Performance Standard for Organisations Undertaking Sampling and Chemical Testing of Water

Part 1 - Sampling and chemical testing of untreated sewage, treated sewage effluents and trade effluents

Environment Agency
January 2013
Version 2

mCERTS
THE ENVIRONMENT AGENCY'S MONITORING CERTIFICATION SCHEME

Record of amendments

Version number	Date	Amendment
1	July 2008	Publication of version 1.
1.1	May 2009	clause 4.1.3 - added to strengthen the concept that treatment works operation should not be manipulated just to ensure compliant samples. 5.3.1.2 and appendix C. - standard required estimation of LOD for all methods, determinands and matrices. Proposed change will simplify so that only one matrix need have an LOD estimate. 5.3.1.3 - clarification that a mixture of CRMs and spikes can be used 5.3.3.2 - incorporation of briefing note1 section 1. 5.5.1 - clarification of status of Environment Agency sampling procedures. 5.5.2 - incorporation of briefing note1 section 4. 5.6.3.2 - additional note regarding update of QC charts.
2	January 2013	Clause 5.2.2.3 – added text to explain requirement to demonstrate appropriate CLOIs. 5.3.1.5 - clarification of requirements for validation of IDMS methods. 5.3.4.3 - incorporate briefing note 3, performance requirements of determinands not listed in Annex A. 5.3.5.1 - further guidance on ongoing validation added. 5.5.6 – incorporation of briefing note 4, temperature control of samples. 5.6.3.2 - review of control sample limits. Annex A - updated. Annex D - inserted to incorporate briefing note 2, portable instruments and test kits. Annex E - previously Annex D

Foreword

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

The standard we focus on in this document sets out what you must do if you carry out the sampling and chemical testing of untreated sewage, treated sewage effluents and trade effluents and have to send the results to us. Over time we expect the standard will be extended to cover other aqueous matrices.

We require organisations carrying out this work to be accredited by the United Kingdom Accreditation Service (UKAS) to international standard, ISO/IEC 17025 for this MCERTS performance standard.

The MCERTS standard provides an application of ISO/IEC 17025 specifically for the sampling and chemical testing of untreated sewage, treated sewage effluents and trade effluents. The standard covers:

- performance targets
- the selection and validation of test methods
- pre-treatment and preparation of samples
- ongoing quality control
- participation in proficiency testing schemes
- how test results and other information are reported
- sampling procedures.

Some of the requirements of this performance standard are described in general terms. This is to allow some flexibility and to allow the organisation to take advantage of technological developments. In this way, an organisation is not excluded simply because, for example, it lacks specific equipment.

However, along with this flexibility we need to ensure that all of the information we require is provided to us. This is particularly important where we assess test data for a specific site over a number of years, so that consistent and meaningful comparisons can be made. Where we assess data for regulatory purposes, all relevant information must be recorded and be available to us, if requested.

The benefits of this MCERTS standard

- MCERTS provides formal accreditation in accordance with European and international standards.
- The standard makes sure that you, the public and other organisations involved in the analysis of untreated sewage, treated sewage effluents and trade effluents can be confident that the information you provide is reliable.
- Everybody in the competitive market of untreated sewage, treated sewage effluents and trade effluents testing will be working towards meeting the same standard. The standard sends the message that the chemical testing of untreated sewage, treated sewage effluents and trade effluents is a critical component in producing reliable information for regulatory purposes;
- By setting quality standards that everybody must work towards, the standard promotes and raises the professional reputation of staff and organisations involved in the testing of untreated sewage, treated sewage effluents and trade effluents.

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

United Kingdom Accreditation Service
21 - 47 High Street
Feltham
Middlesex
TW13 4UN
Tel: 0208 917 8400
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E-mail: info@ukas.com
Web-site: www.ukas.com

For more information on MCERTS and for copies of the performance standards and further guidance, see our web-site at:

www.mcerts.net

If you have any general questions about MCERTS, please contact:

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Introduction

This extension of MCERTS to include the sampling and chemical testing of untreated sewage, treated sewage effluents and trade effluents is built on proven international standards to ensure that the quality of test data is high. This performance standard details the requirements for organisations undertaking the sampling and chemical testing of untreated sewage, treated sewage effluents and trade effluents to the MCERTS performance standard.

The general requirements for the competence of testing and calibration laboratories are described in the international standard ISO/IEC 17025. Where data are submitted to the Environment Agency for regulatory purposes, those data shall be generated using methods that have been accredited to the international standard ISO/IEC 17025 for this MCERTS performance standard. Such methods shall be included within an accredited organisation's scope of activities. This performance standard contains requirements that an organisation must meet if it wishes to demonstrate that it operates a management system, is technically competent and able to generate valid results, and wishes to be considered as an organisation registered under the MCERTS performance standard for the sampling and chemical testing of untreated sewage, treated sewage effluents and trade effluents. In addition, there are also requirements for procurers of analytical services who wish to submit data to the Environment Agency for regulatory purposes.

Note: The term organisation encompasses laboratories, because organisations not normally referred to as laboratories may apply for accreditation to this performance standard for sampling only.

ISO/IEC 17025 recognises - in clause 1.6 (Note 1) - that it might be necessary to explain or interpret certain requirements in the international standard to ensure that the requirements are applied in a consistent manner. This MCERTS performance standard provides criteria for applying ISO/IEC 17025 in the specific field of sampling and chemical testing of untreated sewage, treated sewage effluents and trade effluents. In producing this MCERTS performance standard, guidance given in Annex B of ISO/IEC 17025 has been followed.

This MCERTS performance standard does not restate all the provisions of ISO/IEC 17025 which must be complied with. It states only those additional requirements which must also be complied with, in order for an organisation to become registered under this MCERTS standard.

Annex E in this document is a table of cross-references between this MCERTS standard and ISO/IEC 17025:2005, and may not be the same as those in other dated versions of ISO/IEC 17025. The clause numbers in this document do not align with those of ISO/IEC 17025:2005.

1 Scope

1.1 The chemical testing of untreated sewage, treated sewage effluents and trade effluents can be undertaken for a wide range of determinands using a wide range of methods, including on-site testing methods. The methods that a laboratory or other organisation uses to generate data that are submitted to the Environment Agency for regulatory purposes shall be accredited to ISO/IEC 17025 for this MCERTS performance standard. These methods shall be defined in the organisation's scope of activities. Sampling activities relating to untreated sewage, treated sewage effluents and trade effluents are also covered by this performance standard.

1.2 This performance standard is applicable to all organisations and procurers of analytical and sampling services where results, generated for the chemical testing of untreated sewage, treated sewage effluents and trade effluents, are submitted to the Environment Agency for regulatory purposes.

1.3 This performance standard is applicable to organisations that may wish to undertake sampling and chemical testing, or sampling, or chemical testing, of untreated sewage, treated sewage effluents and trade effluents.

1.4 When an organisation satisfies all of the appropriate requirements of this performance standard, that organisation will have demonstrated that it meets the Environment Agency's MCERTS requirements for the sampling and/or chemical testing of untreated sewage, treated sewage effluents and trade effluents or, if it so chooses, a subset of these different matrices.

1.5 If an organisation complies with the appropriate requirements of this performance standard, it will be regarded by the Environment Agency as demonstrating its competence and of being capable of undertaking the sampling and/or chemical testing of untreated sewage, treated sewage effluents and trade effluents to the Environment Agency's requirements, for its published scope of activities. An organisation's details shall be defined in a scope of accreditation published on the UKAS website.

