Chapter 3 Quality Control and Quality Assurance

3.1 Purpose

To ensure that data generated by WFD physico-chemical and biological monitoring programs is reliable, representative, and facilitates robust assessment of the impacts of Programs of Measures each facility engaged in sampling, or where samples are analysed, is required to put in place a documented Quality Assurance program covering their operations.

3.2 Definitions

A Quality Assurance (QA) programme is a documented system of operating guidelines which, if followed during sample collection, transportation and analysis, will produce reliable data.

Quality Control (QC) is an integral aspect of QA and focuses on ensuring that analytical data are both accurate and precise. The QC programme should encompass all techniques to be used to measure and assess data quality, determination of analytical performance criteria including Limits of Detection / Practical Reporting Limits / Measurement Uncertainty, and remedial actions to be taken when quality criteria are not met.

3.3 Quality Assurance Plan

In preparing their QA programs laboratories are required to develop systems capable of meeting the requirements of the current version of I.S. EN ISO 17025 "General requirements for the competence of testing and calibration laboratories".

The Irish National Accreditation Board (INAB) undertakes assessment to this standard

Laboratories are encouraged to seek accreditation for relevant parameters and matrices tested however those not seeking accreditation are still required to put in place appropriate QA/QC systems in place covering such elements as:

- Sampling, sample transportation, receipt, storage and preservation
- Documented analytical procedures based on recognised National, European or International standards
- In-house Quality Control procedures and participation in relevant external performance testing schemes
- Validation of test methods response, limits of detection, and measurement uncertainty

- Staff training and competency
- Reporting procedures, information storage and data security

Guidance on sampling procedures can be found in the following sources:

Irish Standards:

- I.S. EN 25667-1: 1994 “Water Quality – Sampling – Part 1: Guidance on the design of sampling programmes”.
- I.S. EN 25667-2: 1994 “Water Quality – Sampling – Part 2: Guidance on Sampling Techniques”

International Standards Organisation:

- “Water Quality – Sampling – Part 1 “Guidance on the design of sampling programmes and sampling techniques” is currently under revision (Draft ISO/FDIS 5667-1:2006) is expected to be available from ISO in early 2007.
- IS0 5667-3 “Water Quality – Sampling – Part 3: Guidance on the preservation and handling of samples”
- BS 6068 series of publications relating to water quality. These standards cover sampling of a range of aqueous matrices. Some sections are identical to ISO 5667 publications however not all sections have been adopted by Ireland to date.

In developing their QA / QC procedures laboratories are strongly advised to consult the following document:

- ENV / ISO 13530 “Water Quality - Guide to Analytical Quality Control for Water Analysis (ISO/TR 13530:1997)”.

The EPA operates an inter-calibration programme for several natural water parameters however a number of commercial performance testing (PT) schemes are available. Further information may be obtained at:

http://www.epa.ie/PublicAuthorityServices/LaboratoryIntercalibrationProgramme

and also at www.eptis.bam.de

The use of Certified Reference Materials (CRMs) is encouraged where appropriate to the parameters monitored. These are offered by several commercial companies and can prove useful in validating analytical performance

3.4 Analytical Performance Requirements

The choice of analytical methods available is extensive. It is acknowledged that laboratory facilities will generally utilise in-house documented procedures. These should preferably be based on the following hierarchy of reference sources.

- Irish Standard methods (I.S. EN),
- European Standard Methods (EN),
- International Standard Methods (ISO),

Internationally accepted and documented reference procedures such as those contained in the current edition of APHA / AWWA “Standard Methods for the Examination of Water and Wastewater”

UK Standing Committee of Analysts “Methods for Examination of Waters and Related Materials” (MEWAM) or similar publications.

As a minimum, analytical procedures used should be capable of achieving at least 10% of the concentration of interest (e.g. EQS or other water quality standard) or the lowest measurable value that can be reported with a known statistical confidence. A total error threshold of ± 20% is considered to be the maximum allowable and would be assigned equally to bias and to random variation (standard deviation). For further guidance on method performance refer to Section 6.5 of ISO 13530.

