Performance Standard for Organisations Undertaking Radioanalytical Testing of Environmental and Waste Waters

Environment Agency
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Version 3

mCERTS
THE ENVIRONMENT AGENCY'S MONITORING CERTIFICATION SCHEME

Record of amendement

Version 1 May 2012

Version 2 July 2015

- Amendment of gross beta precision target and clarification of background count monitoring frequency

Version 3 December 2018

- Document reformatted and reordered to comply with changes to ISO 17025.
- Update of contact details

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 radioanalytical testing of environmental and waste waters directly under contract to the Environment Agency and have been required by us to submit results that comply with this MCERTS standard. This may include surface and ground waters, trade effluent, leachate, saline and other waters. Over time this standard may be extended to cover other areas of radioanalytical testing, such as soil and biota.

We require laboratories carrying out this work to be accredited by a National Accreditation Body that is a signatory to the European & International Multilateral Recognition Agreements – the United Kingdom Accreditation Service (UKAS) fulfils this requirement in the UK, to the international standard, ISO/IEC 17025 for this MCERTS performance standard.

The MCERTS standard provides an application of ISO/IEC 17025 specifically for the radioanalytical testing of environmental and waste waters:

- 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

Some of the requirements of this performance standard are described in general terms. This is to allow some flexibility and to allow the laboratory to take advantage of technological developments. In this way, a laboratory 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 laboratories involved in the analysis of environmental and waste waters for radioactive substances can be confident that the information you provide is reliable.

The standard underpins the critical importance of radioanalytical testing of environmental and waste waters in producing reliable information for regulatory purposes, and ensures participating laboratories will be working towards the same standard.

By setting quality standards that are a prerequisite of radiochemical analysis of environmental and waste waters the standard promotes best measurement practice in this area, thus raising the quality of work carried out by laboratories active in this sector and underlining the professionalism of staff involved in such work.

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

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

Telephone: 01784 429000

Email: info@ukas.com

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

www.mcerts.net

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

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Performance standard for organisations undertaking radioanalytical testing of environmental and waste waters

Introduction

This extension of MCERTS to include the radioanalytical testing of environmental and waste waters is built on proven international standards to ensure that the quality of test data is high. It specifies the requirements for laboratories undertaking the radioanalytical testing of environmental and waste waters to meet 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 the Environment Agency has required a contractor to submit data to it for regulatory purposes which complies with this MCERTS standard, 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 laboratory's scope of activities. This performance standard contains requirements that a laboratory 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 accredited laboratory under the MCERTS performance standard for the radioanalytical testing of environmental and waste waters. In addition, there are also requirements for a procurer of analytical services who wishes to submit data to the Environment Agency for regulatory purposes.

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 a laboratory to become accredited under this MCERTS standard.

The clause numbers in this document align with those of EN ISO/IEC 17025:2017, and may not be the same as those in other dated versions of EN ISO/IEC 17025. The text of EN ISO/IEC 17025 is not repeated, and where no additional requirements are needed, this is stated.

1 Scope

For this performance standard environmental and waste waters are taken to include surface and ground waters, trade effluents, leachates, saline and other waters. The radioanalytical testing of environmental and waste waters can be undertaken for a wide range of determinands using a range of methods. Where required, the methods that a laboratory 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 laboratory's scope of accredited activities.

This performance standard is applicable to all laboratories and procurers of analytical services working directly under contract to the Environment Agency where they have been required by us to submit results that comply with this MCERTS standard for the radioanalytical testing of environmental and waste waters.

When a laboratory satisfies all of the appropriate requirements of ISO/IEC 17025 and this performance standard, that laboratory will have demonstrated that it meets the Environment Agency's MCERTS requirements for the radioanalytical testing of environmental and waste waters, or, if it so chooses, a subset of these different matrices, for its published scope of activities. A laboratory'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) "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

b) "MCERTS 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. www.mcerts.net

c) "Quantifying Uncertainty in Analytical Measurement". Eurachem/CITAC Guide, third edition, 2012. ISBN 978-0-948926-30-3 www.eurachem.org

d) "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

e) Handbook for calculation of measurement uncertainty in environmental laboratories, Nordtest Report TR 537 (ed. 4) 2017. Available from www.nordtest.info.