2 References

2.1 Normative references

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

2.2 Text references

a) "Monitoring of Discharges to Water and Sewer" Environment Agency technical guidance note M18, version 2, 2009

b) ISO 5667 Part 3 - Water quality -- Sampling -- Part 3: Guidance on the preservation and handling of water samples

c) ISO TR 13530: "Water Quality - A Guide to Analytical Quality Control for Water Analysis" (currently undergoing revision).

d) “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

e) “Valid Analytical Methods and Procedures”, C. Burgess, Royal Society of Chemistry, 2000. ISBN 0-85404-482-5.

f) “Guidelines for achieving quality in trace analysis”, M. Sargent and G. MacKay, Royal Society of Chemistry, 1995, ISBN 0-85404-402-7.

g) “Quantifying Uncertainty in Analytical Measurement”. *Eurachem/CITAC Guide CG4,* second edition, 2000. ISBN 0-948926-15-5 (www.eurachem.org).

h) “An aid to accreditation” *Eurachem/CITAC* Guide to quality in analytical chemistry, Edition 2002, (www.eurachem.org).

i) “The fitness for purpose of analytical methods”. A laboratory guide to method validation and related topics. *Eurachem Guide* 1998, (www.eurachem.org).

j) “Development and Harmonisation of Measurement Uncertainty Principles – Part (d): Protocol for uncertainty evaluation from validation data.” V J Barwick, S L R Ellison, LGC/VAM/1998/088.

k) “Handbook for Calculation of Measurement Uncertainty in Environmental Laboratories”. Version 1.3, Nordtest Report TR 537 October 2003.

l) “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, the Royal Society of Chemistry 2003.

m) “Quality Control Charts in Routine Analysis”, M J Gardner, WRc Report CO4239 1996.

n) “Guidelines for the In-House Production of Reference Materials” – version 2, B Brookman, R Walker 1998 LGC/VAM/1998/040.

o) “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.

p) MCERTS Standard “Continuous Water Monitoring Equipment Part 1: Performance standards and conformity testing procedures for automatic wastewater sampling equipment” The Environment Agency.

q) BS 1427: Guide to on-site test methods for the analysis of waters

r) MCERTS Standard “Continuous Water Monitoring Equipment Part 2: Performance standards and test procedures for portable water monitoring equipment” The Environment Agency.

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.

Analytical Quality Control (AQC) - The overall process of ensuring that the application of an analytical method is controlled within specified tolerances.

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 and the true or accepted concentration.

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

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) - A reference material, characterised by a metrologically valid procedure for one or more specified properties, accompanied by a certificate that provides the value of a specified property, its associated uncertainty, and a statement of metrological traceability. [ISO Guide 35:2006]

Concentration - Concentration, for chemical testing of waters, is usually expressed as mass per unit volume, for example mg l^{-1}. (In certain circumstances the term concentration is not appropriate, for example in the determination of pH values).

Critical level of interest (CLOI)- 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 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 CLOI.

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

Laboratory - A laboratory, or sub-contracting laboratory, that undertakes the chemical testing of untreated sewage, treated sewage effluents and trade effluents. A laboratory may also undertake sampling activities.

Organisation - In the context of this performance standard the term organisation encompasses analytical laboratories.

Operator - "*Operator*" is defined as: "*in relation to an installation or mobile plant, the person who has control over its operation*"

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.

Precision - This is the distribution of a number of repeated determinations, obtained under specific conditions, 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.

Total standard deviation is obtained from estimates of both within batch and between batch standard deviations, using analysis of variance.

Reference Material (RM) - Material, sufficiently homogenous and stable with respect to one or more specified properties, which has been established to be fit for its intended use in the measurement process. [ISO Guide 35:2006]

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 determinand to a sub-sample, followed by analysis to establish that fraction or percentage recovered by the use of a defined method. Details are given in Annex B.

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

$$\%Bias = \%Recovery - 100$$

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 to be out of statistical control.

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

Traceability - Property of a measurement result whereby the result can be related to a stated reference through a documented unbroken chain of calibrations, each contributing to the measurement uncertainty.

4 Management requirements

4.1 Organisation

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

4.1.2 Organisations conducting sampling shall have arrangements in place to ensure that its management and personnel conducting these activities are free from any undue internal and external commercial, financial and other pressures and influences that may adversely affect the quality of their work.

4.1.3 Organisations shall have policies and procedures in place to ensure operational and sampling practices do not diminish confidence in competence, judgement or integrity.

Note: It would not be acceptable for an organisation to manipulate the operation of their treatment plant or effluent inputs to a treatment plant to take account of sampling dates. The sampling programme should be representative of the normal operation of that treatment plant.

4.2 Review of requests, tenders and contracts

4.2.1 For data to be submitted to the Environment Agency for regulatory purposes, the requirements of the methods to be used shall be clearly and unambiguously defined and documented. The organisation shall demonstrate that the requirements of the methods to be used are understood by those who undertake the sampling and/or analysis.

Note: The organisation may or may not be aware that the data it generates will be submitted to the Environment Agency for regulatory purposes. However, the organisation's customer or procurer of the sampling and 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.

4.2.2 For data to be submitted to the Environment Agency for regulatory purposes, the appropriate sampling, and testing method shall be selected and shall satisfy the requirements of this performance standard.

4.3 Sub-contracting

4.3.1 An operator may sub-contract the sampling and/or chemical testing to another appropriate organisation. It is the responsibility of the operator to ensure that the sub-contracted organisation is accredited 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.

4.4 Technical records

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

5 Technical requirements

5.1 Accommodation and environmental conditions

5.1.1 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 organisation shall have procedures in place and use appropriate practices to ensure that sample transport and storage conditions do not adversely affect the measurement result.

5.2 Test methods and method validation

5.2.1 General

The organisation shall demonstrate and provide justification that suitable methodology (including sample pre-treatment and preparation) has been used in the analysis of a particular matrix and determinand and that it is appropriate with respect to the concentration of the determinand in the sample. The organisation shall demonstrate and provide justification that method validation procedures have been undertaken in such a manner as is appropriate to the sample matrix undergoing analysis. Full details of the method and method validation procedures shall be made available to the Environment Agency, if requested.

5.2.2 Selection of methods

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

5.2.2.2 The description of the method, determinand and matrix shall be sufficiently detailed to allow direct comparisons with similar methods, determinands and matrices that might be used and determined by other analysts or organisations. For example, when an extraction technique is used to isolate or concentrate a particular determinand, the name of the solvent or full details of the composition of the solvent mixture shall be given. In addition, where the analytical determination of an extract is undertaken and, for example, this involves the use of a specific wavelength or mass to charge ratio, then details of these shall also be given.

5.2.2.3 Organisations shall demonstrate that the methods employed for each determinand are appropriate for the CLOI. This may be achieved by submitting a list of the range of regulatory limits to be monitored by each method. Regulatory limits may change, so a mechanism shall be in place to ensure methods are still appropriate when changes take place.

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

5.3 Validation of methods

5.3.1 General

5.3.1.1 Before any method for a particular matrix and determinand is used for generating data for submission to the Environment Agency that method shall be accredited to ISO/IEC 17025 for this performance standard. Only those results generated using these methods will be eligible for submission to the Environment Agency for regulatory purposes. The process of a full method validation provides confidence that the established performance characteristics of the method are based on robust experimental determinations and are statistically sound.

