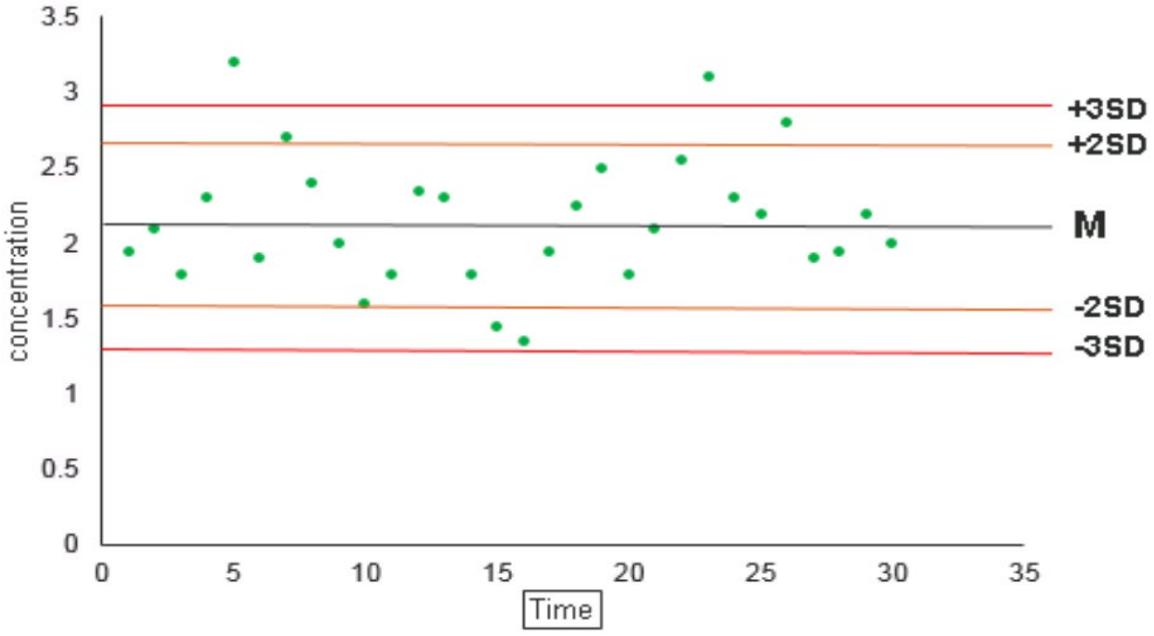
As laboratory control sample results become available, plot them individually and consecutively against date of analysis. They shall not be averaged before plotting.

As you plot them, control rules that indicate a system failure include:

- one laboratory control Standard result outside the control chart action limit
- two consecutive laboratory control Standard results outside the control chart warning limit

In addition, 9 successive laboratory control Standard results on the same side of the chart mean could indicate a change in the bias of the analytical system. Laboratories shall investigate any occurrences. However, this may be due to a small insignificant change and laboratories should use other methods of identifying significant changes in bias. For example, if you measure a number of control standards in each analytical batch of a high throughput method, then you can plot the average value to monitor bias only. However, a separate chart of individual values shall still be required for control of precision.

Example of a Shewhart control chart



The example chart shows the idealised plot of a Shewhart chart, showing a 3S failure and a consecutive 2S failure of control limits.

As further data are obtained, a new chart should be produced based on the latest 60 to 100 results (depending on frequency of analysis), giving a new and more robust estimate of M and SD.

If any of the data points have breached the control rules and a cause is assigned (for example use of wrong standard, or air in flow-cell), then it should not be used. However, since some legitimate results, which are part of the normal distribution, will breach the limits, then these should be used where no specific reason for the breach can be assigned.

The precision and bias shall not be allowed to exceed targets given in Annex A of this performance standard for a given parameter. If required, statistical significance tests should be applied (see Annex B).

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 be established and drawn on the control chart. If no significant changes are detected, then no changes should be made.

At least annually, mean and standard deviation values should be estimated from new data and should be checked to see if any significant changes have occurred. If necessary, the significance of a change in precision (as standard deviation) can be tested using an F test at the 95% confidence level, and if the mean has changed significantly using a student's t test, again at the 95% confidence level (see Annex B).

