MCERTS performance standard for radioanalytical testing of environmental and waste waters

August 2024

LIT 7126

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

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

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

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Introduction

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 to submit results that comply with this MCERTS standard. This may include surface and ground waters, trade effluent, leachate, saline and other waters.

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

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.

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

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

The MCERTS performance standard does not restate all the provisions of EN ISO/IEC 17025 which must be fully complied with. It only states the additional requirements which laboratories must comply with.

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

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

UKAS
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Find more information on MCERTS and copies of the performance standards and further guidance on our website MCERTS page on GOV.UK.

Contact us

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

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Monday to Friday, 8am to 6pm.

1 Scope

For this performance standard environmental and waste waters 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 measurands using a range of methods. The methods that a laboratory uses to generate data that they submit to the Environment Agency for regulatory purposes shall be accredited to EN ISO/IEC 17025 and this MCERTS performance standard. Laboratories shall define these methods in their scope of activities.

This performance standard applies to all laboratories and users of analytical services working directly under contract to the Environment Agency where we require them to submit results that comply with this MCERTS standard for the radioanalytical testing of environmental and waste waters.

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

When a laboratory meets all the appropriate requirements of ISO 17025 and this performance standard, that laboratory will have shown 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 the different matrices, for its published scope of activities. The laboratory shall publish the scope of its accredited activities on the UKAS website.

2 Normative references

We refer to EN ISO/IEC 17025 – General requirements for the competence of testing and calibration laboratories in the text in such a way that some or all their content constitutes requirements of this document.

3 Terms and definitions

In the context of this performance standard, these terms and definitions apply. We recognise 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 by measuring a sample before and after adding a known amount of measurand.

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 measurand being certified to a quoted uncertainty and preferably traceable to an international or 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}).

Measurand – within the sample, this is the determinand, 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 measurand 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 measurand and sample while ensuring that there is no degradation of the measurand.

In-house Reference Material – a sample produced by the laboratory, containing known concentrations of measurands 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 measurand 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.

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 measurand 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 results breach these limits, the method is 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. Details are in chapter 14 of: Multi-Agency Radiological Laboratory Analytical Protocols Manual," Volumes 1–3, NUREG-1576 (MARLAP).

4 General requirements

4.1 Impartiality

No additional requirements to EN ISO/IEC 17025.

4.2 Confidentiality

No additional requirements to EN ISO/IEC 17025.

5 Structural requirements

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

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

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

6 Resource requirements

6.1 General

No additional requirements to EN ISO/IEC 17025.

6.2 Personnel

No additional requirements to EN ISO/IEC 17025.

6.3 Facilities and environmental conditions

6.3.1 The laboratory shall protect equipment, reagents and samples from damage or degradation, during collection, transportation, and subsequent storage, as appropriate.

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

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

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

6.4 Equipment

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

6.4.6 The laboratory shall calibrate equipment, and if appropriate with each batch of samples. Use measurement standards that are traceable to national or international standards except where derived from natural physical constants, or where this degree of traceability is not possible.

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 the instrument needs major repair or maintenance.

Laboratories shall match prepared calibration sources to the samples being measured, in terms of geometry, composition and distribution of sample on a mount or container. In addition, the calibration shall cover the range of interest for the samples being analysed. Laboratories may use internal calibration by the method of standard additions, for example, in liquid scintillation spectrometry.

Note: We recognise that instrument manufacturer's software may restrict the number of calibration points. You should demonstrate and justify the restriction.

6.4.7 Where appropriate, the laboratory shall analyse a minimum of one method blank 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 they utilise results obtained from method blank samples. The laboratory shall investigate method blank sample results that show evidence of contamination and may need to repeat the analysis of the entire batch of samples.

6.4.8 No additional requirements to EN ISO/IEC 17025.

6.4.9 The response of instruments may fall. For example, due to deterioration in a detector. This may not be immediately obvious from internal quality control sample

results. The initial calibration should, therefore, meet with appropriate predefined system suitability limits.

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

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

6.5 Metrological traceability

No additional requirements to EN ISO/IEC 17025.