It is recommended that in-house test procedures be set out in keeping with the ISO 78-2:1999 “Chemistry -- Layouts for standards -- Part 2: Methods of chemical analysis”.

Specific performance criteria and prescription of required analytical approaches may require to be defined for some parameters to ensure data comparability both within Ireland, and across the EU, particularly for empirical procedures such as those used for Chlorophyll or for trace metals / organics analysis.

3.4.1 Sub-contracting of analyses

Where sampling / analyses is sub-contracted, the contracting body shall ensure that any contract documentation makes full reference to all aspects of the monitoring process including (where relevant) choice of sample location, sampling technique (e.g. groundwater purging), sample pre-treatment (e.g. filtration), preservation, storage, transport, reporting criteria and analysis turnaround. This can be especially important for some parameters such as those for microbiology, metals, and trace organics. Reputable companies will generally apply the principles set out above however it is important that all bodies subcontracting work satisfy themselves as to the technical and analytical competence of any third parties engaged by them

Price is an important factor however quality of service and reporting limits can vary markedly between service providers, particularly in the case of organic analysis, where lower reporting concentrations necessitate complex sample pre-concentration and analytical procedures. The contracting body must ensure that its quality objectives are met when sub-contracting such analyses.

3.5 Guidance on reporting and interpretation of data

ISO 13530:1997 provides a robust framework for the evaluation of the performance of analytical measurement systems. The following sections provide guidance on preferred approaches for treatment and reporting of analytical data.

3.5.1 Rounding

It is common practice to truncate (or round) instrumental measured values. Consideration must be given to rounding such data in a manner that does not diminish its usefulness for evaluation of process change. In general rounding should provide a result where the uncertainty exists only in the last significant figure, e.g. 8.05(3) would be rounded to 8.05. Where summed values are reported these should be reported to the significance figures applied to the least accurate measurement. The use of 3 significant figures is generally sufficient for most analytical work.

3.5.2 Limit of Detection / Practical Reporting Limit

The “Limit of Detection” of an analytical system can be defined as the lowest concentration for which a response is measurable above background noise with a defined (typically 95%) statistical confidence. It is desirable that the LoD is based on examination of a series of batches of analyses over time by different analysts and not solely on the evaluation of the best possible performance or lowest detectable signal alone within a single batch of analysis. This approach ensures the most holistic estimate of variability likely to be obtained in routine use.

While the LoD provides a measure lowest signal detectable at the defined confidence it is common for laboratories to apply a somewhat higher value as a “Practical Reporting Limit (PRL)” or “Lower Limit of Quantification (LoQ)”. This is generally a multiple of the LoD (e.g. 2xLoD) and is used as an additional safeguard to ensure that responses to the detection of substances at low concentrations are merited based on a higher confidence of its detection.

3.5.3 Reporting and Interpretation of Low concentrations

A major difficulty with measurement at very low concentrations is that analytical systems can yield responses (sometimes negative) falling below the calculated LoD or LoQ above. Such data is often seen reported in one of the following ways:

- as Not detected (ND)
- as Less than the LoD (<LoD or <Value)
- as zero (0)
- as an arbitrary fraction of the LoD (e.g. LoD/2)
- as the measured value + its measurement uncertainty

The terms “Not Detected” and “Zero” should never be used as they convey no quantitative or qualitative information and are wholly dependent on the characteristics of the measurement system used. In many aqueous matrices it will not be possible to determine, with absolute confidence, the complete absence of a particular substance.

Reporting values as “<LoD” is the most commonly accepted practice however incorporating such values into statistical calculations requires their transposition to a replacement value C_R e.g. LoD/2. These values may facilitate calculations but the calculated statistic may be biased and should always be referenced back to the original LoD.

Recording the actual measured values (including negative responses), plus their estimated measurement uncertainty provides the greatest information however few laboratory data handling systems will store information in this manner. It is important that laboratories determine the measurement uncertainty of their analytical procedures such that this information is available to assist in the evaluation of the significance of any analytical data (see Section 3.5.5 below).