Validation procedures include a number of operations, and shall include assessment of the following:

- selectivity and interference effects
- range of applicability
- linearity
- calibration and traceability
- bias (recovery)
- precision
- limit of detection (LOD)
- uncertainty of measurement

5.3.1.2 Precision and bias (recovery) shall be estimated for each determinand and matrix covered by the method. Limit of detection shall be estimated for each determinand and method (see appendix C). Where available and appropriate, matrix certified reference materials relevant to the matrices, determinands and range of determinand concentrations under investigation shall be analysed. Sample pre-treatment and preparation is an important part in the validation process and shall be considered, as this may not be monitored by the use of certified reference materials. In these cases a separate exercise to determine the effects of sample pre-treatment and preparation shall be undertaken.

Whilst it is not expected that every sample submitted should require its own validated method, it is recognised that a single validated method established for one particular matrix but used for every sample, irrespective of its matrix, is unlikely to be appropriate. For example, it cannot be assumed that one method is appropriate for all effluents. A number of appropriate matrices shall undergo full validation as described in clause 5.3.3, as appropriate to the requirements of the laboratory. In addition to this, ongoing validation of a variety of samples that will in time represent the full range of samples and concentrations received by the laboratory for each accredited matrix shall be undertaken as described in clause 5.3.5.

Note: UKAS will assess the ongoing validation at the time of the annual surveillance visit.

Each sample used in validation or ongoing validation procedures shall be characterised in terms of basic analytical data. This shall include determinands appropriate to the matrix, for example chemical oxygen demand, pH, conductivity, suspended solids, hardness and TOC.

5.3.1.3 In the absence of suitable certified reference materials, recovery estimates relevant to the matrix and determinand under investigation, shall be determined by the use of spiking experiments. Where possible these experiments shall cover the entire method (including pre-treatment, extraction and determination). The addition of a determinand to a sub-sample followed by immediate extraction may not be a satisfactory test for estimating spiking recovery, as insufficient time may elapse to allow possible matrix-determinand interactions to occur. A satisfactory period of time shall be allowed for such interactions to occur. The organisation shall demonstrate that its use of spiking experiments and the spiking procedures employed is appropriate.

It may be appropriate to use a mixture of spiked samples and CRMs to ensure a full coverage of all determinands and matrices, or to validate an additional CRM which may not exactly match spiked matrices but will give further confidence in the method validation.

5.3.1.4 For spiking experiments, the concentrations of the solutions used in the validation procedures shall be appropriate to the concentrations found in samples being routinely analysed. Recovery estimates shall be obtained using two different but appropriate concentration levels, for example, 20 % and 80 % of the expected range, or at a CLOI. The organisation shall justify choice of sample and concentration level. If samples contain a significant amount of a determinand this approach may not be feasible, organisations must be able to find and justify an alternative approach. All solutions shall either be taken from bulk stock solutions that are known (and have been shown) to be stable over the entire period of testing or, if solutions are not stable over the entire period of testing, they may be prepared immediately before the analysis of each validation batch or stabilised by addition of appropriate reagents. The traceability of these solutions shall have been established.

Note: Statistical procedures for dealing with sample instability during validation can be found in reference d).

5.3.1.5 When Isotope Dilution Mass Spectrometry [IDMS] is employed (with appropriate labelled analogues of the determinands spiked into all samples, calibration standards and matrix AQC standards, and equilibrated before sample preparation is undertaken) then the results obtained will be recovery corrected. The recovery corrected values of spiked samples and/or CRMs obtained in this manner shall be used to estimate bias against the certified CRM and/or added spike.

Note: It is good practice to assign acceptable limits for surrogate recovery such that reliability and confidence in results is maintained.

5.3.2 Revalidation

5.3.2.1 After an analytical method has been validated and accredited, it is inevitable that at some time modification of procedures will be necessary. Any modification to a method routinely used within a laboratory may affect the resulting performance. Any changes made to a method already accredited against the MCERTS requirements shall be notified to UKAS. These changes could range from replacing equipment to a fundamental procedural modification, such as using a different extraction procedure.

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

5.3.2.3 If equipment is being replaced by one of the same model, and performance is not expected to fundamentally change, a laboratory need only demonstrate that the new instrument performs as well as the old instrument. This could be achieved, for example, by analysing several replicates of a representative matrix such as a spiked sample, a CRM or a matrix-matched AQC sample.

5.3.2.4 If a fundamental change is made to the analytical procedure or the equipment used then a full validation on all previously validated matrices is required in accordance with this performance standard. These changes may include, for example, replacing ICPOES with ICPMS, using a new extraction technique etc.

5.3.2.5 An intermediate degree of validation shall be carried out if significant changes are made to a method that are not considered fundamental to its performance, or a method is to be reinstated after a voluntary suspension. A partial validation shall be

performed (for example analysis of 6 batches of duplicates), using a low spiked sample or a CRM, for all appropriate matrices. A new estimation of LOD shall also be performed. If a laboratory judges that this level of validation is required, then it shall notify and gain the approval of UKAS. Laboratories shall ensure that the amendments to the analytical system and any procedures that may be affected are included in the revalidation.

5.3.3 Validation procedures

5.3.3.1 For the method, determinand and matrix, the performance characteristics shall be determined with a minimum of ten degrees of freedom. This shall be carried out by analysing each appropriate sample in duplicate in different analytical batches. 11 batches of duplicates will guarantee a minimum of 10 degrees of freedom. However, it may be that 10 degrees of freedom will be achieved in less than 11 duplicate batches, this can be checked after each batch of results (see references a), c), d) and Annexes B and C for appropriate procedures). Validation shall be undertaken in a period of time of not less than six days and no more than three months.

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

Note 2: Any proposed routine control samples can be in the 11x2 test to enable control limits to be set.

5.3.3.2 Precision shall be estimated using analysis of variance (ANOVA), from which different sources of error (for example within batch and between batch random errors) can be estimated and combined to give a total error as a standard deviation. Details of the statistical procedures for ANOVA and bias (recovery) estimation are given in references a), c) and d). See also Annexes B and C of this performance standard.

The following wastewater matrices shall be validated as required:

- Treated sewage effluent (mixed domestic and industrial)
- Untreated sewage
- Trade effluent discharges (from industry sector commonly encountered in the laboratory, for example food processing)

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

If a laboratory does not require accreditation for all three of these matrices, then initial validation shall be on a minimum of 3 matrices that best represent those received and analysed by the laboratory. For example, if a laboratory does not wish to become accredited for untreated sewage then it may substitute that matrix with a second treated sewage effluent or trade effluent discharge. An organisations Schedule of accreditation shall clearly show the matrix types for which Accreditation has been granted.

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

5.3.3.4 When a method has been validated, its stated performance shall reflect the routine capability of the method. That is, when the method is used routinely, its day to day

performance shall be typical of and maintained at the level of the stated validation performance.

5.3.3.5 The limit of detection of a method used to analyse highly contaminated samples may be higher than the limit of detection of a method used to analyse slightly contaminated samples. The reported limit of detection shall be fit for the intended purpose and appropriate to the concentration level of interest required of the analysis. The limit of detection shall be calculated as described in Annex C1. The limit of detection should never be used in isolation of other method validation data to judge the appropriateness of a method.

Laboratories shall demonstrate that the LOD achieved is appropriate to the CLOI of the samples analysed.

