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Preface

This report has been prepared by J.G. Timmerman (RIZA, The Netherlands). The annex on laboratory analyses has been prepared by M.J. Gardner and J.E. Ravenscroft (WRc, United Kingdom). Contributions to the sections on laboratory analyses and data analyses have been made by E. Poroszlai (MERP, Hungary) and J.F.N. Maaskant (RIZA, The Netherlands). The guidance-committee on this report comprised of W.P. Cofino (Institute for Environmental Studies, Vrije Universiteit, The Netherlands), P. Stoks (Water Transport Company Rhine-Kennemerland, WRK, The Netherlands), W.A.J. de Waal (RIKZ, The Netherlands), M. Adriaanse, J.P. Baarsma and L.J. Gilde (RIZA, The Netherlands).

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1. Introduction

1.1 General

The Convention on the Protection and Use of Transboundary Watercourses and International Lakes (hereinafter referred to as the Convention) was drawn up under the auspices the Economic Commission for Europe and adopted at Helsinki on 17 March 1992. The Convention was signed by 25 countries and by the European Community before the period of signature closed on 18 September 1992. It will enter into force 90 days after the date of deposit of the sixteenth instrument of ratification, acceptance, approval or accession. By the time of writing of this report, thirteen countries and the European Community had deposited their relevant instruments of ratification with the United Nations Secretary-General.

To comply with the obligations under the Helsinki Convention, the Parties will, *inter alia*, have to set emission limits for discharges of hazardous substances from point sources based on the best available technology. In addition, they will have to apply at least biological treatment or equivalent processes to municipal waste water. They shall also issue authorizations for the discharge of waste water and monitor compliance. Moreover, they have to adopt water quality criteria and define water quality objectives. To reduce the input of nutrients and hazardous substances from diffuse sources, in particular from agriculture, they shall develop and implement best environmental practices. Furthermore, environmental impact assessment procedures and the ecosystem approach shall be used to prevent any adverse impact on transboundary waters.

Consequently, the Helsinki Convention addresses such issues as monitoring, assessment, warning and alarm systems, and exchange and presentation of information. For example, the Parties bordering the same transboundary waters will have to set up joint or coordinated systems for monitoring and assessment of the conditions of transboundary waters, and set up coordinated or joint communication, warning and alarm systems. The clear objective of monitoring and assessment systems such as the Helsinki Convention is to prove that changes in the conditions of transboundary waters caused by human activity do not lead to significant adverse effects on flora and fauna, human health and safety, soil, air climate, landscape and historic monuments or other physical structures or the interaction among these factors.

The establishment of a system to furnish proof that these objectives are met is a challenging task. Moreover, monitoring compliance with the provisions of the Helsinki Convention demands reliable information on waters and factors influencing water quality and quantity. There is, for instance, a need for information related to in-stream quality, such as conditions of waters (water quantity and quality), aquatic and riparian flora and fauna, and sediment. Information related to extreme conditions in waters, caused by accidents, floods, drought or ice cover, is also needed. Emission sources also have to be monitored to obtain information on the concentration of pollutants in effluents, and to carry out pollution-load assessments. Consequently, information on monitoring of surface waters and significant

emission sources in catchment areas of transboundary waters is required. This includes information on the legal basis of emission monitoring, selection of variables, selection of sampling sites and frequencies and documentation and reporting of the results (both to authorities and to the public at large). Information on monitoring for early warning purposes, including biological warning systems, is required as well.

Following the adoption of the Convention, the Senior Advisers to ECE Governments on Environmental and Water Problems (now known as the ECE Committee on Environmental Policy) entrusted its Working Party on Water Problems with the implementation of the Convention, pending its entry into force. To implement the work plan, the Working Party has set up several task forces and groups of rapporteurs. The topics addressed are:

1. point sources;
2. diffuse sources;
3. legal and administrative aspects;
4. sustainable water management;
5. monitoring and assessment.

The present report has been prepared within the context of the Task Force on monitoring and assessment, which was led by the Netherlands.

This Task Force has been charged with the preparation of draft guidelines to ECE Governments on monitoring and assessment. During the first meeting of the Task Force, a phased approach towards this goal has been approved. During the first phase, the focus will be on 'running-water' transboundary water courses (i.e. rivers, streams, canals), while in later phases, the focus will be on lakes, estuaries and groundwaters.

