Water Quality Monitoring - A Practical Guide to the Design and Implementation of Freshwater Quality Studies and Monitoring Programmes
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Chapter 9 - ANALYTICAL QUALITY ASSURANCE

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This chapter outlines the various techniques that may be employed in analytical quality assurance (AQA), and the reasons why they should be used. Reliability of data for a water quality monitoring programme depends on strict adherence to a wide range of operating procedures for water sampling and analysis. It is the consistent application and monitoring of these procedures that is referred to as quality assurance. The subject can be confusing, especially if more than one reference work is used as an information source. Different authors may use different terms to describe the same thing or the same term to describe different things. A number of the terms used in analytical quality assurance are defined in Table 9.1. The definitions are based on the vocabulary approved by the International Organization for Standardization (ISO) but may not have been universally adopted by those involved in AQA.

In order to demonstrate that a laboratory is producing data of adequate precision, accuracy and sensitivity it is necessary to assess all laboratory procedures at all stages from sampling to reporting. This is a time consuming and costly process and, for this reason, it is important to ensure that the necessary standards of performance are clearly defined and adhered to. In most laboratories, AQA will start with the examination and documentation of all aspects of laboratory management. This will include clearly identifying lines of communication and responsibility, the description and documentation of all procedures which are carried out, and the documentation of instrumental and analytical checks. Within this there should be specific control and assessment procedures designed to monitor quantitatively the accuracy and precision of specific assays.

Analytical quality assurance procedures should be based on a system of traceability and feedback. Traceability, in this context, requires that all steps in a procedure can be checked, wherever possible, by reference to documented results, calibrations, standards, calculations, etc. For example, where a balance is used in a laboratory, the accuracy of measurement must be regularly checked. The weights used for this purpose should either have a certificate demonstrating that they conform to a standard, or the balance must be regularly checked against such standards by the regular use of check weights which are well documented and thus can be linked within the laboratory to the calibration standard. This principle also applies to the calibration of other equipment.

Feedback is the principle that problems or omissions in the AQA system should be brought to the attention of management. Where standards in the laboratory fall below acceptable limits, procedures should ensure that this is easily recognised and corrected. Criteria for recognition and correction of poor performance, as well as responsibilities for corrective

action, must be identified. The procedures for achieving this recognition and correction must be clearly established.

Statistically based assay control systems, as used in internal and external quality control programmes, should also conform to the principles of traceability and feedback to ensure that correct criteria for adequate quality are adopted, and that any problems are quickly recognised and corrected.

Table 9.1 Definitions associated with analytical quality assurance

Term	Definition
Quality	The totality of characteristics of an entity that bear on its ability to satisfy stated and implied needs.
Quality policy	The overall intentions and direction of an organization with regard to quality, as formally expressed by top management. The quality policy forms one element of corporate policy and is authorized by top management.
Quality assurance	All the planned and systematic activities implemented within the quality system and demonstrated as needed, to provide adequate confidence that an entity will fulfil requirements for quality.
Quality system	Organisational structure, procedures, processes, and resources needed to implement quality management.
Organisational structure	The responsibilities, authorities and relationships through which an organization performs its functions.
Procedure	A specified way to perform an activity. When a procedure is documented, the terms “Standard Operating Procedure “written procedure” or “documented procedure & are frequently used’. A documented procedure usually contains the purposes and scope of an activity; what shall be done and by whom; when, where and how it shall be done; what materials, equipment and documents shall be used; and how it shall be controlled and recorded.
Process	A set of inter-related resources and activities that transform inputs into outputs. Resources may include personnel, finance, facilities, equipment, techniques and methods.
Quality management	All activities of the overall management function that determine the quality policy, objectives and responsibilities, and implement them by means such as quality planning, quality control, quality assurance, and quality improvement within the quality system.
Quality control	Operational techniques and activities that are used to fulfil requirements for quality. The terms Internal quality control” and “external quality control” are commonly used. The former refers to activities conducted within a laboratory to monitor performance and the]after refers to activities leading to comparison with other reference laboratories or consensus results amongst several laboratories.
Quality audit	Systematic and independent examination to determine whether quality activities and related results comply with planned arrangements and whether these arrangements are implemented effectively and are suitable to achieve objectives.
Traceability	Ability to trace the history, application or location of an entity by means of recorded identifications. In the context of calibration, it relates measuring equipment to national or international standards, primary standards, basic physical constants or properties, or reference materials. In the context of data collection, it relates calculation and data generated back to the quality requirements for an entity

Properly implemented AQA should demonstrate the standard to which a laboratory is working, ensure that this standard is monitored effectively and provide the means to correct

any deviations from that standard. It is sometimes argued that the value of quality assurance does not justify its cost but, without it, the reliability of data is doubtful and money spent on producing unreliable data is wasted. If 10 per cent of a laboratory's budget is spent on quality assurance, the number of samples that can be analysed will be about 90 per cent of that possible if there were no quality assurance programme. However, the results obtained for that 90 per cent will be accurate, reliable and of consistent value to the monitoring programme.