Note: The maximum value of the limit of detection usually regarded as being fit for purpose is 10 % of the concentration regarded as the CLOI. For example, if the lowest effluent permit level being monitored is 1 mg l^{-1} for a particular determinand, then the LOD should be at least as low as 0.1 mg l^{-1}. It is recognised that this 10% may not be achievable on all matrices. If this situation arises then before submitting results agreement should be sought with the Environment Agency.

5.3.4 Performance criteria

5.3.4.1 The following performance characteristics are acceptable for the validation of methods for the chemical testing of untreated sewage, treated sewage effluents and trade effluents, bearing in mind the need to take meaningful decisions, current analytical capabilities and other likely sources of variation into account.

- 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 – 3) expressed as a percentage. The certified reference materials used shall be of an appropriate uncertainty. If a CLOI is known, the target bias value used can be taken as one-twentieth of the CLOI and either bias value used whichever is the greater. Laboratories shall demonstrate that the bias satisfies the stated requirement at the CLOI.

- The precision, expressed as the percent relative standard deviation of individual results determined for the entire method, shall not be significantly greater than the figure indicated in Annex A (Tables 1 – 3). Precision shall be estimated using ANOVA to determine total standard deviation. If a CLOI is known, the target precision value used can be taken as one-fortieth of the CLOI and either precision value used whichever is the greater. Laboratories shall demonstrate that the precision satisfies the stated requirement at the CLOI .

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

Note: Experience has shown that if a method has borderline performance with respect to the performance requirements of this standard, it may be difficult to maintain the analytical performance of the method when in routine use.

5.3.4.3 Annex A (Tables 1 – 3) specifies the performance characteristics for a selection of determinands (which is not to be regarded as exhaustive).

When a laboratory requests accreditation of additional parameters not listed in Annex A, the following minimum performance requirements shall be enforced:

Metals	–	5% precision and 10% bias
Inorganics	–	5% precision and 10% bias
Organics	–	5% precision and 20% bias

Where there are precision and bias targets for treated sewage and trade effluent discharges to controlled waters and none for the other matrices, the precision and bias targets for treated sewage and trade effluent discharges to controlled waters shall apply.

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 via UKAS for assessment.

If the laboratory is unable to meet requirements due to analysis of a one off nature being required urgently then the laboratory shall report the performance characteristics actually achieved using a partial validation (see clause 5.3.2.5). If this procedure is employed, UKAS shall be informed. If the determinand is subsequently added to Annex A the performance characteristics for the determinand shall be determined in the manner and in accordance with the full validation requirements specified in this performance standard.

Organisations shall not report these results as accredited until UKAS has assessed the method or indeed the Environment Agency has prescribed target performance values.

5.3.5 Ongoing validation

5.3.5.1 Having completed validation to the MCERTS standard, a laboratory shall subsequently undertake a programme of ongoing validation (see also clause 5.3.1.2). Laboratories shall carry out one ongoing validation exercise for each accredited method per year. When performing ongoing validation exercises the effluents assessed shall not have been used for initial validation studies, effluents from a different source shall be used (see note 3).

Note 1: Ongoing validation will ensure that methods will be assessed against a wide range of matrices encountered by a laboratory, without the necessity of performing the full validation procedure on each matrix.

Note 2: If a laboratory can demonstrate that further ongoing validation is unnecessary for a particular method, then ongoing validation may be stopped if UKAS agree. For example, all effluents with a permit limit for a specific determinand have been validated.

Note 3; It is possible that the composition of an effluent may change, for example if manufacturing processes change. Laboratories should ensure that initial validation is still valid.

An ongoing validation exercise shall comprise of a minimum of 7 replicates of a sample and 7 spiked replicates of the same sample undergoing analysis. Precision and recovery shall be estimated and compared with the MCERTS requirements to ensure compliance. A significance test shall be carried out if required (see Annex C2). If MCERTS requirements are not met, and the laboratory undertaking the ongoing validation consider this is due to insurmountable matrix effects, then the ongoing validation data shall be sent to the Environment Agency via UKAS.

Consideration will be given to the performance criteria applied in this MCERTS standard.

5.3.5.2 For some matrices, a high background concentration of the target determinand may make it difficult to assess spiking recovery. An alternative approach may therefore be required, such as pre-dilution of spiked samples before analysis.

5.3.5.3 An alternative to spiking samples for ongoing validation of methods using mass spectrometry detection is the use of isotopically labelled surrogate compounds to establish the recovery of each determinand for each sample (see 5.3.1.5). In these cases a known amount of the isotopically labelled surrogate compound shall be added to every sample prior to sample analysis. The recovery of the surrogate compound shall fall within acceptable limits and be reported with the associated sample results.
If the laboratory is already using an analytical method based on the use of isotopically labelled surrogate standards for each of the determinands being analysed, then there is no need to take any additional measures for the analysis of samples with unvalidated matrices, provided that the recovery of each of the surrogate compound meets acceptable limits. An estimate of precision shall still be required, based on 7 replicate samples.

5.3.6 Estimation of uncertainty of measurement

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

5.4 Measurement traceability (Calibration of equipment)

5.4.1 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.

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

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

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

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

5.5 Sampling

5.5.1 Each organisation that undertakes sampling activities relating to this performance standard shall operate a management system for relevant sampling activities. This may operate independently of a laboratory.

The sampling management system shall include, but not be limited to, the following procedures:

- sampling programme, including procedures for resampling;
- methodologies for taking samples;
- training and audit;
- use of appropriate bottles and preservation techniques;
- sample transport, receipt, handling, storage, retention, delivery and chain of custody;
- operation, maintenance and calibration of equipment used in sampling, including autosamplers;
- operation, maintenance and calibration of on-site test equipment;
- quality assurance procedures for assessing sampling activities.

On site test equipment shall be validated in accordance with Annex D of this standard

Detailed guidance of the sampling procedures is not reproduced in this standard but organisations may wish to take account of the latest Environment Agency guidance, which can be accessed via our website at: www.mcerts.net.

5.5.2 All samplers engaged in accredited sampling activities shall be audited by their own organisation at least once annually.

5.5.3 If automatic sampling devices are used, for example if composite samples are required, then the device shall have been tested and certified to the appropriate MCERTS performance standard (reference p).

5.5.4 When a sample is stabilised, or preserved and subsequently analysed, then this fact shall be recorded and may be reported as shall details of the stabilising or preserving agent. Where a party independent of the analysing laboratory performs this activity the party responsible for this shall inform the laboratory, who shall report it as above. Organisations shall cooperate to ensure that sample preservation and handling procedures (including selection of sample containers) is appropriate for and compatible to the analytical method being employed in the laboratory.

5.5.5 For some determinands on some samples it may be required that the dissolved portion of the determinand in the sample is analysed and reported on. The dissolved portion of the determinand in the sample shall be defined as that which will pass through a 0.45µm membrane filter. Filtration shall take place immediately at the point

of sample collection. Any deviation from this prescribed procedure shall be justified and reported with results.

5.5.6 If preservation of samples by refrigeration is required, then during transportation and subsequent storage of samples, including retention time in an automatic sampling device, the sample storage environment shall maintain a temperature of 4.5 ± 3.5°C. An organisation carrying out sampling shall have appropriate procedures for demonstrating this. It is recognised that some time may be required to bring the sample temperature to within this range.

Note: The temperature range is to allow for the cycling of the refrigeration devices, their opening and closing during normal operation, and effects of adding a number of warm samples. For most analytical purposes best practice is to keep the samples at a constant temperature of not more than 5°C.