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

g) "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

h) "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

i) "A simple fitness-for-purpose control chart based on duplicate results obtained from routine test material." Analytical Methods Committee technical brief No.9, the Royal Society of Chemistry 2002

j) "Quality Control Charts in Routine Analysis", M J Gardner, WRc Report CO4239 1996

k) ISO 8258 - Shewhart control charts

l) "Multi-Agency Radiological Laboratory Analytical Protocols Manual," Volumes 1–3, NUREG-1576 (MARLAP), U.S. Nuclear Regulatory Commission, Environmental Protection Agency, Department of Energy, Department of Defense, Department of Homeland Security, National Institute of Standards and Technology, U.S. Geological Survey, and Food and Drug Administration, Washington, DC, July 2004

m) "Management and technical requirements for laboratories performing environmental analysis: Quality systems for radiochemical testing" – The NELAC Institute 2010

n) "Standardised Reporting of Radioactive Discharges" Radiological Monitoring Standards Working Group Technical guidance note 1 May 2010

o) ISO 11929 - Determination of the characteristic limits (decision threshold, detection limit and limits of the confidence interval) for measurements of ionizing radiation -- Fundamentals and application

2.3 Other references

p) "Monitoring of Discharges to Water and Sewer" Environment Agency technical guidance note M18 www.mcerts.net

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

r) "Nomenclature for Radioanalytical Chemistry," Pure and Applied Chemistry, 66:12, pp. 2513–2526, 1994. International Union of Pure and Applied Chemistry (IUPAC)

s) Eurachem/CITAC Guide: Guide to Quality in Analytical Chemistry: An Aid to Accreditation (3rd ed. 2016). ISBN 978-0-948926-32-7., www.eurachem.org

t) Eurachem Guide: The Fitness for Purpose of Analytical Methods – A Laboratory Guide to Method Validation and Related Topics, (2nd ed. 2014). ISBN 978-91-87461-59-0, www.eurachem.org

u) "General concepts for traceability in environmental radioactivity monitoring" – S. Jerome, J. Eccles and K. Inn. Metrologia 44 (2007) S133-S1389

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 – Difference between the expectation of the test results and an accepted reference value [ISO 3534-1].

Bias can be estimated where appropriate certified reference materials are available and a stated (certified*)* concentration has been quoted, and also by measuring a sample before and after adding a known amount of determinand.

Carrier - A substance in appreciable amount which, when associated with a tracer of a specified substance, will carry the tracer with it through a chemical or physical process, or prevent the tracer from undergoing non-specific processes due to its low concentration. [Nomenclature for radioanalytical chemistry, IUPAC recommendations 1994]

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].

In the context of this standard a CRM is a sample of the target matrix, the activity concentration of determinand being certified to a quoted uncertainty and preferably traceable to an international/national standard.

Concentration - Concentration, for radioanalytical testing of environmental and waste waters, is usually expressed as activity concentration, unit becquerel per litre (Bq L^{-1}).

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

Decision threshold - Value of the estimator of the measurand, which when exceeded by the result of an actual measurement using a given measurement procedure of a measurand quantifying a physical effect, one decides that the physical effect is present. [ISO 11929-10]

Detection limit - Smallest true value of the measurand that is detectable, with a given probability of error, by the measuring method. [ISO 11929-10]

Fortified matrix sample (usually termed matrix 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 this purpose should be from a different source or lot number to that used for calibration. Suitable contact times between addition of the standard and extraction should be determined to provide adequate time for interaction between added determinand and sample while ensuring that there is no degradation of the determinand.

In-house Reference Material – A sample produced by the laboratory, 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.

Laboratory - A laboratory, or sub-contracting laboratory, that undertakes the radioanalytical testing of environmental and waste waters.

Nuclide - An atom specified by its atomic weight, atomic number, and energy state. A radionuclide is a radioactive nuclide.

Operator - "Operator" is defined by The Environmental Permitting (England and Wales) Regulations 2007 No. 3538 as: "the person who has control over the operation of a regulated facility".

Performance characteristics - Those performance values, such as precision, bias and detection limit 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.

Radionuclide - An unstable nuclide capable of spontaneous transformation into other nuclides by changing its nuclear configuration or energy level. This transformation is accompanied by the emission of photons or particles.

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].

This is usually a sample of the target matrix, the concentration of determinand being characterised to a quoted uncertainty.

Sample - That (uniquely identified) material removed from a site and submitted to the laboratory for analysis. See also sub-sample.

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, and analysis results may be questionable.

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.

Tracer – A known quantity of a radioisotope that is added to a solution of a chemically equivalent radioisotope of unknown concentration so that the yield of the chemical separation can be monitored [ref l, p14-90]

4 General requirements

4.1 Impartiality

4.1.1-4.1.5 No additional requirements to EN ISO/IEC 17025.

4.2 Confidentiality

No additional requirements to EN ISO/IEC 17025.

5 Structural requirements

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

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

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

6 Resource requirements

6.1 General

No additional requirements to EN ISO/IEC 17025.