9.1 Quality assurance

Quality assurance (QA) refers to the full range of practices employed to ensure that laboratory results are reliable. The term encompasses internal and external quality control, but these specific aspects of AQA will be covered later. Quality assurance may be defined as the system of documenting and cross referencing the management procedures of the laboratory. Its objective is to have clear and concise records of all procedures which may have a bearing on the quality of data, so that those procedures may be monitored with a view to ensuring that quality is maintained.

Quality assurance achieves these objectives by establishing protocols and quality criteria for all aspects of laboratory work, and provides a framework within which internal quality control (IQC) and external quality control (EQC) programmes can be effective. It is primarily a management system, and as such is analyte-independent, because it deals with the overall running of the laboratory rather than focusing on individual analyses.

Aspects of QA which are specifically applicable to microbiological analyses of water samples are described in Chapter 10.

9.1.1 Components of quality assurance

Given the wide scope of quality assurance, the definition given above provides only the haziest picture of what is required to implement a QA programme. In order to provide a fuller explanation, it is more pertinent to study the components of a quality assurance programme and to examine the procedures that are required for each one.

Management

One of the most important components of the quality assurance programme in a laboratory are the comprehensive management documents which should describe, in detail, the management structure of the laboratory. Such documentation should provide clearly defined communication channels and a clear reporting structure. Within that structure each member of staff should be able to locate his or her own job description and responsibilities and their relationship with other staff members who are subordinate or superior. From a stable management base all the other components of quality assurance can be put in place. Without this the level of control necessary to ensure that all other components are effective is impossible.

Management documents should specify the role of quality assurance within the laboratory and clearly define who is responsible for each area and activity. The documents should also identify the records that should be kept of routine operations, such as equipment calibration and maintenance, thus ensuring that a logical, coherent system of record keeping is adopted. Such documentation should be brought together as a single Quality Manual which will act a reference text for the whole quality assurance programme.

In larger laboratories, proper management of QA will require the appointment of a quality assurance officer to liaise with management, to manage data archives, to conduct regular audits and reviews of the QA system and to report on any QA issues to the programme or institution manager (see also section 4.3.4). The officer is responsible for regularly inspecting all aspects of the system to ensure staff compliance, for reporting on such inspections and audits to management, and for recommending improvements. In practice, this will involve regularly checking facilities and procedures as they are performed and conducting regular audits, by tracing an analytical sample back through the system from report to sample receipt, and ensuring that all appropriate records have been kept.

The QA officer's duties must be clearly defined within the management documents in order for the role to be effective. Appointment of a quality assurance officer may be difficult in a small laboratory for financial or organisational reasons. In such cases the responsibilities for QA should be delegated to a member of staff. This may create conflicts of interest if the member of staff has to monitor the work conducted in his or her section. Senior management, who are always ultimately responsible for QA, should ensure that such conflicts are minimised.

The QA officer's role should be to monitor the system, to report on any deviations from the system, and to recommend to management any changes that might be required. In order to be able to do this effectively the QA officer should be free from management interference, while remaining responsible to management for undertaking the required duties. As a consequence it is better if a QA officer is in a middle management position, thus allowing effective communication with Laboratory Section Heads. In larger organisations QA is the responsibility of a separate section. In such a situation many of the management difficulties are minimised because the QA section is structured in a similar way to other sections of the organisation. Whichever approach is used, it is necessary that management provide adequate resources for this activity and ensure that all staff are clearly informed of their responsibilities within the QA system.

Training

It is important that all staff are adequately trained for the task they have to perform (see also section 4.4). Training must be documented in order that management and other personnel can verify that staff are competent to conduct the duties required of them. The level of training required for each procedure should also be clearly defined to ensure that staff ability and training are matched to procedural requirements. Criteria for the correct levels of training or competence for particular procedures, and job roles, are often specified by national and international agencies and, in some cases, by professional associations. In line with the principle of traceability outlined above, laboratory criteria for training standards should reflect the external criteria which apply. This should be clearly demonstrated in the documentation.

Standard Operating Procedures

Standard Operating Procedures (SOPs) provide the core of most of the day to day running of any quality assurance programme. They are the documents describing in detail every procedure conducted by the laboratory. This includes sampling, transportation, analysis, use of equipment, quality control, calibration, production of reports, etc. They are the laboratory's internal reference manual for the particular procedure to which they are dedicated and, for that reason, SOPs must document every relevant step in the procedure. Thus, anyone of the appropriate training grade should be able to apply the procedure when following the SOP. In addition, the SOP must cross reference and, where necessary, expand any other SOPs which are related to it.

Standard operating procedures often cause confusion when first introduced into a laboratory because many people feel that they are not required by virtue of either experience, availability of manuals or the use of papers from the literature or other published references. In practice, an SOP should present the procedure in a way that avoids all potential differences in interpretation, thereby avoiding subtle changes in the way methods are performed or equipment is used. Such differences can, and do, have a marked effect on accuracy and precision. An SOP should be clear, concise and contain all the relevant information to perform the procedure it describes. In addition, it should include the methods and the frequency of calibration, maintenance and quality control, as well as the remedial action to be taken in the event of malfunction or loss of control.