5.6 Assuring the quality of test results

5.6.1 Having verified that the method performance criteria prescribed in Annex A have been satisfied, on-going performance shall be monitored to:

- demonstrate that the method performance required by this performance standard is maintained in a statistically controlled manner;
- identify at an early stage any changes (especially deterioration) in performance;
- provide historical verification of this performance (records are kept);
- enable aspects of measurement uncertainty to be estimated.

These objectives shall be achieved by carrying out the AQC procedures described in clauses 5.6.2 and 5.6.3.

5.6.2 Participation in interlaboratory comparison or proficiency-testing programmes

5.6.2.1 An organisation 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, or if appropriate, on-site.

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

5.6.2.2 The methods, used by the organisation to generate analytical data for the chemical testing of untreated sewage, treated sewage effluents and trade effluents which are submitted under MCERTS, shall be the same as those methods used by the organisation 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 shall be treated by the organisation in the same manner as normal routine samples submitted for chemical testing of untreated sewage, treated sewage effluents and trade effluents. For example, procedures for registration, storage, analysis and the recording and reporting of results should be similar.

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

5.6.2.4 The organisation 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 shall 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.

5.6.3 Internal Quality Control

5.6.3.1 For internal quality control, the performance of each analytical method shall be verified for each batch of samples analysed. Control samples shall be analysed within the analytical batch with which they have been prepared.

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 monitor trends in analytical performance using a Shewhart chart, a minimum of 30 points plotted in a 12 month cycle, spread evenly over the period, is recommended.

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: Guidance on the production of in-house reference materials can be found in references n) and o).

Note 2: 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 shallbe from a different source or lot number to that used for calibration, unless other independent checks of calibration stocks are undertaken. Suitable contact times between spiking and extraction shall be determined to provide adequate time for interaction between spike and sample while ensuring that there is no degradation of the determinand.

Note 3: 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.

5.6.3.2 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 organisations shall have sufficient data to construct statistically based quality control charts.

As further data are obtained, a new chart shall 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 shall not be used. However, some results, which are part of the normal distribution, will breach the limits, and these shall 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 shall be investigated, even if precision and bias are still within the MCERTS targets. If a statistically significant change to precision or bias has occurred, then the new values shall be used in the control rules, and new control limits established and drawn on the control chart. Any decision made regarding updating of charts shall be justified and recorded.

At least annually, mean and standard deviation values shall be estimated from new data and 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 (bias) has changed significantly using a student's t test, again at the 95% confidence level (see Annex C).

The targets given in Annex A of the MCERTS standard for a given parameter shall not be statistically significantly exceeded, but all significant changes shall 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, and it will be necessary to re-validate the analytical method.

Note: When uncertainty of measurement is reported, it should reflect performance of the method at that time, including current precision as reflected in control charts.

5.6.3.3 For all determinands listed in Annex A (Tables 1-3) quality control results shall be plotted on appropriate control charts.

5.6.3.4 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 the Environment Agency, if requested. Samples in an analytical batch where a laboratory control sample breaches the defined control rules shall be where possible reanalysed. If it is not possible and results are reported a full justification shall be given.

The investigation shall include, but shall not be restricted to, checking:

- changes in concentration of stock standard solutions and reagents and their expiry date;
- calibration of instruments used in the analytical process;
- adherence to documented methods;
- system suitability check data meet the required criteria;
- 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 the affected sample results (analysis repeated or results reported).

5.7 Reporting the results

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

- location of sample;
- unique sample code or reference;
- date/time sample taken;
- name of organisation (including sampling organisation if different);
- name of any sub-contracting organisations, if used;
- date sample analysis completed;
- determinand analysed;
- result of analysis;
- other relevant comments, for example, visual characteristics of sample.

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

5.7.3 Whenever possible and where appropriate, individual compounds shall 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.

6. Status of this document

6.1 This version of the MCERTS performance standard will be subject to review and amendment following publication. The latest version of the standard is available on the Environment Agency's web site at:

www.mcerts.net

6.2 If you have any questions regarding the accreditation process, including how to make an application, please contact UKAS at the address given in the foreword to this document.

Annex A (normative): Performance Characteristics

Table 1 - Metals (total and dissolved)

	Treated sewage and trade effluent discharges to controlled waters		Trade effluent discharges to sewer		Untreated sewage	
	precision[1]	bias[2]	precision[1]	bias[2]	precision[1]	bias[2]
Aluminium	5	10	7.5	10	-	-
Antimony	7.5	10	7.5	10	-	-
Arsenic	7.5	10	10	10	10	10
Barium	5	10	7.5	10	-	-
Beryllium	5	10	7.5	10	-	-
Boron	5	10	10	10	10	10
Cadmium	5	10	7.5	10	-	-
Calcium	5	10	7.5	10	-	-
Chromium	5	10	7.5	10	-	-
Chromium hexavalent	5	10	7.5	10	-	-
Cobalt	5	10	7.5	10	-	-
Copper	5	10	7.5	10	-	-
Iron	5	10	7.5	10	-	-
Lead	5	10	7.5	10	-	-
Magnesium	5	10	7.5	10	-	-
Manganese	5	10	7.5	10		
Mercury	7.5	10	7.5	10	10	15
molybdenum	5	10	7.5	10	-	-
Nickel	5	10	7.5	10	-	-
Potassium	5	10	7.5	10	-	-
Selenium	7.5	10	10	10	10	10
Silver	7.5	10	7.5	10	-	-
Sodium	10	10	10	10	10	10
Strontium	5	10	7.5	10	-	-
Thallium	5	10	7.5	10	-	-
Tin	5	10	10	10	10	10
Titanium	5	10	7.5	10	-	-
Uranium	5	10	7.5	10	-	-
Vanadium	5	10	7.5	10	-	-
Zinc	5	10	7.5	10	-	-

1. Precision expressed as percent relative standard deviation.
2. Bias expressed in percentage terms.

Note: Where there are precision and bias targets for treated sewage and trade effluent discharges to controlled waters and none for the other matrices, the precision and bias targets for treated sewage and trade effluent discharges to controlled waters apply(but see clause 5.3.4.3).

Table 2 – General determinands

	Treated sewage and trade effluent discharges to controlled waters		Trade effluent discharges to sewer		Untreated sewage	
	precision[1]	bias[2]	precision[1]	bias[2]	precision[1]	bias[2]
Alkalinity (to pH 4.5)	5	10	-	-	-	-
Ammonia	5	10	5	10	5	10
BOD	8	10	8	10	8	10
COD	5	10	5	10	5	10
Chloride	5	10	-	-	-	-
Chlorine (all forms)	10	10	-	-	-	-
Cyanide(all forms)	5	10	-	-	-	-
Detergents (anionic, MBAS)	7.5	10	-	-	-	-
Dissolved oxygen	2	2	-	-	-	-
Fluoride	5	10	-	-	-	-
Formaldehyde	5	10	-	-	-	-
Nitrite nitrogen	5	10	-	-	-	-
Nitrogen total oxidised	5	10	-	-	5	10
Nitrogen kjeldahl	5	10	5	10	5	10
Nitrogen total			-	-	5	10
Optical density	5	10	-	-	-	-
pH	0.2	0.2	0.2	0.2	0.2	0.2
Phosphorus total	5	10	-	-	5	10
Phosphorus soluble reactive	5	10	-	-	-	-
Specific conductivity	2	2	2	2	2	2
Sulfide	7.5	10	7.5	10	7.5	10
Sulfate	5	10	5	10	5	10
Suspended solids (105°C)	7.5	10	7.5	10	7.5	10
Turbidity	5	10	-	-	-	-

1. Precision is expressed as percent relative standard deviation, except for pH, which is in terms of pH units.
2. Bias is expressed in percentage terms, except for pH, which is in terms of pH units

Note: Where there are precision and bias targets for treated sewage and trade effluent discharges to controlled waters and none for the other matrices, the precision and bias targets for treated sewage and trade effluent discharges to controlled waters apply (but see clause 5.3.4.3).