6.2 Personnel

No additional requirements to EN ISO/IEC 17025.

6.3 Facilities and environmental conditions

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

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.

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.

6.4 Equipment

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

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

Calibration shall take place before an instrument's initial deployment in a laboratory. Thereafter recalibration shall occur at appropriate intervals documented in procedures, or when other control measures suggest the method is out of control, or major repair or maintenance is undertaken

Prepared calibration sources shall be matched to the samples to be determined, in terms of geometry, composition and distribution of sample on a mount/container. In addition, the calibration shall cover the range of interest for the samples being analysed. Internal calibration by the method of standard additions may be used, for example, in liquid scintillation spectrometry.

Note: It is recognised that the number of calibration points may be restricted by instrument manufacturer's software. Here the restriction should be demonstrated and justified.

6.4.7 Where appropriate a minimum of one method blank shall be analysed with each batch of samples. This sample shall be of a similar matrix to the other samples in the batch, and shall be taken through the entire analytical procedure wherever possible. Laboratories shall demonstrate, according to written procedures, how the results obtained from method blank samples are utilised. Method 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.

6.4.8 No additional requirements to EN ISO/IEC 17025.

6.4.9 The response of instruments may fall due to, for example, deterioration in a detector. This may not be immediately obvious from internal quality control sample results. The initial calibration should, therefore, meet with appropriate predefined system suitability limits (see section 7.1.1).

6.4.10 Where appropriate, 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 should be investigated and if necessary the instrument shall be fully recalibrated and affected samples reanalysed

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

6.5 Metrological traceability

No additional requirements to EN ISO/IEC 17025.

6.6 Externally provided products and services

No additional requirements to EN ISO/IEC 17025.

7 Process requirements

7.1 Review of requests, tenders and contracts

7.1.1 For data to be submitted to the Environment Agency under this performance standard, the requirements of the methods to be used shall be clearly and unambiguously defined and documented. The laboratory shall demonstrate that the requirements of the methods to be used are understood by those who undertake the analysis.

Where required, for data to be submitted to the Environment Agency, the appropriate testing method shall be selected and shall satisfy the requirements of this performance standard.

A laboratory may sub-contract the testing to another appropriate laboratory. It is the responsibility of the laboratory to ensure that the sub-contracted laboratory 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.

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

7.2 Selection, verification and validation of methods

7.2.1 Selection and verification of methods

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

7.2.1.2 Selection of standard nuclear data

Laboratories shall have procedures for regular update of standard nuclear data used in the analytical determination and calculation of results. It is recommended that data should be obtained from the Decay Data Evaluation Project website at www.nucleide.org/DDEP.htm wherever possible.

However, it is recognised that there are some omissions in the above source of data that may be relevant for Environment Agency requirements, namely Ru-106 , Cs-134, Ce-144, Ca-47, Tc-99 and Th-230. The alternative ENSDF (Evaluated Nuclear Structure Data File) data source can be used for these nuclides, at http://www.nndc.bnl.gov/nudat2/

7.2.1.3 No additional requirements to EN ISO/IEC 17025.

72.1.4 The Environment Agency will not prescribe those analytical methods that a laboratory 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.

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 laboratories. For example, when a radiochemical separation technique is used to isolate or concentrate a particular determinand, the separation steps shall be detailed

(for example whether ion exchange or solvent extraction) including details of the chemicals and reagents used.

The detailed description of the method shall be made available to the Environment Agency, if requested.

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

7.2.2 Validation of methods

7.2.2.1 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. The process of 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
- Precision
- Decision threshold and detection limit
- Uncertainty of measurement

Precision and bias shall be estimated for each determinand and matrix covered by the method. Decision threshold and detection limit shall be estimated for each determinand and method (see Annex C1). Where available and appropriate, matrix certified reference materials relevant to the matrices, determinands and range of determinand activity 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 environmental and waste waters.

Each sample used in validation procedures shall be characterised in terms of basic analytical data. This shall include determinands appropriate to the matrix, for example pH, conductivity, suspended solids, dissolved solids and total organic carbon (TOC).

In the absence of suitable certified reference materials, bias estimates relevant to the matrix and determinand under investigation, shall be determined by the use of matrix fortifying 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 bias, 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 laboratory shall demonstrate that its use of matrix fortifying experiments and the procedures employed is appropriate.

For matrix fortifying experiments, the laboratory shall justify choice of sample and concentration level. If samples contain a significant amount of a determinand this approach may not be feasible, laboratories 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 (excepting radioactive decay) 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 a).