The targets given in Annex A of the MCERTS standard for a given parameter shall not be statistically significantly exceeded. However, all significant changes should be investigated, even if precision and bias are still within the MCERTS requirements. If the MCERTS targets are significantly exceeded and cannot be corrected, then a statistically significant change in performance has occurred. It will be necessary to re-validate the analytical method.

C3 Reporting

Laboratories shall not report results associated with failed AQC samples as MCERTS accredited results. In some circumstances customers may request the release of the results. Whenever results associated with failed AQC are required by the customer they should only be issued under the direct authority of an appropriate manager.

Any report issued, which contains results associated with failed AQC samples shall include a printed disclaimer as to this effect.

Annex D (informative): Estimation of soil organic matter (SOM)

The Environment Agency has published soil guideline values (SGVs) to aid the risk assessment of contaminated land. SGVs for contaminant organic compounds such as toluene, ethylbenzene and phenol address the fact that these compounds tend to adsorb onto soil organic matter (SOM), and so reduce plant uptake and volatilisation to air. As SOM increases less contaminant is available for these exposure pathways. The SGV calculated for these compounds varies with the SOM, the higher the SOM the higher the SGV. This means that SOM needs to be estimated.

The Environment Agency considers that the most appropriate way to proceed is to measure the fraction of organic carbon (foc) and then calculate an estimate of the SOM.

The definition of SOM used in the CLEA model is:

%SOM = foc x (100/0.58)

This assumes that SOM has a carbon content of 58%.

A method of estimation of foc is by the determination of total organic carbon (TOC) after prior removal of inorganic carbon with acid by dry combustion at 900°C, and measurement of released carbon dioxide. This does not preclude other appropriate analytical methods.

foc = TOC x 10^{-6} where TOC is expressed in units of mg/kg

therefore %SOM = TOC / 0.58 where TOC is expressed as a percentage

Laboratories can estimate SOM from the loss on ignition method. However, laboratories will need to develop a conversion factor that will depend on the soil matrix and the temperature of ignition.

Annex E (normative): Accreditation of hydrocarbon banding

E1 Introduction

Many laboratories have obtained accreditation for TPH (total petroleum hydrocarbons) or EPH (extractable petroleum hydrocarbons). However, reporting of petroleum hydrocarbon concentrations in soils using bands that are defined by carbon number is becoming increasingly important for contaminated land assessment.

Note 1: The term EPH is often used to describe the fraction C10 to C40, and VPH (volatile petroleum hydrocarbons) the fraction C6 to <C10 and the sum of the two fractions being reported as TPH. This convention is not strictly adhered to, and some laboratories quote different ranges. It is not the purpose of this document to define these terms or fractions or how these fractions are divided into specific bands. Laboratory methods and their associated scopes should do this. The requirements of the Environment Agency will be stated elsewhere.

Note 2: TPH analysis is usually performed on an as received sample, rather than a dried and crushed sample, to minimise loses of the volatile fraction.

E2 Validation

E2.1 Hydrocarbon banding (without separation into aliphatic and aromatic fractions)

A laboratory that requires accreditation for hydrocarbon banding without separation into aliphatic and aromatic fractions shall use the following procedure:

- the bands that are reported will contain both aliphatic and aromatic hydrocarbons
- the beginning and end for integration of each band shall be defined by running a mixture that contains n-alkanes (straight chain, unsaturated hydrocarbons) with carbon numbers whose range covers the bands defined in the method

Note: It is not acceptable to report bands to odd carbon numbers using solely even numbered hydrocarbons.

- a minimum of three soil matrices shall be used in the validation
- if available and appropriate, matrix CRMs shall be used
- the performance characteristics shall be determined with a minimum of 10 degrees of freedom by analysing batches of duplicates
- if CRMs are not available, each matrix should be spiked at two significantly different but appropriate concentration levels, for example, at 20 % and 80 % of the range of the method, using a spike composed predominantly of a mixture of petroleum hydrocarbon fractions to ensure that there are adequate amounts of appropriate hydrocarbons in each of the bands for which accreditation is sought

- this oil mixture may be fortified with n-alkanes or PAHs if necessary but use of a spike containing individual n-alkanes or PAHs alone or containing predominantly individual n-alkanes or PAHs alone is inappropriate and shall not be used
- soil matrices should be extracted, analysed and the resulting chromatogram interpreted using the method for which accreditation is sought

Performance targets:

- the precision of the method for the sum of the bands shall not significantly exceed 15% and the bias of the method for the sum of the bands shall not significantly exceed 30%
- the precision of the method for each individual band shall not significantly exceed 15%

E2.2 Aliphatic and aromatic fractions and subsequent banding

The validation protocol is the same as that outlined in E2.1 and the performance targets are as follows:

- if total TPH is derived from summing the aliphatic and aromatic fractions, or the bands of those fractions, then the precision of the method for the sum of the bands shall not significantly exceed 15% and the bias of the method for the sum of the bands shall not significantly exceed 30%
- the precision for the aromatic and aliphatic fractions shall not significantly exceed 15%
- the precision of the method for each individual band shall not significantly exceed 15%

In this case the precision obtained by laboratories for each band will be reviewed and changed if deemed necessary.

Accreditation for banding and splitting into aliphatic and aromatic fractions and subsequent banding will only be granted if each and all of the bands within the range defined by ‘total’ EPH or TPH can be shown to meet the specified targets.

E2.3 Limit of Detection (see also Annex B1)

A soil containing a small but detectable amount of the parameter of interest shall be analysed for determining the limit of detection for TPH (total, aromatic/aliphatic split and banded) in soils. This sample can be prepared by spiking.

The low spiking solution for LOD estimation should use a spike composed predominantly of a mixture of petroleum hydrocarbon fractions. You should ensure that there are adequate (but not greater than 5 times the resulting LOD) amounts of appropriate hydrocarbons in each of the bands for which accreditation is sought. This oil mixture should be the same as that used for the spiking experiments and may be fortified with n-alkanes or PAHs if necessary. Use of a spike containing individual n-alkanes or PAHs alone or containing predominantly individual n-alkanes or PAHs alone is inappropriate and shall not be used.

The low spiked sample shall be put through the entire analytical process (including, as necessary, drying, grinding, extraction, clean-up and measurement). The extraction and measurement of blank solutions based only on solvent or reagent blanks is not sufficient for estimating LODs for the purpose of satisfying MCERTS requirements. The low spiked samples shall be processed in the same manner and using the same equipment as other samples.

The limit of detection shall be calculated as described in Annex B1.

E3 Quality assurance for hydrocarbon banding; aliphatic and aromatic split and subsequent banding

E3.1 Quality control

AQC samples shall be representative soils spiked at an appropriate level with an oil mixture as described in the validation protocol.

This shall be extracted and analysed, a minimum of 1 sample in every 20 samples shall be an AQC sample. AQC performance targets are 15% for precision and 30% for bias.

With respect to the evaluation of AQC results obtained the minimum that is expected is:

- for TPH (Total) Plot AQC Data
- for TPH (Bands) Monitor AQC Data
- for Aliphatic (Total) Plot AQC Data
- for Aliphatic (Bands) Monitor AQC Data
- for Aromatic (Total) Plot AQC Data
- for Aromatic (Bands) Monitor AQC Data

The frequency at which AQC data is monitored (where plotting is not mandatory) is at the discretion of the laboratory. However, if at the monitoring or review stage laboratories find that the targets have not been met, any associated results shall be treated as non-conforming work and it may be necessary to reissue reports. If a laboratory wishes to plot for all AQCs analysed, this is acceptable.

For AQC data that requires plotting laboratories shall plot it on a chart and shall follow the statistical acceptance rules as detailed in Annex C.

For AQC data that requires monitoring, AQC samples shall include the parameters of interest and AQC results shall be recorded. Laboratories shall review performance of monitored AQC as part of regular AQC performance review and precision and bias shall not statistically exceed the targets given in this Annex.

E3.2 System suitability

When splitting into aliphatic and aromatic fractions there are additional requirements for system suitability checks to ensure adequate separation column efficiency.

With every batch of new column material, a synthetic aliphatic and aromatic mixture shall be separated and analysed. This mixture shall cover the range of hydrocarbons analysed and shall be composed of aliphatic and aromatic components. A full range of hydrocarbons shall be present in the mixture and shall include critical compounds in each fraction (such as naphthalene, decane and corresponding compounds in the C30 to C40 range).

Laboratories shall estimate recoveries for the aliphatic and aromatic fractions concurrently with the method validation and use the estimates to set limits for subsequent analysis. As a minimum, laboratories shall maintain records of the recovery of the critical compounds in each fraction.