6.6 Externally provided products and services

No additional requirements to EN ISO/IEC 17025.

7 Process requirements

7.1 Review of requests, tenders, and contracts

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

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

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

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

7.2 Selection, verification, and validation of methods

7.2.1 Selection and verification of methods

7.2.1.1 The laboratory shall demonstrate and provide justification that they use suitable methods (including sample pre-treatment and preparation) for the analysis of a particular matrix and measurand. They shall also show that it is appropriate for the concentration of the measurand in the sample. The laboratory shall demonstrate and provide justification that method validation procedures have been undertaken in such a manner as is appropriate to the sample matrix undergoing analysis. The laboratory shall make full details of the method and method validation procedures available to the Environment Agency, if requested.

7.2.1.2 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.

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

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

For example, when a radiochemical separation technique is used to isolate or concentrate a particular measurand, the separation steps shall be detailed (for example whether ion exchange or solvent extraction) including details of the chemicals and reagents used.

If requested, a laboratory shall make a fully documented method available to the Environment Agency.

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

7.2.2 Validation of methods

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

Validation procedures include a number of operations, 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

Laboratories shall estimate precision and bias for each measurand, and matrix covered by the method. They shall also estimate decision threshold and detection limit for each measurand and method (see Annex C1). Where available and appropriate, the laboratory shall analyse matrix certified reference materials relevant to the matrices, measurands and range of measurand activity concentrations under investigation. Laboratories shall consider sample pre-treatment and preparation as an important part in the validation process. Certified reference materials may not need any pre-treatment. In these cases, they shall do a separate exercise to determine the effects of sample pre-treatment and preparation.

We do not expect that every sample submitted should require its own validated method. However, we recognise that a single validated method established for one particular matrix, but used for every sample, irrespective of its matrix, is unlikely to be appropriate. We cannot assume 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 measurands 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, the laboratory shall make bias estimates relevant to the matrix and measurand under investigation, using matrix fortifying experiments. Where possible these experiments shall cover the entire method (including pre-treatment, extraction, and determination). The addition of a measurand 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-measurand 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 measurand 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 stable (excepting radioactive decay) over the entire period of testing
- if solutions are not stable over the entire period of testing, the laboratory may prepare them immediately before the analysis of each validation batch or stabilised by addition of appropriate reagents

The laboratory shall have established the traceability of these solutions.

Note: You can find statistical procedures for dealing with sample instability during validation in “A Manual on Analytical Quality Control for the Water Industry,” R. V. Cheeseman and A. L. Wilson, revised by M. J. Gardner, NS 30, Water Research Centre, 1989. ISBN 0-902156-85-3.

7.2.2.2 Revalidation

After validation and accreditation of an analytical method, it is possible that in time some modification of procedures will take place. Any modifications to a method used within a laboratory may affect the resulting performance. Laboratories shall notify UKAS of any changes made to a method already accredited against the MCERTS requirements. These changes could range from replacing a piece of equipment to a fundamental procedural modification, such as using a different extraction procedure.

Minor changes to the analytical system may not require revalidation, but laboratories shall take care to make sure the cumulative effects of several changes do not affect system performance. For example, by closely monitoring internal and external AQC, and reanalysing CRMs used for validation.

If 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 or 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.

Laboratories should carry out an intermediate degree of validation if any significant changes made to a method are not considered fundamental to performance. The laboratory shall perform a partial validation (using 7 replicates of a single fortified matrix sample or a CRM, for all appropriate matrices. If a laboratory judges that the method needs this level of validation, then it shall notify and gain the approval of UKAS. Laboratories shall make sure that they include amendments to the analytical system and any procedures that they may affect, in the revalidation.

7.2.2.3 Validation procedures

Validation procedures for radiometric methods

For each method and each measurand the laboratory shall estimate the performance characteristics (precision and bias) 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 the laboratory uses a fortified matrix experiment, then they shall replicate both sample and fortified samples 7 times, so collecting 21 results per matrix. The laboratory shall use a CRM if available and appropriate. See also Annex B.

Note 1: You may include proposed routine control samples to enable control limits to be set.