7.2.2.2 Revalidation

After an analytical method has been validated and accredited, it is possible that at some time modification of procedures will be required. 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.

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

If equipment is being replaced, and performance is not expected to fundamentally change, or an instrument has to be taken out of service to undergo a repair, a laboratory need only demonstrate that the new/repaired instrument performs as well as the old instrument.

If a fundamental change is made to the analytical procedure or the equipment used, for example, using a new radioanalytical separation technique, then a full validation on all previously validated matrices is required in accordance with this performance standard.

It is recognised that an intermediate degree of validation should be carried out if significant changes are made to a method that are not considered fundamental to its performance. A partial validation shall be performed, using seven replicates of a Single fortified matrix sample or a CRM, for all appropriate matrices. If a laboratory judges that this level of validation is required, then it shall notify and gain the approval of UKAS. Laboratories shall ensure that the amendments to the analytical system and any procedures that may be affected are included in the revalidation.

7.2.2.3 Validation procedures

Validation procedures for radiometric methods

For each method and each determinand the performance characteristics (precision and bias) shall be estimated by analysing 7 replicates of each chosen matrix at 2 different but appropriate concentrations. The laboratory shall test matrices representing the range of matrices routinely analysed by the laboratory. The laboratory shall demonstrate that the concentrations and matrices chosen are appropriate. If a fortified matrix experiment is used then both sample and fortified samples should be replicated 7 times, therefore 21 results per matrix required. A CRM shall be used if available and appropriate. See also Annex B.

Note 1: Any proposed routine control samples should be included to enable control limits to be set.

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

Note 3: Previously obtained accredited data may be usable, validity and traceability must be demonstrated, and must have been obtained using the present method (i.e. no major method changes). It is unlikely data more than 4 years old would be acceptable (a UKAS reassessment cycle).

Sample replicates shall wherever possible and appropriate be analysed in different analytical batches, by different analysts (if available), using different equipment and be randomly placed in different detectors. The data shall be collected over a period of time that reflects the frequency of and time taken to carry out the analysis.

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

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

The decision threshold and detection limit of a method shall be fit for the intended purpose and appropriate to the concentration level of interest required of the analysis. The decision threshold and detection limit shall be calculated as described in Annex C1. The decision threshold and detection limit should never be used in isolation of other method validation data to judge the appropriateness of a method.

Validation procedures for non-radiometric methods

Radiometric methods use instruments that have a fixed calibration, which is used over many batches of analysis. Non radiometric methods, such as inductively coupled plasma mass spectrometry (ICP-MS), require regular within batch calibration. Therefore, to fully assess precision an estimate of both within and between batch random errors should be obtained.

Laboratories shall use the validation procedures described in reference b), which is available for download at www.mcerts.net

For estimation of detection limit and decision threshold (critical limit) in non radiometric methods see Annex C2 of this performance standard.

Performance criteria

The following performance characteristics are acceptable for the validation of methods for the radioanalytical testing of environmental and waste waters, 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 10%. For group/total methods (e.g. gross alpha and gross beta), the bias shall not be greater than 20%. If certified reference materials are used in bias determination, their specified uncertainties shall be sufficiently small to make a valid assessment at this level. Laboratories shall demonstrate that the bias satisfies the stated requirement at appropriate concentrations.

The precision, expressed as the percent relative standard deviation of individual results determined for the entire method, shall not be significantly greater than 7.5%. For gross alpha and gross beta methods the precision shall not be significantly greater than 15%. Laboratories shall demonstrate that the precision satisfies the stated requirement at appropriate concentrations. It is recognised that this performance is not achievable at the detection limit of the method.

When validating gross alpha and gross beta methods, the radionuclides used for calibration shall be used to estimate the performance characteristics.

If required, testing for significance shall be carried out as described in Annex C3. 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.

Annex A specifies the determinands covered by this standard.

When a determinand that is not listed in Annex A is measured, the laboratory shall apply the performance characteristics in clause 7.2.2.3. 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.

Note: Laboratories should be aware that unless flexible scopes are employed they would not be able to report these results as accredited until UKAS has assessed the method or indeed the Environment Agency has prescribed target performance values.

Validation of further matrices

Having completed validation to the MCERTS standard, a laboratory may subsequently be required to analyse samples of environmental or waste waters that have a significantly different matrix to the samples used in the initial studies. Where this is the case, a separate validation will be required for each of the new water types.

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.

7.2.2.4 No additional requirements to EN ISO/IEC 17025.

7.3 Sampling

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

7.4 Handling of test or calibration items

7.4.1 A sample shall be analysed using either all of the sample or a representative or homogenised sub-sample. If a determinand is known to be unstable, or suspected of being unstable, or begins to degrade once the sample has been taken, then the analysis shall be carried out without undue delay. The analysis shall be undertaken on a sub-sample of the sample as removed from the site or preserved or stabilised on site.