The present report is one in a series of 5 background documents to be used for the drafting of guidelines on monitoring and assessment of running-water transboundary water courses. These reports deal with the following themes:

1. inventory of transboundary rivers and international lakes in Europe;
2. inventory of current monitoring and assessment practices in UN/ECE countries;
3. preparation of draft guidelines for biological assessment of rivers;
4. preparation of draft guidelines for quality assurance;
5. inventory of State of the Art practices in monitoring and assessment.

The present report is the result of the activities under item number 4: Quality Assurance.

1.2 Outline of the report

This report will give an overview of the subjects that have to be dealt with in quality assurance in monitoring and assessment. Chapter 1 gives general information on quality assurance and describes the different elements in monitoring and assessment. Chapter 2 gives an outline of the quality assurance aspects of the distinguished monitoring and assessment elements. Chapter 3 will give a short overview of the report and gives recommendations. An overview of analytical quality control and quality management in water laboratories is given in the Annex.

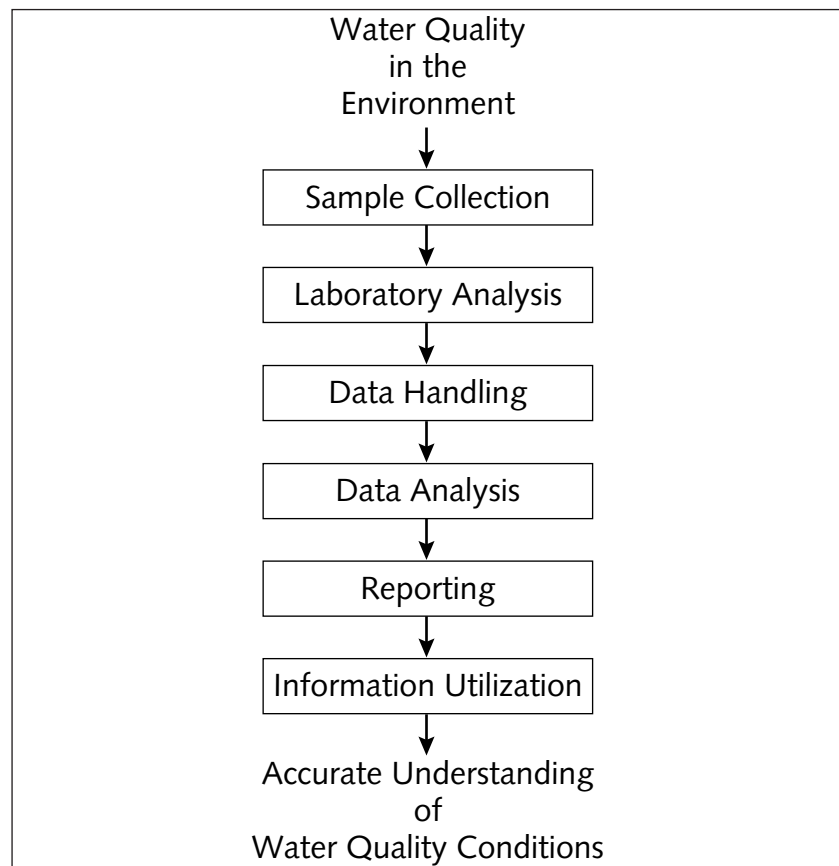
2. Quality management

2.1 General

The major challenge in monitoring and assessment is making the information obtained fit the information needed. The design of a monitoring system starts with defining the information needed to make decisions on water management; the monitoring objective strongly determines the kind of data to be collected and the kind of information to be extracted from the data [Buishand and Hooghart, 1986]. This information becomes the information “product” of the entire monitoring system [Ward, 1994b]. Only by defining the information needed, can the designer of the monitoring system have confidence that the information system has a good chance of being accountable to supporting water management decision making.

A way to ensure that the information needs as specified by decision makers will be met by the monitoring system and the information obtained from it, is by managing and assuring the quality of the monitoring system. In this chapter, first an overview will be given on the different aspects that have to be accounted for in carrying out monitoring and assessment (section 2.2). The next section is on the principles of quality management and quality assurance (section 2.3). The last section will deal with quality assurance in monitoring and assessment (section 2.4).

Figure 1
Flow of information through a monitoring system [Ward, 1994a].