Note 2: The use of a validated method for one 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 measurand.

Note 3: Previously obtained accredited data may be usable. You must have obtained it using the present method (with no major method changes) and prove validity and traceability. 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 show that the certified reference material for the matrix, methodology, measurand and concentration of analysed measurand is appropriate.

When validated, a method’s stated performance shall reflect the routine capability of the method. Thus, when used routinely, the methods 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 calculation of the decision threshold and detection limit shall be 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. So, to assess precision you need to get an estimate of both within and between batch random errors. Laboratories shall use the validation procedures

described in MCERTS standard for organisations sampling and chemically testing water.

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 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 (gross alpha and gross beta), the bias shall not be greater than 20%. If the laboratory uses certified reference materials 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. We recognise that this performance is not achievable at the detection limit of the method.

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

If required, carry out testing for significance as described in Annex C3. If, for a particular measurand, testing shows a significant difference exists between achieved and required performance, then the laboratory shall do further method development or refinement, or they shall use a different analytical method.

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 measurands covered by this standard.

When a laboratory measures a measurand that is not in Annex A, it 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 they use a flexible scope, they would not be able to report these results as accredited until UKAS has assessed the method, and the Environment Agency has prescribed target performance values.

Validation of further matrices

Having completed validation to the MCERTS standard, a laboratory may subsequently need 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, the laboratory will need a separate validation for each of the new water types.

If the new validation does not meet the MCERTS requirements, and the laboratory considers this is due to insurmountable matrix effects, then the ongoing validation data shall be sent to the Environment Agency via UKAS.

We will consider 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 Laboratories shall analyse samples using either all the sample or a representative or homogenised sub-sample. If a measurand is unstable, or suspected of being unstable, or begins to degrade after sampling, then laboratories shall do the analysis 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 undergoes stabilisation, or preservation before analysis then the laboratory shall record this fact, and details of the stabilising or preserving agents used. Where a party independent of the analysing laboratory performs this activity (provides the samples) the laboratory shall get this information and report it as above.

Laboratories shall ensure that sample preservation and handling procedures (including selection of sample containers) are appropriate for and compatible with the analytical method that they use. Laboratories shall be able 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 measurands on some samples it may be required that the dissolved portion of the measurand in the sample is analysed and reported on. The dissolved portion of the measurand in the sample shall be defined as that which will pass through a 0.45µm membrane filter. Filtration shall, whenever possible take place immediately at the point of sample collection. Any deviation from this prescribed procedure shall be justified and reported with results

If samples need preservation by refrigeration, 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 that it may take some time to bring the sample temperature to within this range.

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

7.5 Technical records

7.5.1 The laboratory shall retain records for a minimum of 6 years. This period shall take into account the need of the customer (user of the analytical services) and the need to submit these records to the Environment Agency, if requested.

7.5.2 No additional requirements to EN ISO/IEC 17025.

7.6 Evaluation of measurement uncertainty

No additional requirements to EN ISO/IEC 17025.

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

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

7.7 Ensuring the validity of results

7.7.1 Internal quality control

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

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 20, one laboratory control sample per batch is still required.

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

Note 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 measurand concentration and matrix of the material to those of samples normally encountered in the laboratory.

Note 2: You can find guidance on the production of in-house reference materials in references:

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

Note 3: You may achieve traceability for this material by characterisation against a certified reference material, for example during method validation or by comparison with the analysis of the material by accredited third-party laboratories.

For fortified matrix samples, the sample to which a known quantity of a measurand 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 measurand and sample while ensuring that there is no degradation of the measurand.

Note 4: Sourcing of separate standards may not always be possible, but 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 2 or more aliquots of the same sample or 2 or more separate samples if the analysis uses the whole sample. This procedure may be useful when a laboratory carries out a test 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 use techniques to correct for losses of measurand radionuclides during sample processing. Techniques employed may include:

- the addition and measurement of a radioactive isotope of the measurand 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 measurand during the analytical process
- the addition and measurement of a stable element of the measurand

- the addition and measurement of a stable element that has been demonstrated to be a chemical analogue of the measurand during the analytical process
- processing duplicate samples, one to which you add a known quantity of measurand and one which remains unchanged

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

Note 5: Acceptance criteria for carrier yield or tracer yield may be matrix dependent.