When a sample is stabilised, or preserved and subsequently analysed, then this fact shall be recorded, as should 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. Laboratories shall ensure that sample preservation and handling procedures (including selection of sample containers) are appropriate for and compatible to the analytical method being employed in the laboratory. Laboratories shall be in a position to supply suitable sampling containers to whoever collects the samples.

If the method requires the addition of substances to estimate chemical yield, they shall be added after sub-sampling and before any stabilising of the sample (see also 7.7.1.1).

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 0.45 µm membrane filter. Filtration shall, whenever possible and appropriate take place immediately at the point of sample collection. Any deviation from this prescribed procedure shall be justified and reported with results.

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 between 1 and 8°C. A laboratory 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.

7.4.2 - 7.4.4 No additional requirements to EN ISO/IEC 17025.

7.5 Technical records

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

7.5.2 No additional requirements to EN ISO/IEC 17025.

7.6 Evaluation of measurement uncertainty

7.6.1 Measurement uncertainty shall be estimated in accordance with accepted best practice.

Note: Useful information regarding the estimation of measurement uncertainty is given in references c), d) and e).

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

7.7 Ensuring the validity of results

Having demonstrated 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 7.7.1 and 7.7.2.

7.7.1 Internal Quality Control

7.7.1.1 For internal quality control, the performance of each analytical method shall be verified for each batch of samples analysed. Laboratory 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 fortified matrix 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: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.

For in-house reference materials 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 2: Guidance on the production of in-house reference materials can be found in references f) and g).

Note 3: 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.

For fortified matrix samples, the sample to which a known quantity of a determinand standard solution is added before analysis shall be representative of the matrix being analysed. Standards used for fortifying the sample shall be from a different source or lot number to that used for calibration. Suitable contact times between addition and extraction shall be determined to provide adequate time for interaction between added determinand and sample while ensuring that there is no degradation of the determinand.

Note 4: Sourcing of separate standards may not always be possible, however laboratories will need to demonstrate how they have tried to address this.

Other Options - Replicate analyses of individual samples as submitted to the laboratory can be considered, either two or more aliquots of the same sample or two or more separate samples if the whole sample is used in the analysis. This procedure may be useful when a test is carried out infrequently, as should the use of 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.

Where appropriate, laboratories shall employ techniques to correct for losses of determinand radionuclides during sample processing. Techniques employed may include:

- the addition and measurement of a radioactive isotope of the determinand that is not likely to be present in the sample
- the addition and measurement of a radionuclide that has been demonstrated to be a chemical analogue of the determinand during the analytical process
- the addition and measurement of a stable element of the determinand
- the addition and measurement of a stable element that has been demonstrated to be a chemical analogue of the determinand during the analytical process

- processing duplicate samples, one in which a known quantity of determinand is added and one which remains unchanged

Each sample shall have the chemical yield of determinand radionuclide estimated and recorded. This shall be assessed against statistically derived acceptance criteria. Laboratories shall have documented procedures to deal with yields that do not meet the acceptance criteria.

Note 1: Acceptance criteria for carrier yield or tracer yield may be matrix dependent.

Note 2: For elements with multiple oxidation states, ensure the tracer and target radionuclide are in the same oxidation state.

7.7.1.2 In order to monitor the variation of laboratory control samples and the method blank, results shall be recorded or plotted on statistically based quality control charts. After initial validation procedures laboratories shall have sufficient data to construct statistically based quality control charts. These charts shall be reviewed regularly for trends, and the control limits updated as necessary. Various forms of chart may be suitable, including Shewhart charts (individual results), cusum charts, zone control charts (J-chart), and duplicate charts. Use of the various charts is discussed in references h), i), j), and k).

To be able to monitor trends in analytical performance using control charts, it is recommended that wherever possible a minimum of 30 points are plotted in a 12 month cycle, spread evenly over the period. It is recognised that this may not be possible for infrequently used methods.

Note: When uncertainty of measurement is reported, it should reflect performance of the method at that time.

7.7.1.3 For all radionuclides monitored, quality control results shall be plotted on appropriate control charts. For gamma spectroscopy, where a large number of radionuclides are being determined simultaneously, a minimum of three of the radionuclides shall be used for laboratory control samples, and their choice shall be justified.

7.7.1.4 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, where possible, be reanalysed. If it is not possible and results are reported a full justification shall be given.