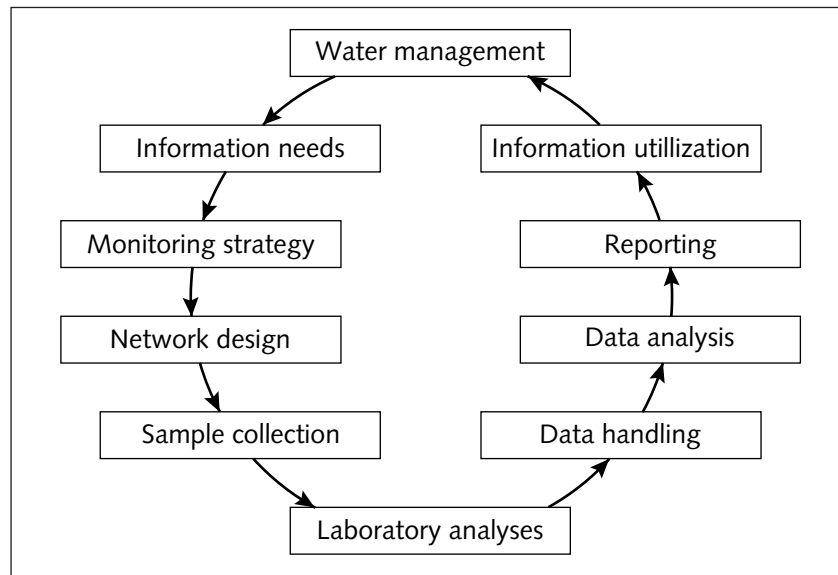


2.2 Activities in monitoring and assessment

Going from information required to information obtained, different steps can be distinguished. Ward [1994a] defines the information “product” between ‘Water Quality in the Environment’ and the ‘Accurate Understanding of Water Quality Conditions’ as a monitoring system with six steps: ‘Sample Collection’, ‘Laboratory Analysis’, ‘Data Handling’, ‘Data Analysis’, ‘Reporting’ and ‘Information Utilization’ (figure 1).

Adriaanse and Lindgaard-Jørgensen [1995] define additional elements in the information system; in ‘Information needs’, design criteria for ‘Monitoring strategy’ and ‘Network design’ are set. After the network design, sample collection, laboratory analyses, etc. can be carried out. The elements are arranged in a circle (figure 2), signifying that each element of the monitoring information system can be derived and designed from the former one. This chain of activities is changing with changes in the information needs. The last element, ‘Information utilization’, is input to the ‘Water management’ of the water system, which may lead to changes in the information need, leading to reentering the cycle by specification of the altered information need.

.....
Figuur 2
Chain of activities in monitoring and assessment
[Adriaanse & Lindgaard-Jørgensen, 1995].



In going through the circle, each element imposes conditions on the type and quality of information flowing from the previous element. This implies that in each element acceptance criteria for the results of the previous element have to be established [Cofino, 1993]. Also, each element is subject to changes and enhancements over time, reflecting changes in knowledge or goals, or improvements in methods and instrumentation. Thus, each element must have defined quality assurance activities to monitor these changes [Groot and Villars, 1995]. This means that in defining a monitoring system, the various elements have to be considered to specify all the conditions. The information is obtained as the result of a chain of activities, the strength of this chain being determined by its weakest link [Stroomberg *et al.*, 1995].

The content and level of detail of the required information is depending upon the political importance of an issue, or, connected with this, the level

of control of the problem. At first there is an awareness of a problem. This awareness results in the formulation of measures to be taken. These measures are implemented, and after some time there is a certain level of control. This is called the 'policy life cycle' [Winsemius, 1986]. Witmer [1994] defines 5 phases:

0. Scientific recognition, in which the awareness of a problem arises. The information need is focused on the scale of the problem.
1. Political recognition, in which a decision is made to put effort into reducing the problem. A policy is delineated with short-term and long-term objectives, possible measures are outlined and legislation is adopted. The impacts of the problem and the measures to be taken are the focus of the information need.
2. Elaboration, in which government institutions work out the new policy and legislation for the area they control, and objectives are translated into tasks for target groups involved. Surveys and monitoring programmes are started to determine the actual situation.
3. Implementation, in which plans and decisions are converted into action, legal and financial instruments are applied, target groups are informed and convinced, projects are organized and carried out. In this phase, it becomes apparent whether or not the policy objectives and proposed measures are realistic and can be achieved. Information on the effectiveness of the measures is gathered.
4. Evaluation, in which the policy is reviewed based on relevant information and, if necessary, adjusted. The problem is incorporated in the general information need or additional information is needed. Eventually, the problem can no longer be relevant, making information obsolete.