The SOP is the laboratory's reference to a given procedure and, therefore, it must be regularly reviewed and, if necessary, updated. Issue and availability of SOPs should be carefully controlled to ensure that they are used only by appropriately trained staff and to ensure that out of date copies of SOPs do not remain in circulation (thereby defeating their original objective). When a new or amended SOP is published in a laboratory all copies of the old SOP must be taken out of circulation. Consequently, it is necessary to have an issue log for all SOPs in the system, so that all copies of each SOP can be located.

While all procedures require SOPs, it is not necessary to generate new documents where appropriate ones exist. For example, standard analytical methods published by recognised authorities (such as the United States Environmental Protection Agency), or manufacturers manuals for specific pieces of equipment, may be adopted as SOPs if they meet the need of the laboratory and if this is properly documented and sanctioned by the management and, or, the QA officer.

Laboratory facilities

Resources are required for regular laboratory work as well as for the additional workload associated with quality assurance (see also section 4.1). It is essential that these resources, i.e. space, staff, equipment and supplies, are sufficient for the volume of work to be done. Space should be adequate and sufficient equipment should be available to allow the procedures performed in the laboratory to be conducted efficiently. The environment in which the work is conducted must be well controlled. It should be clean and tidy, have adequate space in which to work without risk to personnel or to the analytical sample, and there should be sufficient storage space for glassware, chemicals, samples and consumables. It is also essential that there are adequate numbers of appropriately trained staff available to undertake all the required tasks. Management policy should ensure that these facilities are available before any laboratory work is commenced. In practice, anything that restricts the efficient running of the laboratory would be a cause for concern, and should lead to noncompliance with the quality assurance system.

Equipment maintenance and calibration

All equipment must be maintained on a regular basis, consistent with the documented criteria of the laboratory and normally accepted codes of practice. The laboratory must apply standards which are well within the limits normally established and recommended for the care of the particular piece of equipment. This should be checked by the quality assurance officer, and be corrected if inappropriate. These principles apply to general laboratory equipment such as glassware as well as to sophisticated analytical instruments. The care and cleaning of this type of equipment is extremely important to ensure quality and should not be overlooked. Frequent checks on the reliability of equipment must also be performed. This includes calibration checks on all relevant equipment, such as balances, pipettes, etc. The frequency of these checks will depend on the stability of the equipment in question. In

some instances calibration checks may be done as a part of normal maintenance. Again, the criteria for checking should be based on established acceptable practice.

Equipment calibration and maintenance records should be kept for all equipment, thus allowing the repair status of each piece of apparatus to be monitored. This reduces the likelihood that malfunctioning equipment will be used for analysis (thereby leading to poor analytical data), and allows any problems with equipment to be more quickly diagnosed and corrected.

Sampling

Procedures for sampling operations should be carefully documented. In particular, clear details should be given for precautions to be taken while sampling and the sampling strategies to be employed. Careful documentation during sampling is required so that all relevant information on the nature of the sample (when it was taken, where it was taken and under what conditions it was taken) are clearly recorded on site at the time of sampling by the person conducting the sampling. This is necessary because variations in sampling procedures can have a marked effect on the results of analysis. It is very difficult to quantify these effects and, therefore, the most practical way to control this stage of the analytical process is to document sampling conditions as fully as possible. It is very important to ensure that all relevant information is made available to the analyst. Quality assurance of sampling can be achieved in the following ways:

- Strictly adhere to standard operating procedures for sampling.
- Ensure all equipment is clean and in working order.
- Record all conditions which applied during sampling.
- Take strict precautions to avoid contamination.

Following those simple procedures should help to ensure that the quality of samples matches the quality of analysis.

Sample receipt, storage and disposal

Almost as important as proper sampling, is the proper storage of samples prior to analysis. It is important to ensure that the passage of a sample through the laboratory's analytical systems is fully documented, and corresponds to the practices laid down in the relevant SOPs. Equally important are the arrangements for disposal of samples. This should be done when the sample exceeds its stable storage time. With some forms of analysis which are required for legal or for regulatory reasons there may be a requirement to store a suitable aliquot of a sample safely, for a given time, to allow for re-examination should this be considered necessary. The systems in place should take these factors into account.

Procedures for sample handling should ensure that the sample is not compromised. The sample should be logged in and stored in such a way as to minimise its deterioration. The condition of each sample and its storage location should be recorded and, where appropriate, the analyses to which it is to be subjected should also be recorded. Sub-sampling, splitting of the sample to allow for different storage conditions, or sample pretreatment to increase stability must be recorded and the samples clearly and uniquely marked to ensure that no confusion exists about the source and identity of any sample.

Reporting of results

The final products of the laboratory are the data that it reports. It, therefore, follows that the efforts of quality assurance are directed towards seeing that these data are suitable for use

in an assessment. This includes the final stage of reporting and interpreting the results which have been generated.

The first stage in this process is examination of the data to determine whether the results are fit to report. Data should be examined at many stages in the quality assurance system and no data should be reported from assays that are out of control (see sections 9.2 and 9.3 below). However, once data are ready to report it is important to ensure that they are reported accurately and in a manner that facilitates interpretation. Consequently, it is often necessary to include information which may have a bearing on interpretation, such as that related to the nature of the sample or the analytical procedure which was applied. All such information must be available to the reporting analyst. Reports must be prepared according to an agreed procedure and they must accurately reflect the findings of the study. They should include reference to all calibration and quality control data and to any problems that were encountered during the study (e.g. rejected analytical batches, loss of sample, etc.). All data included should have been comprehensively checked by an experienced analyst.