The investigation shall consider but shall not be restricted to the following areas:

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

7.7.1.5 System suitability checks

System suitability checks shall be carried out as quality control measures to ensure acceptable performance of an analytical system. Where appropriate the results of these checks shall be recorded on a statistically based control chart. Laboratories shall have fully documented procedures of actions to be taken when system suitability checks fail assigned control limits, measures may include recalibration of the analytical instrument. Procedures should be in place to assess trends, and take action where appropriate. Depending on method employed, the following should be monitored.

Background counts;

Gamma ray and alpha particle spectroscopy - carry out checks monthly, gas-proportional and scintillation counters - weekly.

Wherever possible, the sample containers, geometries and counting times should be the same as used for routine samples. Once sufficient data points are available to demonstrate stability, it may be possible to reduce the frequency of background counting.

Detector efficiency;

- For gamma ray spectrometers, gas-proportional and scintillation counters - check daily when in use, or at the start of an analytical run that continues for more than one day.
- For alpha spectrometers - check monthly.

Verification of energy calibrations;

- For gamma ray spectrometers - check daily when in use, or at the start of an analytical run that continues for more than one day.
- For alpha spectrometers - check weekly, or at the start of an analytical run that continues for more than one week.

Peak resolution and tailing;

- For gamma ray spectrometers - check daily when in use, or at the start of an analytical run that continues for more than one day.

This list is not exhaustive; all analytical systems shall undergo system suitability checks as appropriate. A laboratory may use different frequencies to those recommended, but if numbers are reduced, the change must be justified, for example if extremely long count times are used.

Note: The frequency suggested is as recommended in references l) and m).

7.7.2 Participation in interlaboratory comparison or proficiency-testing programmes

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

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.

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

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

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

This review procedure should take into consideration the relevance of the matrices and concentrations provided by the scheme, the number of other laboratories participating in the scheme and whether these laboratories use the same or similar analytical methods.

7.7.3 No additional requirements to EN ISO/IEC 17025.

7.8 Reporting the results

7.8.1 General

No additional requirements to EN ISO/IEC 17025.

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

No additional requirements to EN ISO/IEC 17025.

7.8.3. Specific requirements for test reports

7.8.3.1 For data submitted to the Environment Agency for regulatory purposes, 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 counted, analysis completed
- determinand analysed
- result of analysis
- uncertainty
- any decay correction applied,whether supported or unsupported for short lived nuclides
- other relevant comments, for example, visual characteristics of sample, source thickness
- sample filtration details
- particulate loading

Reporting requirements shall be defined by the environment Agency

7.8.3.2 No additional requirements to EN ISO/IEC 17025.

7.8.4 – 7.8.8 No additional requirements to EN ISO/IEC 17025.

7.9 Complaints

No additional requirements to EN ISO/IEC 17025.

7.10 Non conforming work

No additional requirements to EN ISO/IEC 17025.

7.11 Control of data – information management

No additional requirements to EN ISO/IEC 17025.

8 Management system requirements

No additional requirements to EN ISO/IEC 17025.

Annex A (Normative): Radionuclides covered by this standard

Americium -241
Antimony -125
Caesium -134
Caesium -137
Calcium -45
Calcium -47
Carbon -14
Cerium -144
Chromium -51
Cobalt -60
Curium -242
Curium -243/244
Europium -152
Europium -154
Europium -155
Iodine -125
Iodine -129
Iodine -131
Iron -55
Manganese -54
Neptunium -237
Nickel -63
Niobium -95
Plutonium -238
Plutonium -239/240
Plutonium -241
Plutonium - total alpha emitters
Polonium -210
Potassium -40
Promethium -147
Radium -226
Ruthenium -103
Ruthenium -106
Samarium -151
Silver -110m
Strontium -89
Strontium -90
Sulfur -35
Technetium -99
Thorium -230
Thorium -232
Tritium
Uranium -233
Uranium -234
Uranium -235
Uranium -236
Uranium -238
Uranium - total alpha emitters
Yttrium -90
Zinc -65
Zirconium -95

Group / total activity methods

Gross Alpha

Gross Beta

Annex B (informative): Validation Protocol

B1 A typical validation protocol for radiometric methods:

Performance tests to estimate precision, bias, decision threshold and detection limit can only be carried out on a stable calibrated analytical system. In this example three matrices represent the range of sample types analysed by the laboratory. Samples should be put through the entire analytical procedure in a random order.

Wherever possible, samples within each set of sample types shall be prepared on and analysed on different days. 7 replicates of each sample is required. Further information can be found at section 7.2.