Note 6: For elements with multiple oxidation states, make sure the tracer and target radionuclide are in the same oxidation state.

7.7.1.2 To monitor the variation of laboratory control samples and the method blank, laboratories shall record or plot results on statistically based quality control charts. After initial validation procedures laboratories shall have enough data to construct statistically based quality control charts. The laboratory shall review these charts regularly for trends and update the control limits 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 given in the following references:

- A Manual on Analytical Quality Control for the Water Industry, R. V. Cheeseman and A. L. Wilson, revised by M. J. Gardner, NS 30, Water Research Centre, 1989. ISBN 0-902156-85-3
- The J-chart: a simple plot that combines the capabilities of Shewhart and cusum charts, for use in analytical quality control". Analytical Methods Committee technical brief No.12, Royal Society of Chemistry 2003
- Quality Control Charts in Routine Analysis, M J Gardner, WRc Report CO4239 1996

To be able to monitor trends in analytical performance using control charts, we recommend that wherever possible laboratories plot a minimum of 30 points in a 12-month cycle, spread evenly over the period. We recognise that this may not be possible for infrequently used methods.

Note: The uncertainty of measurement reported with results should reflect performance of the method at the time of reporting.

7.7.1.3 For all radionuclides monitored, laboratories shall plot quality control results on appropriate control charts. For gamma spectroscopy, where many radionuclides are being determined simultaneously, laboratories shall use a minimum of 3 of the radionuclides for laboratory control samples. Laboratories shall justify their choice.

7.7.1.4 Laboratories shall have documented procedures that define loss of statistical control and specify actions they shall take (control rules) when control limits are breached. They shall investigate all breaches, and the findings and actions recorded and made available to the Environment Agency, if requested. Laboratories shall, where possible, reanalyse samples in an analytical batch where a laboratory

control sample breaches the defined control rules. If it is not possible and a laboratory reports the results, it shall give a full justification.

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

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

Records shall include:

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

7.7.1.5 System suitability checks

Laboratories shall conduct system suitability checks as quality control measures to make sure of acceptable performance of an analytical system. Where appropriate they shall record results of these checks on a statistically based control chart. Laboratories shall have documented procedures of actions they will take 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, monitor the following.

Background counts:

- for 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 enough 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
- 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
- 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 it must justify the change if they reduce numbers, for example, if they use extremely long count times.

Note: The frequency suggested is as recommended in:

- "Management and technical requirements for laboratories performing environmental analysis: Quality systems for radiochemical testing" – The NELAC Institute 2010
- "Standardised Reporting of Radioactive Discharges" Radiological Monitoring Standards Working Group Technical guidance note 1 May 2010

7.7.2 Participation in interlaboratory comparison or proficiency-testing programmes

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

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

7.7.2.2 The methods, used by the laboratory to generate analytical data for radioanalytical testing of environmental and waste waters, shall be the same as those methods used by the laboratory for the analysis of samples distributed by the proficiency-testing scheme organiser. In addition, as far as is possible, the laboratory should treat samples distributed by the proficiency-testing scheme organiser in the same manner as normal routine samples submitted for radioanalytical 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, measurands, analyses to be undertaken by the laboratory and the types of matrices to be analysed, shall be made available. The reports of the results of all analyses submitted by the laboratory to the scheme organiser shall be made available.

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

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

7.7.3 No additional requirements to EN ISO/IEC 17025.

7.8 Reporting of results

7.8.1 General

No additional requirements to EN ISO/IEC 17025.

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

No additional requirements to EN ISO/IEC 17025.

7.8.3 Specific requirements for test reports

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

- location of sample
- unique sample code or reference
- date and time sample taken
- name of laboratory (including sampling organisation if different)
- name of any sub-contracting laboratories, if used
- date sample counted
- date sample analysis completed
- measurand analysed, including any sample preservation or stabilisation at sampling site
- result of analysis
- 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.