In all cases it is essential that a clear distinction is made between recorded (measured) values and any subsequently reported results.

Reference:

Royal Society of Chemistry (Analytical Methods Committee), AMC Technical Brief No.5, April 2001

3.5.4 Estimation and Use of Recovery Factors

Use of recovery factors to correct analytical results is a contentious issue. It is very relevant to trace organic analysis where liquid / liquid or solid phase extraction is used to pre-concentrate samples. It also applies however to inorganic parameters defined as “totals” e.g. Total Phosphorus, Total Cyanide etc. In such cases the recovery should be confirmed from complexed forms of the analyte.

The International Union of Pure & Applied Chemistry (IUPAC), International Standards Organisation (ISO) and AOAC International recommend the following approach.

Quantitative results should be corrected for recovery unless there are specific reasons for not doing so. These may include situations where: (a) the analytical method is regarded as empirical, (b) a contractual or statutory limit has been established using uncorrected data, or (c) recoveries are known to be close to unity.

It is of over-riding importance that all data, when reported, should be clearly identified as to whether or not a recovery correction has been applied and if a recovery correction has been applied, the amount of the correction and the method by which it was derived should be included with the report.

Recovery values should be established as part of method validation. When the use of a recovery factor is justified, the method of its estimation should be specified in the method protocol.

QC charts for recovery should be established during method validation and used in all routine analysis. Runs giving recovery values outside the control range should be considered for re-analysis in the context of acceptable variation, or the results reported as semi-quantitative.

Reference:

Pure Appl. Chem., 1999, 71, 337-348

3.5.5 Measurement Uncertainty

All analytical measurements have an associated uncertainty arising from sampling and analysis. For environmental samples the overall uncertainty arising from sampling variability is less able to be accurately estimated than that for analytical measurements however it has the potential to be a more significant component, particularly if the matrix sampled is not homogenous, e.g. downstream of a mixing zone of two waters, in a stratified water body etc. or where phyisco-chemical parameters are influenced by biological activity e.g. Chlorophyll measurement.

The use of replicate randomised sampling and/or the use of auto-samplers can provide more representative samples however where these approaches are employed it is essential to consider the selection of sites and their potential impact on the measurement achieved. This may require the use of preservatives for auto-sampler bottles and should be taken into account in designing monitoring programs

Analytical measurement uncertainty may be calculated from an evaluation of all contributory factors in a “bottom-up” approach however this can be a complex and lengthy process. It may be appropriate in some circumstances but does not lend itself to use as a routine tool.

A more practical approach to estimation of the analytical uncertainty is to use a “top-down” approach in which the performance of routine control standards is used to assess overall variability. This utilises the standard deviation of controls expressed as a relative standard deviation. A coverage factor of 2 (95%) is commonly applied. It is much simpler to apply but may require additional validation across the range of concentrations to be measured.

References:

“Quantifying uncertainty in Analytical Measurement” 2nd Ed. 2000 Eurachem/Citac Guide CG4.

“Estimation and Expression of Uncertainty of Measurement in Chemical Analysis”, Nordic Committee on Food Analysis, NMKL Procedure No. 5 (1997)

“The Expression of Uncertainty and Confidence in Measurement” (Dec 1997), United Kingdom Accreditation Service (UKAS), Document M3003.

3.5.6 Plausibility Checks / Data Validation

Data should always be checked prior to reporting for overall plausibility and comparability with previous samples. The use of comparative ratios such as BOD:COD, Na:K, Ionic Balances etc., is recommended.

Plotting of trends in such ratios can be of assistance in the early detection of trends in natural variations or step changes due to analytical factors. This may be particularly relevant when assessing parameters which are naturally low e.g. as trace metals concentrations. In addition such checks may also serve to highlight differences in reporting units e.g. Nitrate as NO_3 or as N, Phosphate as P or as PO_4 etc. especially where data from a range of sources is being aggregated.