Obtain an adequate volume of each of the three matrix samples (for example a final effluent, a saline water and a surface water). Stabilise the sample if required by the documented analytical procedure. If present, the concentration of target determinand in the matrix sample should be close to the expected detection limit.

For each matrix, add an appropriate amount of standard. The concentrations chosen should be appropriate for the sample concentrations normally encountered in each matrix (if practical), any regulatory limit and the range of the analytical method employed. Other suggestions are: 10 times the detection limit, mid range concentration or 80% of concentration range

Wherever possible, measure the matrix samples(3) and fortified matrix samples(6) in one analytical batch. Carry out blank and recovery corrections as directed by the documented analytical procedure.

Repeat the above measurements on 7 different occasions in seven different analytical batches. For 3 different matrices, a total of 63 samples will require analysis.

Estimate the precision for each matrix as a relative standard deviation (n=7) and compare with the performance targets specified in this standard. If required carry out significance tests (see Annex C3.3).

Estimate systematic error (bias) as described in Annex C3.4

Detection limit and decision threshold shall be calculated using the procedure outlined in Annex C1.

Results of these validation tests can then be presented with method documentation.

Annex C (normative): Statistical Analysis

C1 Decision threshold and detection limit for radiometric methods

For radiometric methods it is possible to determine a method decision threshold and detection limit from the measurement of a single blank sample (using the method in this section). However, the method decision threshold and detection limit may also be based on the uncertainty in the measurement of a number of 'blank' samples – see section C2.

Laboratories shall be required to estimate decision threshold and detection limit using the procedures below. Where multiple detectors are in use, each shall be assessed. The procedures below were adapted from references n) and o).

C1.1 Choice of blank sample and blank sample pre-treatment

The blank sample used for estimating decision threshold and detection limit shall be as similar as possible to the matrix being analysed. Using a single sample for these estimations for a given method will not take into account different matrix effects.

Note: If appropriate, blank sample may only include reagents and containers and holders used in counting.

It is recognised that laboratories may wish to estimate decision threshold and detection limit using just a detector background (i.e. counting with an empty detector) rather than producing a blank sample. The laboratory shall demonstrate and provide justification of the equivalence of using an empty detector rather than producing a full blank sample.

Where appropriate the blank shall be put through the entire analytical process (including, as necessary, extraction, clean-up and measurement). The blank samples shall be processed and analysed in the same manner and using the same equipment and reagents as other samples in a batch.

C1.2 Calculation

Definitions and differences

There are many formulations of the decision threshold and detection limit in use for measuring radioactivity. Key points leading to differences are:

a) For gamma spectrometry the activity present in the sample itself increases the spectrum continuum background and hence the detection limit which is achievable for that sample. Therefore for gamma spectrometry a detection limit based on a blank sample would only be an indication of that which is best achievable. Thus for gamma spectrometry it is good practice to define the decision threshold and detection limit on the basis of the continuum background of the sample measurement and measurement of the blank sample (see note in section on parameter definitions).

b) Radiometric spectrums are normally assumed to follow a Poisson distribution, due to the integer nature of the measurement. However, at low counts, the distribution tends to be binomial. Although, revised methods are available to take account of this, the correction provided is less than 10% where there are ten background/blank counts or more. For fewer than ten background/blank counts, deciding how many counts are in the background/blank is likely to provide the greatest source of error. Hence, for simplicity, the same method

shall be used to derive decision thresholds and detections limits, whatever the number of background/blank counts.

c) The probability of error used in the formulation of the decision threshold and detection limit varies between methods. A confidence level of 95% shall be assumed. This gives a so called 'coverage' or 'k' factor of 1.96 for a two-tailed distribution and 1.645 for a one-tailed distribution.

d) Analytical instruments have embedded software for calculating decision thresholds and detection limits. However, these quantities are often given different names and are derived in different ways. The best fit to the formulations below shall be selected, and the rationale demonstrated. Methods which use the uncertainty in the gross or net sample counts to derive the detection limit shall not be used. Some embedded software will have algorithms for accepting and rejecting peaks. If a peak is rejected by such an algorithm then the counts of the rejected peak shall be included with the continuum background counts when calculating decision thresholds or detection limits.