The phases 1 to 4 make up the policy life cycle. After the evaluation the policy objectives can be adjusted and a new cycle starts.

2.3 Quality assurance

From the definition of quality (see Text 1) it can be derived that quality can only be achieved (and measured) when the requirements of a product are clear. The first (and usually most difficult) thing to do is to explicitly state, in detail, the requirements of a product (or service). This will be the touchstone in quality assurance.

The goal of quality assurance is ensuring that a product complies with the requirements, which in turn should reflect the intended objective (Text 2). This means that in quality assurance, consideration must be given to the intended use of a product. There are *general features* of a product in relation to the general use of the product, e.g. a chair is used to sit in. Then there are the *specific features* related to *specific use* of a product, e.g. a desk chair has to be adjustable.

This brings us to the different views to a product: the *intrinsic features* of a product and the purpose of the product. The *intrinsic features* are related to expectations at one side and regulations at the other side. A product is expected to fulfil some kind of general use, e.g. a car is expected to transport people from one place to another. Next to this, a product can be subject to regulations of some kind; e.g. a car has to comply with various safety measures. Usually, e.g. when buying a car, these kinds of expectations and regulations are not made explicit. This will be referred to here as the 'intrinsic quality' of a product.

Text 1

Definition of quality [ISO, 1986].

Quality:

The totality of features and characteristics of a product or service that bear on its ability to satisfy stated or implied needs.

NOTES:

- 1 In a contractual environment, needs are specified, whereas in other environments, implied needs should be identified and defined.
- 2 In many instances, needs can change with time; this implies periodic revision of specifications.
- 3 Needs are usually translated into features and characteristics with specified criteria. Needs may include aspects of usability, safety, availability, reliability, maintainability, economics and environment.
- 4 The term "quality" is not used to express a degree of excellence in a comparative sense nor is it used in a quantitative sense for technical evaluations. In these cases a qualifying adjective shall be used. For example, use can be made of the following terms:
 - a) "relative quality" where products or services are ranked on a relative basis in the "degree of excellence" or "comparative" sense;
 - b) "quality level" and "quality measure" where precise technical evaluations are carried out in a "quantitative sense".
- 5 Product or service quality is influenced by many stages of interactive activities, such as design, production and service operation and maintenance.
- 6 The economic achievement of satisfactory quality involves all stages of the quality loop (quality spiral) as a whole. The contributions to quality of the various stages within the quality loop (quality spiral) are sometimes identified separately for emphasis. Two examples: "quality attributable to design", "quality attributable to implementation".
- 7 In some reference sources, quality is referred to as "fitness for use" or "fitness for purpose" or "customer satisfaction" or "conformance to the requirements". Since these represent only certain facets of quality, fuller explanations are usually required that eventually lead to the concept defined above.

The *purpose* of the product is related to the specific use of the product; e.g. a car has to be used transporting a family with six children and two dogs or maybe off-the-road driving or racing. All these different uses put different requirements on the product. This will be referred to here as the 'user-requirements'. Also, a certain use can imply certain regulation, e.g. there can be legislation on the requirements of racing cars.

The two aspects of a product have to be applied through the process in which the product is manufactured. The intrinsic quality is input to the process through standards and procedures and maybe specific tools. The user-requirements are also input to the process, but require tailor-making activities. In quality assurance it is important that a procedure is defined to implement the user-requirements in the product.

In the elaboration of a monitoring network, the ISO-standards for sample collection and laboratory analyses can be an example of the intrinsic quality. After choosing the variables, locations, frequencies, etc. (reflecting the purpose of the product and the requirements of the users, i.e. the decision-makers), the use of standard methods, if applicable, should be self-evident.

Quality is not just a matter related to a product, it is a matter of the total organization. It is the top management that is responsible for defining and

Text 2

Definition of quality assurance [ISO, 1986].

Quality assurance:

All those planned and systematic actions necessary to provide adequate confidence that a product or service will satisfy given requirements for quality.

NOTES:

- 1 Unless given requirements fully reflect the needs of the user, quality assurance will not be complete.
- 2 For effectiveness, quality assurance usually requires a continuing evaluation of factors that affect the adequacy of the design or specification for intended applications as well as verifications and audits of production, installation and inspection operations. Providing confidence may involve producing evidence.
- 3 Within an organization, quality assurance serves as a management tool. In contractual situations, quality assurance also serves to provide confidence in the supplier.

documenting its quality policy (see Text 3) and to ensure that this policy is understood, implemented and maintained at all levels in the organization [ISO, 1991c]. This means that, first of all, the top management has to commit to the concept of quality. Commitment from the top management is important because of the costs of quality assurance which can be seen as investments, that will certainly pay off later. The next step is that all levels in the organization adopt to this concept. These are the preconditions for quality management (see Text 4) to be possible. Quality policy is an integral part of the corporate policy [ISO, 1986]. Quality management has to be embedded in an organization's quality policy. Supervision on the application of the quality policy should be carried out by an independent group within the organization (see section 2.4).