Table 3 – Organic Determinands

	Treated sewage and trade effluent discharges to controlled waters		Trade effluent discharges to sewer		Untreated sewage	
	precision[1]	bias[2]	precision[1]	bias[2]	precision[1]	bias[2]
Acid herbicides[3]	15	20	15	20	-	-
Alcohols/Ketones	10	15	-	-	-	-
Explosive substances[4]	15	20	15	20	-	-
Hexachloro-1,3-butadiene	15	20	15	20	-	-
Hydrocarbon oils(IR)	10	12.5	10	12.5	10	12.5
Mothproofers[3]	15	20	-	-	-	-
Nitroaromatics[3]	15	20	-	-	-	-
Nonyl phenols[3]	15	20	-	-	-	-
Organochlorine compounds[3]	15	20	15	20	-	-
Organophosphorus compounds[3]	15	25	15	25	-	-
Organotin compounds[3]	15	20	-	-	--	-
Phenols [3]	15	20	-	-	-	-
Phenols Monohydric colorimetric	6	10	-	-	--	-
Polyaromatic hydrocarbons[3]	15	20	-	-	-	-
Polychlorinated biphenyls[3]	15	20	-	-	-	-
Volatile organic compounds[3]	15	20	-	-	-	-
Pyrethroids[3]	15	20	-	-	-	-
Triazines[3]	15	20	-	-	-	-
Urons/carbamates[3]	15	20	-	-	-	-

1. Precision expressed as percent relative standard deviation.
2. Bias expressed in percentage terms.
3. 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.
4. Covers organic explosive compounds as listed in Environment Agency guidance.

Note: Where there are precision and bias targets for treated sewage and trade effluent discharges to controlled waters and none for the other matrices, the precision and bias targets for treated sewage and trade effluent discharges to controlled waters shall apply (see clause 5.3.4.3).

Annex B (informative): Validation Protocol

A typical validation protocol is described below:

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

- Matrix blank or sample with determinand concentration close to the expected LOD.
- Samples of appropriate matrices.
- AQC material.
- CRMs and/or samples of appropriate matrices + spike if CRM not available.

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

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

Recovery should be assessed as follows:

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

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

where: U = measured conc. in unspiked sample
C_m = measured conc. in spiked sample
C_s = conc. of spiking solution
W = volume of spiking solution added
V = volume of sample to which spike is added

Then calculate the mean recovery of each analytical batch. Calculate the mean recovery of all analytical batches and its standard deviation (s) (the standard deviation of the 11 batch means).
The standard error (S) of this estimate of the mean recovery can now be calculated from:

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

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

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

Results of these validation tests can then be presented with method documentation in a tabular format, for example:

		As appropriate				
Sample type	Blank for LOD	Sample	spiked sample 1	spiked sample 2	AQC material	CRM
mean						
degrees of freedom						
Standard deviation						
%RSD	-					
Precision target	-					
Pass?(Y/N)						
Recovery	-					
Pass?(Y/N)						
LOD		-	-	-	-	-

Annex C (normative): Statistical Analysis

C1 Limit of detection

C1.1 Introduction

The limit of detection (LOD) is widely but inappropriately used as the primary performance measure of an analytical system. However, 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. The LOD is not specified in this performance standard. However, a common approach to the estimation of LOD is desirable in order 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.

C1.2 Choice of sample and sample pre-treatment

The sample used for estimating LOD shall 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.

As a minimum LOD shall be estimated for one appropriate effluent matrix. It may be necessary to estimate LOD using different effluents for different methods due to background concentration of target determinands. When reporting results, it shall be made clear that the reported LOD may not be appropriate for samples with a 'complex' matrix.

If a more complex sample matrix is analysed, for example a crude sewage, and an estimation of matrix LOD is considered crucial, then the procedure for an on-going check in C1.3 below shall be used.

Ideally analysis of the blank sample will produce normally distributed results scattered around zero; both negative and positive results will be generated. It is usually possible for the blank sample to have a sufficiently small background concentration of the determinand 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 shall be spiked with a small amount of the determinand, as close as possible to zero but sufficient to produce a small but significant response from the analytical system.

The blank or spiked sample shall be put through the entire analytical process (including, as necessary, extraction, cleanup 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 manner and using the same equipment and reagents as other samples in a batch.

Note 1: For commonly occurring substances such as iron, zinc, chloride and sulfate etc., where waters may contain a significant amount of these substances, the method used to determine an LOD for that substance using blank can give an optimistic (lower concentration) LOD. Alternatively if an "uncontaminated natural" sample is used to determine the LOD and it contains a significant amount of these substances then a pessimistic (higher concentration) LOD will be obtained.

Note 2: 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 3: For substances of this type 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 CLOI.

C1.3 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 zero concentration of the determinand 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 determinand being determined and shall 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 shall 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, if at validation 11 batches of 2 blanks are analysed:

$$\mathbf{s_w}\ (\text{pooled}) = \sqrt{\frac{\sum s_i^2}{11}}$$ with 11 degrees of freedom

Since $\mathbf{t}_{(\alpha = 0.05)}$ for a one sided t-test with 11 degrees of freedom is 1.796

Then $LOD = 2\sqrt{2}.\mathbf{t}.\mathbf{s_w} = 5.08\mathbf{s_w}$

Note: at infinite degrees of freedom the value of $\mathbf{t}_{(\alpha = 0.05)}$ becomes 1.645 and $LOD = 4.65\mathbf{s_w}$

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 estimating the LOD. Further data shall be collected during routine analysis, and pooled with the data obtained during validation to give a more robust estimation of LOD.

As an ongoing check, an estimate of LOD can be obtained by analysing 11 blank or spiked (at or close to the LOD)samples in the same batch, here $\mathbf{s_t}$ (total standard deviation) equates to $\mathbf{s_w}$, with 10 degrees of freedom. This procedure shall be used when a matrix is analysed by a method that has not been fully validated for that matrix.

C1.4 Form of expression

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

For TPH and similar determinands, 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 determinands they represent. The calculated value may be rounded up for convenience and ease of use.

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

C2.1 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.
After the validation has been carried out as described in clause 5.3 and Analysis of Variance (ANOVA) has been applied to the results, there will be sufficient data to assess whether method performance complies with Annex A criteria (see clause 5.3.3).

C2.2 Assessment of precision

The convention in analysis has been to consider precision to be satisfactory if the measured standard deviation is found not to be statistically significantly larger than the target standard deviation.
This implies there is uncertainty about the measured standard deviation value, although this uncertainty is minimised by specifying its calculation with at least 10 degrees of freedom.

Assessment of precision is in three stages:

1. Determine the target standard deviation at the concentration of interest, in accordance with clause 5.3.3.

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

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

C2.3 F-Test of standard deviation.