Many laboratories have a system which requires checking of data records and countersigning of analytical reports to act as a safeguard against erroneous or misleading data leaving the laboratory. This type of system is only effective when conscientiously applied. Automatic signing of reports with minimal checking is all too common and should be avoided.

9.1.2 Implementation of quality assurance

The ultimate objective of a QA programme is to ensure that the laboratory functions efficiently and effectively. The benefits in terms of increased reliability of results has already been mentioned. A number of other benefits are also evident. The clear assignment of duties and adherence to written and agreed protocols ensure that staff clearly understand their responsibilities. This allows lines of communication to be clearly identified, making staff management easier. Calibration, maintenance and record keeping, in general, assist laboratory staff to identify developing problems with equipment earlier than would otherwise be the case. In addition, the sources of analytical problems can be more rapidly identified leading to their rapid solution.

The implementation of a QA programme is, in principle, very simple and involves putting in place the components listed above. In practice, this requires a considerable amount of effort and commitment from all staff and takes a long time to set up. A clear plan of action must be formulated and clear objectives and time scales identified for each stage. Staff who are involved with the implementation should be well briefed on what is required of them. It is also wise to ask for the opinion of staff on the proposed QA system, as this ensures that impractical procedures are avoided.

One logical way to tackle the task is first to write the Quality Manual, then to put in place documentation such as SOPs and laboratory records, then to test run the system for a limited period (i.e. three to six months) and then, finally, to conduct a detailed review which identifies successes and failures within the system. This is best done by inspection of key areas such as laboratory records and by conducting audits. An efficient auditing system is to pick data at random and then trace the documentation pertaining to those data back to sampling and sample receipt. Any breaks in the traceability of the data will become apparent as a gap in the linking documentation. Deficiencies that become apparent should be corrected at this stage. The review should also seek to identify and to remove any inefficient or bureaucratic systems which serve no useful purpose.

A common method of implementing a QA programme is to apply for accreditation. Accreditation is the implementation of a QA programme in conformity with a recognised QA system, such as Good Laboratory Practice (GLP) or the National Measurement Accreditation System (NAMAS). Quality Assurance is often linked with accreditation although this does not have to be the case. While implementing QA in this way allows the programme to be independently assessed against an agreed standard, it can be costly. Alternatively, QA can be implemented by reference to international standards such as ISO 9000 without necessarily going to the expense of accreditation. However, commercial, legal or political considerations may require that formal accreditation is adopted by the laboratory because this formally records compliance with a recognised QA system (i.e. compliance that has been validated by an official third party).

9.1.3 Checking compliance

In order to maintain the quality assurance system it is necessary to check periodically each area of the laboratory for compliance with the QA system. This involves auditing of the component parts to assess whether they continue to meet the original criteria. As with any other aspect of quality assurance the procedures to be adopted for checking compliance should be formally documented. Reports on all audits should be made available to management, and to the individuals responsible for the work concerned. Deviations from required standards must be corrected immediately. As with any check of such a complicated structure, the audit must be extensive and systematic in order to test every part of the system. Such audits are also better done in a way that makes them hard to predict, thereby minimising abuse of the system.

The audit must also be independent, hence the need for a quality assurance officer who reports directly to the highest level of management. Regular comprehensive audit often requires a large input of resources in order to be effective.

9.2 Internal quality control

Internal quality control (IQC) consists of the operational techniques used by the laboratory staff for continuous assessment of the quality of the results of individual analytical procedures. The focus is principally on monitoring precision but also, to a lesser degree, on accuracy. It is necessarily part of the wider quality assurance programme, but differs from it by virtue of the emphasis placed on quantifying precision and accuracy. Whereas quality assurance strives to achieve quality by regulating procedures using what are essentially management techniques, IQC focuses on the individual method and tests its performance against mathematically derived quality criteria.

9.2.1 Choice of analytical method

A variety of different analytical methods are usually available for determining the concentration of any variable in a water sample. The choice of method is critical for ensuring that the results of the analysis meet the laboratory's requirements, because different methods have different precisions and sensitivities and are subject to different potential interferences. Consideration must be given to these parameters before a method is chosen, although the technical literature does not always provide adequate information. Nevertheless, a number of standard methods which have procedures described in sufficient detail are available for most of the analytical determinations involved in water quality monitoring. These standard methods frequently include extensive validation data that allows them to be easily evaluated and many are sanctioned by appropriate international or national organisations. It is not recommended, however, that a laboratory purchases equipment and reagents and starts to follow the procedure of a standard method without considering

whether the method meets the programme requirements. The performance of a method can be unpredictably affected by many factors which can lead to serious problems. Before any analytical method is put into routine use it is essential that it is properly validated. The following experiments should be performed as a minimum programme of validation.