Text 3

Definition of quality policy [ISO, 1986].

Quality policy:

The overall quality intentions and direction of an organization as regards quality, as formally expressed by top management.

NOTE:

The quality policy forms one element of the corporate policy and is authorized by top management.

Introduction of quality management urges a need for change in the culture of the organization. All levels in the organization should have an orientation on quality. This means for instance that work should be checked on a regular basis, not to reward or reprimand, depending on the quality of the work, but to correct mistakes in the work and avoid them in the future. It should be based on the notion that everybody makes mistakes and that mistakes can be learned from.

Striving for quality is not equal to striving for perfection. The level of quality to be reached has to be defined. Quality has to be a balance between perfection and preconditions like time and expenses. A product has a good quality when it is 'fit for use'. Not complying with the objectives makes it useless, higher specifications makes it more expensive but not better to use. Basically, quality is concerned with the concept of effectiveness and the concept of efficiency. In monitoring this can be translated into 'the degree to which the information obtained meets the monitoring objectives' respectively 'provide the user(s) with sufficient information against minimal costs' [Buishand and Hooghart, 1986]. The quality policy has to set the

goals for the quality management to reach; what is the effort to be put in quality assurance? Quality assurance has to ensure that these goals are reached.

.....
Text 4

Definition of quality management [ISO, 1986].

Quality management:

That aspect of the overall management function that determines and implements the quality policy.

NOTES:

- 1 The attainment of desired quality requires the commitment and participation of all members of the organization whereas the responsibility for quality management belongs to top management.
- 2 Quality management includes strategic planning, allocation of resources and other systematic activities for quality such as quality planning, operations and evaluations.

In quality management, the responsibilities and competence of all persons involved in carrying out activities and in verifying activities in monitoring and assessment have to be defined. This is especially important for those that supervise the process and products and consequently have the competence to conclude on quality problems and to take the appropriate measures to ensure that the products meet the requirements [ISO, 1987b]. The means and capacity to perform quality control (see Text 5) have to be appointed.

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Text 5

Definition of quality control [ISO, 1986].

Quality control:

The operational techniques and activities that are used to fulfil requirements for quality.

NOTES:

- 1 In order to avoid confusion, care should be taken to include a modifying term when referring to a sub-set of quality control such as "manufacturing quality control", or when referring to a broader concept, such as "company-wide quality control".
- 2 Quality control involves operational techniques and activities aimed both at monitoring a process and at eliminating causes of unsatisfactory performance at relevant stages of the quality loop (quality spiral) in order to result in economic effectiveness.

To achieve quality management, all procedures and standards should be documented. Furthermore, all decisions should be documented. The reason for this is that it should always be possible to trace how a product is realised. When a product does not comply with the intended objective, there is always the possibility to find the origin of the discrepancy. This element is called traceability.

Quality management in monitoring and assessment requires an overall quality system (see Text 6), dealing with, as already stated, the total organization, with procedures, processes and responsibilities and the level of quality that is to be reached. This quality system should deal with the whole process from specification of the information need to the information utilization. This does not necessarily mean that the quality system should deal with all the details. If, for instance, a laboratory that is involved in the monitoring programme, has its own quality system, the overall quality system should only deal with connecting to this quality system. Note that in such a situation connection is required both at the point of samples going in and at the point of analyses data coming out.

Text 6

Definition of quality system [ISO, 1986].

Quality system:

The organizational structure, responsibilities, procedures and resources for implementing quality management.

NOTES:

- 1 The quality system should only be as comprehensive as needed to meet the quality objectives.
- 2 The quality system of an organization is primarily designed to fulfil the internal managerial needs of the organization.

The process is done by the personnel. Without skilled personnel, a product cannot reach a higher level of quality. This implies that requirements have to be set up for the personnel and a plan has to be made for training and coaching of personnel.