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

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

where $\mathbf{s_t}$ 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 $\mathbf{s_t}$ and **Z**.

Z is a target standard deviation and therefore has infinite degrees of freedom. In the case of $\mathbf{s_t}$, 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:

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

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

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

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

C2.4 Assessment of systematic error or bias

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

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

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

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 = $\frac{\sum R_i}{m} = \mathbf{M}$

Standard Error of Recovery = $\frac{s_R}{\sqrt{m}} = s_e$

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

Where:

m = number of batches
$\boldsymbol{R_i}$ = %Recovery of the ***i***th batch
$\boldsymbol{S_R}$ = standard deviation of batch recoveries
$\boldsymbol{t_{(0.05,m-1)}}$ = single-sided Student's t value at 5% probability level and (**m-1)** degrees of freedom

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

Note: When a bias is estimated it is either positive or negative, therefore a one sided t-test at the 95% confidence level is used to assess if observed bias is greater than permitted bias. However, by definition, a confidence interval is two sided, therefore the significance test is at the 95% confidence level but the resulting confidence interval is 90%.

Example

An example is presented below to illustrate the application of the statistical tests mentioned above. It considers a spiking exercise for ammonia, a low level spike of a sewage effluent, and a higher level spike of an industrial discharge. Spiking solution concentration was 5000 mg l^{-1} N; for the sewage sample 1 ml of this solution was made to 1 litre with sample, for the trade effluent, 3 ml of the spiking solution was made to 1 litre with sample.

Example 1: Ammonia mg l^{-1} as N in wastewater – spiked samples

	Test sample	Sewage effluent sample	spiked sewage sample	Recovery	Trade effluent sample	Spiked trade effluent sample	Recovery
Batch	Replicate						
1	1	0.327	5.073	4.746	9.133	22.899	13.766
1	2	0.450	5.311	4.861	9.550	22.330	12.780
	Batch Mean.	0.3885	5.1920	4.80350	9.3415	22.6145	13.273
	Batch S.Dev.	0.08697	0.16829	0.08132	0.29486	0.40234	0.69721
2	1	0.614	5.431	4.817	9.688	24.227	14.539
2	2	0.519	5.138	4.619	9.376	23.380	14.004
	Batch Mean.	0.5665	5.2845	4.7180	9.5320	23.8035	14.2715
	Batch S.Dev.	0.06718	0.20718	0.14001	0.22062	0.59892	0.37830
3	1	0.281	5.427	5.146	9.560	23.637	14.077
3	2	0.412	5.394	4.982	9.417	24.336	14.919
	Batch Mean.	0.3465	5.4105	5.0640	9.4885	23.9865	14.498
	Batch S.Dev.	0.09263	0.02333	0.11597	0.10112	0.49427	0.59538
4	1	0.430	5.870	5.440	9.770	21.871	12.101
4	2	0.557	6.086	5.529	9.564	21.039	11.475
	Batch Mean.	0.4935	5.9780	5.48450	9.6670	21.4550	11.788
	Batch S.Dev.	0.08980	0.15274	0.06293	0.14566	0.58831	0.44265
5	1	0.698	5.289	4.591	10.189	23.114	12.925
5	2	0.744	5.899	5.155	10.882	23.565	12.683
	Batch Mean.	0.7210	5.5940	4.8730	10.5355	23.3395	12.804
	Batch S.Dev.	0.03253	0.43134	0.39881	0.49002	0.31891	0.17112
6	1	0.495	5.395	4.900	10.055	23.389	13.334
6	2	0.415	5.845	5.430	10.720	22.773	12.053
	Batch Mean.	0.4550	5.620	5.165	10.3875	23.0810	12.6935
	Batch S.Dev.	0.05657	0.31820	0.37477	0.47023	0.43558	0.90580
7	1	0.787	5.414	4.627	9.239	22.304	13.065
7	2	0.570	5.735	5.165	9.678	23.836	14.158
	Batch Mean.	0.6785	5.5745	4.896	9.4585	23.0700	13.6115
	Batch S.Dev.	0.15344	0.22698	0.38042	0.31042	1.08329	0.77287
8	1	0.940	5.391	4.451	10.271	23.437	13.166
8	2	0.647	5.201	4.554	10.310	23.736	13.426
	Batch Mean.	0.7935	5.2960	4.5025	10.2905	23.5865	13.296
	Batch S.Dev.	0.20718	0.13435	0.07283	0.02758	0.21142	0.18385
9	1	0.364	5.574	5.210	9.501	22.513	13.012
9	2	0.490	4.934	4.444	10.149	23.835	13.686
	Batch Mean.	0.4270	5.2540	4.827	9.8250	23.1740	13.349
	Batch S.Dev.	0.08910	0.45255	0.54164	0.45821	0.93480	0.47659
10	1	0.434	5.102	4.668	9.802	22.552	12.750
10	2	0.588	5.219	4.631	9.920	23.382	13.462
	Batch Mean.	0.5110	5.1605	4.6495	9.8610	22.9670	13.106
	Batch S.Dev.	0.10889	0.08273	0.02616	0.08344	0.58690	0.50346
11	1	0.516	5.249	4.733	10.172	22.952	12.780
11	2	0.468	5.047	4.579	10.277	22.642	12.365
	Batch Mean.	0.4920	5.1480	4.656	10.2245	22.797	12.5725
	Batch S.Dev.	0.03394	0.14284	0.10889	0.07425	0.21920	0.29345
Overall mean		0.53391	5.410		9.874	23.080	
Overall mean recovery				4.876			13.206

Precision test (From ANOVA)	Sewage effluent	Spiked Sewage effluent	Trade effluent	Spiked trade effluent
Mean	0.53391	5.410	9.874	23.080
Within-Batch sd	0.104619	0.249369	0.293543	0.594442
Between-Batch sd	0.121437	0.186605	0.365231	0.534918
Total sd	0.160288	0.311459	0.468574	0.799687
Relative sd %	30.02%	5.76%	4.75%	3.46%
Target sd:	0.125	0.2705	0.4937	1.154
Tabulated F 0.05 value	1.67	1.60	1.69	1.64
Calculated F-Value	1.64	1.33	0.90	0.48
Estimate degrees freedom	15.14	18.02	14.68	16.86
Assessment	PASS	PASS	PASS	PASS

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

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

In this example the precision in terms of the observed relative standard deviation of the sewage effluent is much higher than the target value of 5%, so an F test is performed. For this particular sewage effluent the CLOI is known to be 5 mgl^{-1} so the target standard deviation can be increased to one-fortieth of the CLOI (that is 0.125 mgl^{-1}). The 95% calculated F value (1.64) for the sewage sample is less than the tabulated reference F value of 1.67, so the standard deviation of the sewage sample is not significantly different from the target value, and therefore meets the MCERTS requirement. With the spiked sewage effluent the observed relative standard deviation (5.76%) is higher than the 5% target value of the mean (that is 0.2705). Following the F test calculation, the data for the spiked sewage sample passes and therefore meets MCERTS requirements. Again the sample passes the F test. The trade effluent sample and spiked trade effluent are within the target values and the F test does not need to be carried out.