- *Linearity:* The calibration point should be determined and a linear response curve demonstrated if possible. If the calibrants do not show a linear response, linear transformation of the data should be investigated.

- *Limit of Detection:* The lowest concentration of the variable that can be distinguished from zero with 95 per cent confidence should be determined.

- *Precision:* Within day and between day coefficients of variation should be performed at three concentration levels.

- *Accuracy:* Analysis of reference materials with known concentrations of the variable (i.e. CRMs, see below) or comparison analyses with existing methods in other laboratories where possible.

9.2.2 Validity checking

After a method has been validated, found to be suitable and introduced into routine use in the laboratory, it is necessary to ensure that it continues to produce satisfactory results. Validity checks should be made on every batch of samples or at frequent, regular intervals if batches are large or if testing is continuous. Validity checking is an extension of the checks carried out before the method was selected and is intended to confirm regularly the conclusions reached at that time.

Calibration check

If a calibration curve is being used, standard solutions should be analysed from time to time within the required range of concentration. The ideal calibration curve is linear within its most useful range, with a regression coefficient of 0.99 or greater. The response of the measuring equipment to the concentration of the variable in a standard solution (in terms of absorbance or some other physical parameter) should be recorded when it is expected that this parameter will be comparable from assay to assay. In addition, the deviation of individual calibration points from the line of best fit can be used to assess the precision of the calibration, which should be within the mean precision limits for the method.

Use of blanks

Method blanks and, where possible, field blanks should be analysed with each batch of samples. A method blank consists of reagent water, usually double-distilled water. A field blank is reagent water that has been bottled in the laboratory, shipped with sample bottles to the sampling site, processed and preserved as a routine sample and returned with the routine samples to the laboratory for analysis. The analysis of a blank should not yield a value higher than that allowed by the acceptance criteria. This procedure checks interference and the limit of detection of the assay.

Recovery checking

A specimen spiked with a known amount of the variable should be tested in each batch and the closeness of fit to the expected value calculated. In most cases this procedure provides a

check on accuracy but, in assays where a variable is extracted from the original matrix (such as in many sample clean-up procedures used prior to chromatographic analysis), it can be used to monitor the extraction step. It is important that the matrix of the spiked specimen matches the real sample matrix as nearly as possible. Many laboratories use real samples with low natural values of the variable for this purpose, spiking them with known amounts of the variable and including both the spiked and natural samples in the same assay batch.

9.2.3 Precision and accuracy checks

Precision and accuracy checks are an extension of the validity checking described above. They have been dealt with separately because these checks allow the quality of the assay to be monitored over time using techniques such as control charting that will be described below. The validity checks described in the previous section only allow acceptance or rejection of the assay data to be decided. Precision and accuracy checking should allow slow deterioration of data quality to be identified and corrected before data have to be rejected. This results in increased efficiency and reduced costs for the laboratory.

Control by duplicate analysis

Use of duplicate analysis as a method of precision checking has two distinct advantages:

- quality control materials are matrix-matched, and
- the materials are readily available at no extra cost.

Since the samples are analysed using the same method, equipment and reagents, the same bias should affect all results. Consequently, duplicate analyses are only useful for checking precision; they provide no indication of the accuracy of the analyses. Results from duplicate analyses can be used to calculate a relative range value, *R*, by using the equation:

$$R = \frac{(X_1 - X_2)}{(X_1 + X_2)/2}$$

where X_1 and X_2 are the duplicate results from an individual sample and X_1-X_2 is the absolute difference between X_1 and X_2. These values are then compared with the mean relative range values previously calculated for the assay during validation. The simplest method of assessment is to use the upper concentration limit (UCL), where UCL = 3.27 × mean *R* value. When any value is greater than the UCL, the analytical procedure is out of control. This method, although statistically valid, provides no indication of deteriorating precision. A better and more sophisticated approach is to use acceptance criteria based on warning and action limits (as described below).

Precision control using pooled reference material

This method has the advantage of providing some monitoring of accuracy but is a viable control only if the material to be used will be stable in storage for a sufficiently long period of time. The reference material is normally prepared by taking previously analysed samples with known concentrations of the variable under investigation, mixing them and aliquoting the resultant pool. The aliquots are then stored in readiness for analysis. A small sample of the aliquots is analysed to determine the mean concentration of the variable, and the standard deviation and the coefficient of variance at that concentration level. Data may be used only if they come from analyses that are in control. This requires that the original pool materials must have been prepared during method validation, and that new materials must be prepared before the old ones are finished.

A typical precision control exercise would involve the analysis of four aliquots from each pool in each of five assays, thus obtaining 20 results. It is important that the material from the pool be analysed at several different times with different batches because between-batch variance is always slightly greater than within-batch variance.

Once 20 or more analyses have been made on this pool of material, the mean and standard deviations of the results are calculated. Any result that is more than three standard deviations from the mean is discarded and both of the statistics are recalculated. The mean is the “target” value and, ideally, will be a close approximation of the true concentration of the variable in the reference material. The mean and standard deviation become the basis of the acceptance criteria for the assay method and may be used to draw up control charts.