Parameter definitions

k = coverage factor (at defined confidence level)

b = background/blank count rate (S^{-1})

t_s = sample count time (s)

t_0 = background/blank count time (s)

w = 1 / (e V f) or 1 / (e M f)

e = detector efficiency (0-1), including branching ratio for radionuclide where appropriate

V = volume (L)

M = mass (kg)

f = other factors (e.g. quench correction)

$u_{rel}(w)$ = total relative standard uncertainties for all the factors making up w

Note: It needs to be recognised that for some techniques the detection limit is unique for individual samples (for example gamma spectrometry). In these cases, the background (b) comprises the continuum background counts at the appropriate energy of the radionuclide of interest in the spectrum when the sample is present and any net peak counts of the specific radionuclide for the blank sample (see C1.2a). The first component is sample specific, the second component is detector/method specific. For other radiometric methods (for example alpha spectrometry) the background/blank (b) would be the gross peak counts at the appropriate energy of the radionuclide of interest for the most recent appropriate blank sample.

Generic formulae

The generic formulae for the decision threshold and detection limit where the coverage factor (k) is the same for the decision threshold and detection limit are:

Decision threshold (L_c) (activity concentration / Bq L^{-1}) = $kw\sqrt{\frac{b}{t_s}+\frac{b}{t_0}}$

Detection limit (L_d) (activity concentration / Bq L^{-1}) = $\frac{2L_c+\frac{k^2 w}{t_s}}{1-k^2u_{rel}^2(w)}$

$$= \frac{\frac{k^2w}{t_s}+2kw\sqrt{\frac{b}{t_s}+\frac{b}{t_0}}}{1-k^2u_{rel}^2(w)}$$

Simplified formulae

The generic formulae can be simplified by setting a value for the coverage factor (usually chosen to be 1.645 for 95% probability); assuming that the count time (t_s) is the same as the background/blank count time (t_0); and that there is negligible relative error in *w* (u_{rel} (*w*)):

Decision threshold (L_c) (activity concentration / Bq L^{-1}) = $2.3w\sqrt{\frac{b}{t_s}}$

Detection limit (L_d) (activity concentration / Bq L^{-1}) = $\frac{2.7w}{t_s}+4.7w\sqrt{\frac{b}{t_s}}$

These simplified formulae shall be used under the following conditions:

The sample count time is the same as or shorter than the background/blank count time. If the sample count time is longer than the background/blank count time, then the background/blank count time should be used in the formulae.

The relative error in (u_{rel} *(w))* is less than 10% at one standard deviation (coverage factor equals one).

Any variation on the procedures shall be fully justified.

C2 Detection and critical limits for non radiometric methods

For non radiometric methods, such as ICP-MS, the detection limit shall be calculated using the method prescribed in the latest version of the MCERTS standard, reference B, available for download at www.mcerts.net

If required, the critical limit (L_C) shall be calculated:

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

where: df = the number of degrees of freedom (minimum 10)

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

S_w = within-batch standard deviation of results

This is based on reference a)

C3 The use of significance tests in the interpretation of method performance.

C3.1 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 section 5.3 and calculations have been applied to the results, there should be sufficient data to assess whether method performance complies with this standard.

C3.2 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 could be minimised by specifying its calculation with at least 10 degrees of freedom.

Assessment of precision is in three stages:

Determine the target standard deviation at the concentration of interest.

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

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

C3.3 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 S_t is the measured total standard deviation, and Z is the target standard deviation.

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

Z is a target standard deviation and therefore has infinite degrees of freedom. For S_t use (n-1), where n = number of samples.

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 i.e. performance passes.

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

C3.4 Assessment of systematic error or bias

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

The assessment of bias depends on independent knowledge of a "true" value with which to compare the average of measured data. This is accomplished by the use of reference materials or by addition of known amounts of determinand to matrix samples.

To assess bias and its associated uncertainty the procedure is to calculate the mean result for each sample tested and to estimate the overall bias 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.

When using determinand fortified matrix samples, estimate % recovery for each matrix sample in each analytical batch, using the equation:

$$R = \frac{E(V+W) - UV}{CW} \times 100\ \%$$

Where: U = measured conc. in original sample (after method corrections applied)

E = measured conc. in fortified sample (after method corrections applied)

C = conc. of solution

W = volume of standard solution added

V = original volume of sample

R = % Recovery (of determinand added to sample)

Overall mean $M = \frac{\sum \boldsymbol{R_i}}{\boldsymbol{n}}$

Standard Error of mean $S_e = \frac{S_R}{\sqrt{n}}$

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

Where:

$\boldsymbol{n}$ = number of samples

$\boldsymbol{R_i}$= Recovery (%) of the **I** th sample

$\boldsymbol{S_R}$ = standard deviation of $(R_1, R_2 \ldots\ldots R_i)$

$\boldsymbol{t}_{\textbf{(0.05,n-1)}}$ = single-sided Student's t value at 5% probability leveland (n-1) degrees of freedom

If there is an overlap (i.e. one or both of the target bias limits is within the confidence interval), the bias is not significantly worse than required and should 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%.

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