There has been a progress in the ways to ensure the product to meet its requirements. At first, the purpose of quality assurance was mainly to inspect and correct. The ready-made product was inspected and measures were taken to improve the process when the product did not meet the requirements. Later, the principle became the prevention of mismatches. Both the product and the process were analyzed and observed¹⁾. Measures were taken in changing the process when deviations from the standards and requirements occurred. Nowadays there is a tendency towards meeting the needs. This implies not only analyzing and observing the process and the product, but also the establishment of feedback mechanisms, ensuring the product meeting the requirements. The implication is that quality assurance is a continuum of planning, acting, inspecting, observing and making adjustments. This is called the quality loop or quality spiral (see Text 7).

Text 7

Definition of quality loop [ISO, 1986].

Quality loop; quality spiral:

Conceptual model of interacting activities that influence the quality of a product or service in the various stages ranging from the identification of needs to the assessment of whether these needs have been satisfied.

2.4 Quality assurance in monitoring and assessment

The product of monitoring and assessment is a combination of what can be expected (by regulations, standards and expectation) and the requirements for the use of the product. The major challenge is to specify and document all of these expectations and requirements. "There should be no information expectations that are not documented - no future disappointments for the public, their elected representatives, or the professional staff operating the water quality management program" [Ward, 1994b].

In monitoring and assessment targets may be reached or policies may change and new methodologies become available; quality assurance in monitoring and assessment can be presented as a spiral of continuous adjusting the monitoring system (figure 3).

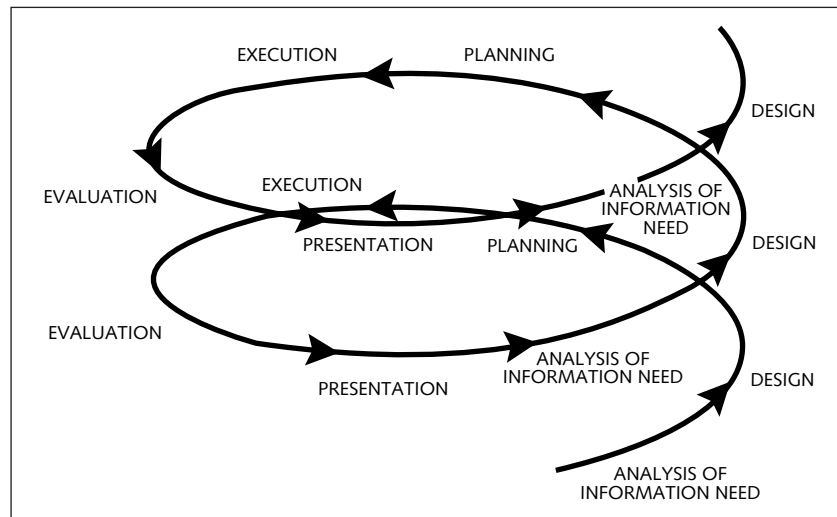
The design and optimization of monitoring networks is an iterative process: the optimal (future) network is based on the information gained from the present one [Buishand and Hooghart, 1986]. The spiral reflects the dynamic,

.....
Note

¹⁾ The term 'observe' suggests viewing from some distance. In quality management the process and the product should be observed closely. 'Monitoring' might be a better term in the text, but is not used because of the possible confusion with monitoring of the water system.

ongoing nature of monitoring and incorporates and uses feedback mechanisms to assure and control the level of quality required [Cofino, 1994].

.....
Figure 3
 A quality spiral for the monitoring process [Cofino, 1994].



The quality assurance in monitoring and assessment, and with this the quality system, can be viewed from two different levels:

- On the top level, there is the need to ensure that the results from the monitoring and assessment programme meet the requirements, i.e. that the monitoring and assessment programme gives the answers to the questions about water quality.
 This requires a specified information need and a defined monitoring strategy to ensure that the information is used in the right way. The overall quality system should deal with this.
- On the second level, there is concern with carrying out the monitoring network, sampling or laboratory analyses, according to the requirements. On this level, expertise in one of the fields is important. A laboratory quality system is the best known example but quality systems for sample collection and for data handling are equally important.

Both of the levels need specific requirements and each level has to perform specific activities and use specific techniques to make sure that the required quality is fulfilled.

This means that the quality system will have different levels. One level is concerned with the whole of the monitoring cycle, another level is concerned with specific elements, like for instance data-analysis. Since in the different levels, usually different organisations or parts of organisations are involved, the development of a comprehensive quality system will be very difficult, if not impossible. Therefore any quality system should deal with only that part for which the management involved is responsible. The quality system sets criteria for products that are input to or output from the process under the quality system. Output criteria from one quality system should not conflict with input criteria from the adjoining quality system.