At least three separate reference materials with different mean values of variable concentration should be in use at any one time in order to provide control of the analytical method across a range of concentrations. If precision is checked at only one concentration of the variable, it is impossible to detect whether precision is deteriorating at other concentrations. Use of several reference materials also allows their preparation to be staggered so that they become exhausted at different times. This assures greater continuity of control because two or more old pools will still be in use during the first few assays of a new reference material.

Although the monitoring of accuracy by assessing deviation from the reference material mean (target value) is possible, care must be taken because the target value is only an approximation, albeit a good one, of the true value. As reference materials become exhausted and new ones are made, there will be a slow deterioration in accuracy. Accuracy can be safeguarded by regular participation in external quality control exercises and by the regular use of certified reference materials.

Accuracy control using certified reference materials

Certified reference materials (CRMs) are matrix-matched materials with assigned target values and assigned ranges for each variable, reliably determined from data obtained by repeated analysis. Target and range values may be generated from data produced by several laboratories using different analytical methods or calculated from data obtained by the use of one analytical method (usually a reference method). Consequently, there may be bias in the target value. The target values assigned to each variable in the matrix in certified reference materials are generally very close to the true value. For some variables, however, there is an appreciable difference in bias between different analytical methods and this may lead to wide assigned ranges. When a laboratory is not using one of the reference methods the “all method” range may be so wide that it is practically meaningless. Certified reference materials are also only practical for variables that are stable in long-term storage.

Since CRMs are prepared and checked under carefully controlled conditions, they are costly to produce and correspondingly expensive to purchase. Some authorities advocate the routine use of CRMs as precision control materials, rather like the pooled materials prepared in-house as described above, but it is more cost effective to use them for the periodic checking of accuracy, in combination with a rigorous IQC programme.

9.2.4 Use of control charts

Control charts have been used for recording internal quality control data for many years and are one of the most durable ways of using quality control data. The principle of control charts is that IQC data can be graphically plotted so that they can be readily compared and

interpreted. Consequently, a control chart must be easy to use, easy to understand, and easy to act upon.

The Shewhart chart is the most widely used control chart. It is a graph with time (or assay batch) on the x-axis and the concentration of the variable in the reference material on the y-axis. Target, warning and action lines are marked parallel to the x-axis. Data obtained from precision control using reference materials (as described above) are usually plotted on a Shewhart chart. In this application the target line is at the mean concentration of the variable for that specific pool of material, warning lines are placed at two standard deviations to either side of the target line. Provided the distribution is normal, 95 per cent of results from assays in control will fall between the two warning lines. Action lines are normally placed at three standard deviations to either side of the target line and 99 per cent of normally distributed results should be between the action lines. Examples of typical Shewhart charts are shown in Figure 9.1.

In the regular day-to-day use of a Shewhart chart, an aliquot from an appropriate reference material is analysed with every batch of samples and the measured concentration of the variable in the aliquot is plotted on the chart. Normally, no more than 1 in 20 consecutive results should fall outside the warning lines. If this frequency is exceeded, or if a result falls outside the action lines, the method is out of control.

The scatter of the assay results for the reference material around the target line provides an indication of the precision of the method, while the mean of the assay results relative to the target value indicates whether there is any bias (consistent deviation) in the results.

The following general rules give guidance on the action to be taken should the analysis on one or more of the control specimens yield a result that is outside the warning or action lines on the chart.

A single result outside the warning lines should lead to careful review of data from that analytical batch and two or three subsequent batches.

Results outside the warning lines more frequently than once every 20 consecutive analyses of control specimens should prompt detailed checking of the analytical method and rejection of the assay data.

A result outside the action limits should prompt detailed checking of the analytical method and rejection of the assay data.

9.2.5 Summary of an internal quality control programme

A summary of the internal quality control programme recommended by the GEMS/Water programme is given below. This programme offers a simple but effective introduction to IQC and is described in more detail in the *GEMS/WATER Operational Guide*.

For each variable:

1. Analyse five standard solutions at six different known concentrations covering the working range to develop a calibration curve or, when a calibration curve already exists, analyse two standard solutions at different known concentrations covering the working range to validate the existing calibration curve.

2. Analyse one method blank per set of 20 samples.

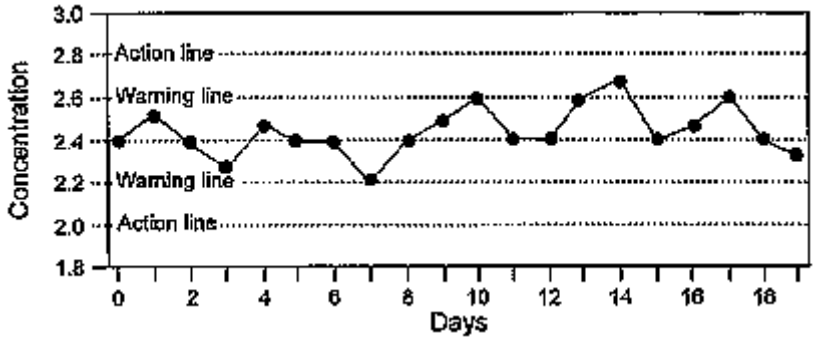
3. Analyse one field blank per set of samples.