Recovery	Sewage effluent	Trade effluent
Expected recovery concentration	4.9995	14.9704
Mean measured recovery	4.8763	13.2057
Overall mean recovery	97.5%	88.2%
sd of mean recovery	5.5192	5.11
Standard error of mean recovery	1.664	1.5402
90 % Confidence interval of recovery	3.015	2.7909
Recovery range	94.52% - 100.55%	85.42% - 91.0%
Assessment	PASS	PASS

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

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

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

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

Annex D: (normative) Validation and use of portable instruments and test kits

D1. Introduction

If portable instrumentation or test kits are to be used in the field for regulatory compliance monitoring of effluents then procedures and practices shall comply with MCERTS and ISO 17025.

Where available, instruments certified to the MCERTS "Performance Standards and Test Procedures for Portable Water Monitoring Equipment" should be used. Manufacturer's instructions for calibration and operation shall be followed as appropriate, field AQC requirements are given below.

All tests kits and instruments with or without MCERTS certification to the MCERTS "Performance Standards and Test Procedures for Portable Water Monitoring Equipment", shall undergo a validation procedure, as well as routine calibration and AQC, to ensure they can achieve the required performance.

One of the main criticisms of the use of portable instruments and test kits in the field is the lack of training given to staff that use them. Hence inconsistent and erroneous results from their misuse often occur, which is not acceptable for regulatory compliance monitoring. Manufacturer's training resources shall be used if available and appropriate. At least one member of staff shall be fully trained in the use of the instrument and/or test kit, have a good understanding of its basis of operation, fault finding and quality control, and be able to train others in its use. All who operate portable instruments and test kits shall have a training record including objective evidence of competency.

Operating procedures shall be fully documented and available in the field for users.

As the analytical systems are used outside of a controlled laboratory environment, particular care shall be given to their cleaning, storage and maintenance.

D2. Validation

pH, specific conductivity and dissolved oxygen field instruments

The full validation procedure detailed in clause 5.3 shall be carried out for each model and probe/electrode combination in use. For each determinand one validation exercise could encompass all instruments used in the field, if all of the model and probe/electrode combinations are identical. Validation may be performed under laboratory conditions. If it is not appropriate to use spiking experiments, matrix samples and standards may be used.

Further limited verification tests shall be carried out on any additional instrumentation (if it has the same model and probe/electrode combination) using clause 5.3.5.1. This can be carried out after instrument calibration before first use in the field. An appropriate standard and one appropriate matrix sample shall be used. Seven replicates of each would be considered acceptable.

For dissolved oxygen it is acceptable to test matrix solutions at 0% and 100% oxygen saturation. Precision and bias targets only need to be met at 100% saturation.

Chlorine test kits

The full validation procedure detailed in clause 5.3 shall be carried out for each model in use. Further limited verification tests shall be carried out on any additional instrumentation (same model) using clause 5.3.5.1. This can be carried out after instrument calibration before first use in the field. An appropriate standard and one appropriate matrix sample shall be used. Seven replicates of each would be considered acceptable.

D3. Performance requirements

Performance requirements are given in Annex A.

For pH and conductivity bias can be determined from standard solutions used in validation. Precision shall be determined from samples used in validation.

For dissolved oxygen bias can be estimated by comparison with winkler titrations, for which traceability shall be demonstrated.

D4. Calibration

- Each piece of equipment shall be uniquely identified and recorded.
- A calibration timetable shall be drawn up, and each instrument clearly labelled as to when recalibration is required. It may not be necessary to calibrate pH and Electrical Conductivity [EC] meters daily (see AQC checks).
- A record of calibration events shall be kept.
- For pH, conductivity and dissolved oxygen measurements, thermocouples and thermometers shall also be calibrated.
- Clause 5.4 shall apply.

D5. AQC requirements

Quality assurance checks using AQC samples shall be carried out during sampling runs when the instrument or test kit is in use. Results shall be recorded and plotted on appropriate control charts after analysis of the AQC and checked against current control chart limits before the associated sample results are reported.

Clauses 5.6.3.2. and 5.6.3.4 shall apply where appropriate.

Note 1: An example of good practice is measuring an AQC sample at the beginning of the day before the first sample reading is taken and at the end of the day after the last sample has been analysed. Others approaches can be used if adequate control can be demonstrated.

Sufficient AQC samples should be measured to ensure that AQC samples comprise at least 5% of the samples measured.

If making pH measurements in low conductivity samples then a low conductivity pH check solution shall be used.

Note 2: For Conductivities of $<100 \mu S.cm^{-1}$ Ph 4 dilute acid buffers are reccommended, Other buffers are available for samples with conductivity around $500 \mu S.cm^{-1}$. Some electrodes may not be appropriate for measurement of pH in low conductivity waters.

If measuring specific conductivity in low conductivity or saline water then an additional more appropriate conductivity AQC sample shall be used.

Note: It is possible to use the same check/AQC solutions for conductivity and pH.

In addition, for all instruments, manufacturer recommended system suitability checks shall be carried out and the results recorded.

Proficiency testing shall be undertaken for all parameters for which appropriate schemes are available and shall be undertaken on-site.

D6. Instrument care

The following procedures shall be documented, and where appropriate records of implementation shall be kept:

- Storage conditions for instruments and probes, when in use and when not, short term and long term.
- Replacement of consumables, such as reagents, o-rings and membranes.
- Cable and connector inspections and replacement.
- Cleaning of instruments and probes.
- Updating firmware and software.

D7. Temperature

Temperature measurement is not in Annex A but accreditation for the MCERTS (waters) standard can be granted for this parameter provided the relevant requirements of ISO 17025 are met.

Annex E (informative): Nominal cross references with ISO/IEC 17025:2005

The table below cross-references the clauses in this MCERTS performance standard with the clauses of ISO/IEC 17025:2005.

This MCERTS performance standard	**ISO/IEC 17025:2005**
1	1
2	2
3	3
4.1	4.1.2
4.2	4.4
4.1.2	4.4.1(a)
4.2.2	4.4.1(b)
4.3	4.5
4.3.1	4.5
4.4	4.13.2
4.4.1	4.13.2.1
5	5
5.1	5.3
5.11	5.3.1
5.2	5.4
5.2.1	5.4.1
5.2.2 (5.2.2.1, 5.2.2.2, 5.2.2.3)	5.4.2
5.3	5.4.5
5.3.1 (5.3.1.1, 5.3.1.2, 5.3.1.3, 5.3.1.4)	5.4.5.2
5.3.2 (5.3.2.1, 5.3.2.2, 5.3.2.3, 5.3.2.4, 5.3.2.5)	5.4.5.2
5.3.3 (5.3.3.1, 5.3.3.2, 5.3.3.3, 5.3.3.4, 5.3.3.4)	5.4.5.3
5.3.4 (5.3.4.1, 5.3.4.2, 5.3.4.3)	5.4.5.3
5.3.5 (5.3.5.1, 5.3.5.2, 5.3.5.3)	5.4.5.3
5.3.6	5.4.6
5.4	5.6
5.4.1, 5.4.2, 5.4.3, 5.4.4, 5.4.5	5.6.2.2
5.5	5.7
5.5.1	5.7.1
5.5.2	5.7.1
5.5.3	5.7.1
5.5.4	5.7.1
5.6	5.9
5.6.1	5.9
5.6.2 (5.6.2.1, 5.6.2.2, 5.6.2.3, 5.6.2.4)	5.9
5.6.3 (5.6.3.1, 5.6.3.2, 5.6.3.3, 5.6.3.4)	5.9
5.7	5.10
5.7.1	5.10.3.1
5.7.2	5.10.3.1
5.7.3	5.10.3.1