The action of ensuring the desired quality should be carried out by an independent group within the organization. Independence is necessary for this group to be able to judge objectively. The Quality Assurance Group should observe the processes and the obtained product and should give advice if deviations occur. The Quality Assurance Group should work directly under and be accountable to the top management.

Text 8

Five definition of quality [ISO, 1986].

Transcendent

According to the transcendent view, quality is synonymous with 'innate excellence'. It is both absolute and universally recognizable, a mark of uncompromising standards and high achievement.

Product-Based

Quality is a precise and measurable variable. Differences in quality thus reflect differences in the quantity of some ingredient or attribute possessed by a product.

User-Based

User-Based definitions start from the premise that quality 'lies in the eye of the beholder'. Individual consumers are assumed to have different wants or needs, and the goods that best satisfy their preferences are the ones they regard as having the highest quality.

Manufacturing-Based

Manufacturing-Based definitions primarily focus on engineering and manufacturing practices. Virtually all manufacturing-based definitions identify quality as 'conformance with requirements'.

Value-Based

Value-based definitions define quality in terms of costs and prices. Thus, a quality product is one that provides performance or conformance at an acceptable price or cost.

The key is that every element in the circle of activities in monitoring and assessment, as shown in figure 2, must be "designed", specified, detailed, described, or documented to be sure that the monitoring system produces the desired information [Ward, 1994b].

Text 9

Proposed terms of reference for an NSTF/JMG working group on Quality Assurance [NSTF/JMG, 1989].

1. The purpose of the Quality Assurance Group is to develop, implement and maintain a system to achieve and maintain comparability of environmental data, to provide confidence in these data, to provide continuing surveillance of the monitoring programme and to advise on corrective actions as required.

[...]

3. The QAG should report to the NSTF (North Sea Task Force) and the JMG (Joint Monitoring Group of the Oslo and Paris Commissions).

By continuous evaluation and feedback the circle becomes a spiral, leading to a better quality of the information. The monitoring cycle will be used as the basis for quality assurance in the different monitoring and assessment activities. In the next chapter each of these elements will be specified.

.....
Text 10

Institutional arrangements to control the quality of information [Cofino, 1994].

“Information on aquatic systems is the result of a chain of activities (e.g. design, sampling, analysis, evaluation). The quality of the entire monitoring process has to be managed in order to obtain information that meets the needs. Frequently, this is a complex task owing to the large number of different parties involved. In international programmes, each country has its own responsibilities. Within each country various institutes may take part, often taking care for just a specific part in the process or for a certain region. In these circumstances, quality management has two dimensions. On the international level, a clear quality policy needs to be formulated covering all elements of the monitoring process. This policy needs to be undersigned by all countries involved. This policy has to be elaborated into a quality system, important elements being a clear description of guidelines, procedures and criteria that all parties have to adhere to or fulfil, arrangements aimed to control and verify the quality of the information supplied and a communication programme to ensure adequate flow of information between the organizing body and participants about criteria, procedures, guidelines and difficulties encountered. The second dimension consists of the participants (institutes and laboratories) which on the national level acquire the information needed. These organizations need to have their own quality systems, which assure that the requirements posed on the international level are satisfied.

[...]

Quality management of monitoring programmes is an ongoing task and should be addressed systematically. Any programme, be it national or international, should appoint a quality manager or quality managing group. In international programmes, national organizations and laboratories should set up quality systems attuned to the international requirements. In this way, individual laboratories are embedded in an infrastructure, the totality producing the information which environmental management needs at reasonable costs.”

3. Quality assurance in monitoring and assessment

3.1 General

In quality assurance, it is important that processes are carried out in a verifiable way. Different people, carrying out the same process must obtain the same result. This is obvious for laboratory analyses but it also counts for sample collection and making calculations.

This means that there is a need for standards and standardized procedures [Ward, 1994a]. Next to this, if there are differences between the outcomes of similar processes, there must be a way to account for the difference. This means that there is a need for protocols [Ward, 1994b]. The use of protocols makes it possible to trace back the processes to the point where the deviation starts. In this way the absence of a measurement in a series can be traced back to, for instance, the breaking of a sample bottle.