4. Analyse one duplicate of a sample chosen at random from each set of up to 20 samples. Interpret using the UCL method.

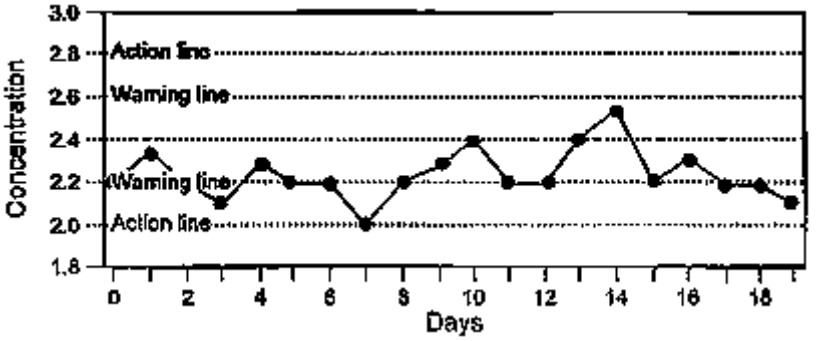
5. Analyse one specimen that has been spiked with a known amount of the variable as a recovery check. This specimen should have a matrix similar to those of the samples being processed.

Figure 9.1 Examples of typical Shewhart charts

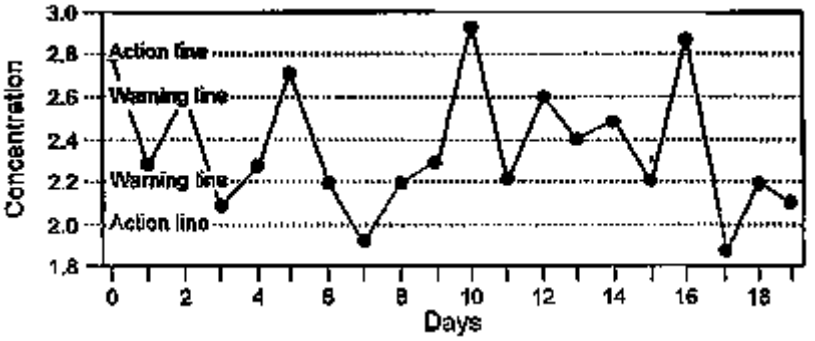
Assay in control



Poor accuracy



Poor precision



9.2.6 Remedial action

If any of the quality control procedures indicates that a method is out of control or that a problem exists, corrective action must be taken. The main checks to make are calculations and records, standard solutions, reagents, equipment and quality control materials (Table 9.2).

9.3 External quality control

External quality control (EQC) is a way of establishing the accuracy of analytical methods and procedures by comparing the results of analyses made in one laboratory with the results obtained by others conducting the same analysis on the same material. This is usually accomplished by one laboratory, the reference laboratory, sending out sets of specimens with known and unknown concentrations of variables to all of the participating laboratories. Each participant analyses the specimens for the specified variables and reports the results to the reference laboratory.

The results from all participating laboratories are collated by the organisers of the EQC programme and then subjected to detailed statistical analysis. A report to each laboratory is generated, giving a target value for the reference sample or samples (usually consensus mean or median), a histogram illustrating distribution of results for each material, and an individual performance score relating the individual laboratory results to the target value. The calculations for performance indicators are often quite complex because multiple specimens have to be considered and the method variance varies with the concentration of the variable. However, the general principle of providing a method of performance comparison remains the same in all EQC exercises. An example of an external quality control report is shown in Figure 9.2.

Table 9.2 Necessary checks to be carried out when a problem is detected with an analytical method

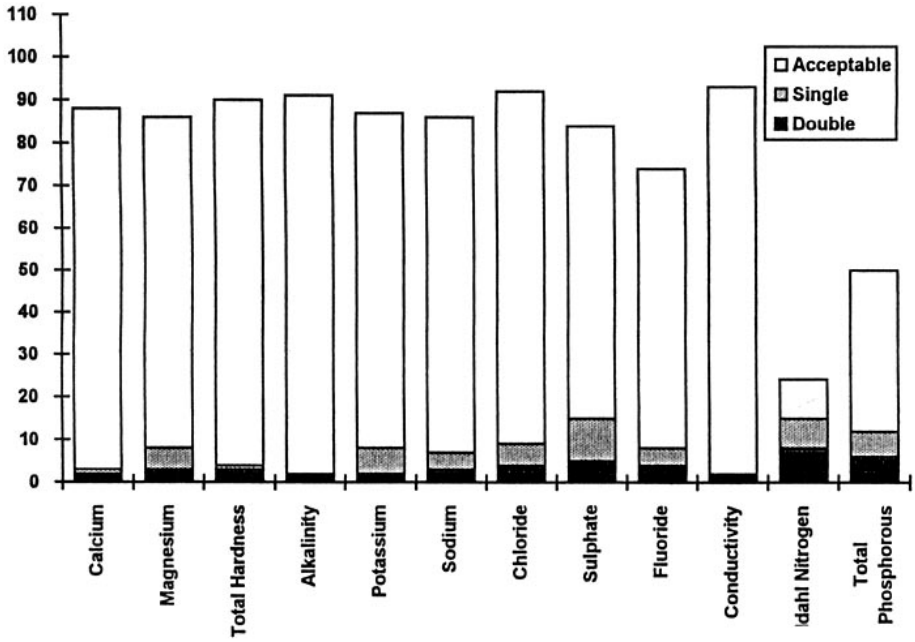
Item	Checks
Calculations and records	Check calculations for a transposition of digits or arithmetic errors. Confirm that results have been recorded in the proper units and that any transfer of data from one record to another has been made correctly.
Standard solutions	Check the standard solutions that are used for calibrating equipment. Old solutions may have deteriorated and errors may have occurred in the preparation of new ones. Check on storage conditions, the age of solutions and their expected shelf-life.
Reagents	Check whether old reagents have deteriorated. Check fresh reagents to ensure that they have been properly prepared. Check the storage conditions of reagents, especially those that must be stored away from the light or at a controlled temperature. Check the shelf-life of reagents, discarding any that are outdated or have been improperly stored.
Equipment	Check calibration records and maintenance records for all reagent dispensers and measuring equipment used for the analysis of the variable where the method is out of control. Items such as automatic pipettes, balances and spectrophotometers should be checked and recalibrated if appropriate. Ascertain that equipment is being properly used.
Quality control materials	Check on the storage conditions of quality control materials, ensuring that bottles are tightly sealed and that they are not being subjected to extremes of temperature. Run analyses on several aliquots to determine whether the concentration of the variable remains within two standard deviations of the target value and close to the mean of the last 20 determinations.