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

7.8.3.2 No additional requirements to EN ISO/IEC 17025.

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

7.9 Complaints

No additional requirements to EN ISO/IEC 17025.

7.10 Non conforming work

No additional requirements to EN ISO/IEC 17025.

7.11 Control of data – information management

No additional requirements to EN ISO/IEC 17025.

8 Management system requirements

No additional requirements to EN ISO/IEC 17025.

Annex A (normative): 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 - 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

Plutonium -239/240

Plutonium -241

Zirconium -95

Group / total activity methods

Gross Alpha

Gross Beta

Annex B (informative): validation protocol

B1 A typical validation protocol for radiometric methods:

Laboratories shall only do performance tests to estimate precision, bias, decision threshold and detection limit on a stable calibrated analytical system. In this example 3 matrices represent the range of sample types analysed by the laboratory. Samples should go through the entire analytical procedure in a random order.

Wherever possible, you shall prepare and analyse samples within each set of sample types on different days. You need 7 replicates of each sample. Further information is in section 7.2.

Obtain an adequate volume of each of the 3 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 measurand 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 separate occasions in 7 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.

Calculate detection limit and decision threshold using the procedure outlined in Annex C1.

You can then present results of these validation tests 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 estimate decision threshold and detection limit using the procedures below. Where multiple detectors are in use, laboratories shall assess each of them. We adapted the procedures below from:

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

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, containers, and holders used in counting.

We recognise that laboratories may wish to estimate decision threshold and detection limit using just a detector background (that is 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 laboratory shall put the blank through the entire analytical process (including, as necessary, extraction, clean-up, and measurement). They shall process blank samples and analyse them 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. Main 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 10 background and blank counts or more. For fewer than 10 background and blank counts, deciding how many counts are in the background and blank is likely to provide the greatest source of error. Hence, for simplicity, laboratories shall use the same method 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. But these quantities are often given different names and derived in different ways. The best fit to the formulations below shall be selected, and the rationale demonstrated. Laboratories shall not use methods which use the uncertainty in the gross or net sample counts to derive the detection limit. Some embedded software will have algorithms for accepting and rejecting peaks. If an algorithm rejects a peak, 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 and blank count rate (S^{-1})

t_s = sample count time (s)

t_0 = background and 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 (for example quench correction)

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

Note: 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 and 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

By setting a value for the coverage factor (usually chosen to be 1.645 for 95% probability), you can simplify the generic formulae if:

- the count time (t_S) is the same as the background/blank count time (t_0)
- there is negligible relative error in 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}) = $\frac{2.7w}{t_s}+4.7w\sqrt{\frac{b}{t_s}}$

Laboratories may use these simplified formulae under the following conditions if the:

- the sample count time is the same as or shorter than the background and blank count time. If the sample count time is longer than the background and blank count time, then use the background and blank count time used in the formulae
- relative error in (u_{rel} *(w))* is less than 10% at one standard deviation (coverage factor equals one)

Laboratories shall justify any variation to these procedures.

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 MCERTS standard for organisations sampling and chemically testing water.

If required, laboratories shall calculate the critical limit (L_C):

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

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

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 doing the validation as described in section 5.3 and applying the calculations 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 not 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 3 stages:

1. Determine the target standard deviation at the concentration of interest.
2. The target is achieved If the measured standard deviation is less than the target standard deviation.
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. You will need to do a statistical test to assess this significance

C3.3 F-Test of standard deviation.

The F-test or variance ratio test is a way of determining whether 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.

Compare the calculated value of F with a reference value obtained from statistical tables. Obtain the reference value of F 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 so 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, so 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. Accomplished this by using reference materials or by addition of known amounts of measurand 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).

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

When using measurand 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 measurand 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 ith 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 level and (n-1) degrees of freedom

If there is an overlap (that is one or both target bias limits are within the confidence interval), the bias is not significantly worse than required and is acceptable.

Note: An estimated bias is either positive or negative, so use a one-sided t-test at the 95% confidence level to assess if the observed bias is greater than permitted bias. But, by definition, a confidence interval is two sided, thus the significance test is at the 95% confidence level, but the resulting confidence interval is 90%.