External quality control reports should clearly indicate whether performance is satisfactory or not. If it is not satisfactory, two general actions must be taken. First, the analysis at fault must be examined to determine the cause of poor performance. Once found, the problem must be corrected. Secondly, the internal quality control programme that allowed the deterioration to progress unchecked must be closely examined to establish where inadequacies exist. Any inadequacies must be corrected.

Number of laboratories producing acceptable, flagged and double flagged results for Group 1 Hard Water

Group 1 Hard Water	Total	Acceptable	Single Flagged	Double Flagged
Calcium	88	85	1	2
Magnesium	86	78	5	3
Total Hardness	90	86	1	3
Alkalinity	91	89	0	2
Potassium	87	79	6	2
Sodium	86	79	4	3
Chloride	92	83	5	4
Sulphate	84	69	10	5
Fluoride	74	66	4	4
Conductivity	93	91	0	2
Kjeldahl Nitrogen	24	9	7	8
Total Phosphorous	50	38	6	6

Figure 9.2 Example of an external quality control report. Supplied by Dr. Ian Taylor of Aquacheck, WRc, UK.



The general objective of EQC is to assess the accuracy of analytical results measured in participating laboratories and to improve inter-laboratory comparability. For an individual laboratory, participation in an EQC exercise is the only way to ensure that accuracy is independently monitored. Wherever possible, laboratories should participate in EQC programmes for each variable that is routinely analysed. This is only worthwhile where internal quality control is also part of a laboratory's normal procedures. Participation in relevant EQC programmes, and maintenance of adequate performance in those programmes, is often a requirement for laboratory accreditation (see section 9.1.2).

The organisation of an EQC exercise requires substantial resources. Large quantities of stable reference materials must be prepared, these materials must be transported to the participating laboratories, data must be analysed and detailed reports on performance must be prepared. Consequently, these exercises are usually managed and run by large organisations which have adequate resources. Participating laboratories are usually charged for the service provided.

Distribution	89	Overall mean:	9.46
Group 1 - Hard water - Sodium		Reference value:	9.46 - Mean of a
Units	- $mgNa.l^{-1}$	Relative standard deviation:	7.10%
Number of laboratories reporting:	86	Range of reported concentrations:	1.46 to 16.05
		Lower and upper flagging limits	7.85 to 11.07

	Z-Score	Laboratory numbers
Double flagged	>2.00	(153) (185)
Single flagged	1.80 to 2.00	
	1.60 to 1.80	
	1.40 to 1.60	
	1.20 to 1.40	10 54
	1.00 to 1.20	
	0.80 to 1.00	**284**
	0.60 to 0.80	**359**
	0.40 to 0.60	**112 61 419 56**
	0.20 to 0.40	**65 25 34 55 50 464 45 8 140 286 <106 414 421 416 182 46 478**
	00 to 0.20	**165 133 471 33 119 193 44 457 108 109 399 128 358 36 424 200 283 178**
	0.00 to -0.20	**101 134 35 60 143 455 332 96 214 164 197 21 395 272 23 63**
	-0.20 to -0.40	**466 355 9 47 472 113 418 213 275 216 177 154 422 202**
	-0.40 to	**100 120 42 62 222**

	-0.60		
	-0.60 to -0.80	**38**	**339**
	-0.80 to -1.00	**141**	
Single flagged	-1.00 to - 1.20	398	477
	-1.20 to -1.40		
	-1.40 to -1.60		
	-1.60 to -1.80		
	-1.80 to -2.00		
Double Flagged	<-2.00	(129)	

Laboratories number enclosed in brackets indicates that the lab's results were flagged as outliers

9.4 Source literature and further reading

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