It may often be necessary to carry out a preliminary sampling and analysis programme in order to obtain a better understanding of the problem, before the final objectives can be defined [ISO, 1980]. This should be treated in the same way the monitoring network is designed. The objective in the survey, a better understanding of the processes, is not directly related to the information need, but will give information for the monitoring network design. For instance, a survey to find out the distance it takes for the water at the confluence of two rivers to mix completely will give information on choosing sampling locations.

3.2 Specification of information needs

As stated in section , quality assurance can only be performed when the requirements of the product are made explicit. The requirements of monitoring and assessment are the information needs. Only when the information needs are clear, can a monitoring and assessment programme satisfy its users and can the effectiveness of information be verified. The information need is the starting point for the elaboration of the monitoring strategy; it is the scope of information the monitoring system should provide.

There is no general information need that is valid for all monitoring and assessment programs. On the other hand there are many different questions that have to be answered by a monitoring and assessment programme [Ward, 1994a] [Hofstra, 1994]. The monitoring and assessment programme has to be tailor-made to the specific needs of the people involved. But there are some factors that complicate the defining of the information needs, especially in international cooperation [Ward, 1994a]:

- There is a lack of definitions, e.g. what is water quality? Many organizations work on defining their terminology in order to avoid misunderstandings in communicating with other organizations.
- Agreement has to be accomplished on how monitoring systems should be designed, and what common components can be shared
- Experts tend to be blinded by their discipline. There is a need for integral approaches, combining different disciplines. This requires a clear, agreed upon, information goal.

-
- Too often too much information has to be obtained from one and the same monitoring system. Next to the information needs, the limitations of a monitoring system should be made clear. One way to overcome this problem is to connect different water quality measurement efforts. The Intergovernmental Task Force on Monitoring Water Quality (ITFM) in the United States is developing a strategy to be adopted by US Federal and State agencies. The information resulting from implementing the strategy is expected to be greater than the sum of the measurements produced by the individual organizations [Fellows *et al.*, 1994]. More information on different variables is known and with this knowledge it becomes clear what is actually measured and what are the connections between different variables.

These elements will have to be accounted for in developing a joint transboundary monitoring programme.

How should the information need be defined? There are various ways to do this. Most important is to stay at the right level. This means that we should not be concerned with what variable we want to measure at what location. The information need should reflect the current policy in water management and should involve tactic and strategic considerations. The first and major sources for defining information needs are the national and international laws and agreements. These provide the legal basis for setting up a monitoring programme. Also, policy preparation, next to opinions of current managers and reviews of regulations, are sources of information goals [Ward, 1994b].

There is no generic method for defining information needs. Nevertheless there are some criteria that account for the defining of information needs. First, decision-makers have to be responsible for the defining of the information needs. Directly related to this is the aspect of accountability; the information needs have to be documented and these documents have to be explicitly (e.g. by means of a signature) approved by the decision-makers. There shall not be any confusion about the basic assumptions.

Another criterium is the quantification of the information needs. Information needs should be stated in terms like "Twenty percent reduction of pollution in the next five years", or "No more interruptions in the intake of drinking water within two years". There should be an element of relativity ('percentage reduction of ...') or quantity ('no more ...' or 'less than ...') in the specification. Next to that an element of time ('... within two years') is imperative. 'The salmon back in the river Rhine in the year 2000'²⁾ is a statement that can be measured to some extent. There is an element of quantity (a more or less stable population of salmon) and an element of time (the year 2000). Naturally, the quantity element must have a link to water management measures. In this case, the element of quantity should be expressed in terms of a specific water quality and to physical factors like suitable spawning grounds and migration paths. When these criteria are quantified, the elements can be converted into a monitoring strategy. The effectiveness of a monitoring network can only be tested when the information need is quantified.

Five different approaches for defining information needs can be distinguished, which should all be considered (after [Witmer, 1994] and [Enderlein, 1994]):

.....

Note

²⁾ The aim is that by the year 2000 the ecosystem of the Rhine should be improved to such an extent that higher species, such as the salmon, may become indigenous [Hogervorst, 1993]

- the effect-approach: there can be an adverse effect of some kind that has to be reduced within a certain period. The element of relativity can be used here.
- the source-approach: there are sources that cause adverse effects. These sources have to reduce their effect, e.g. by reducing their loads on the environment. This is closely related to the effect-approach.
- the achievement-approach: there is a goal to be achieved within a given time period. This approach gives an impression of how far the intended actions will be after some time. 'The salmon back in the river Rhine' is an example of this approach.
- the background-approach: "there may be no change in" a given parameter or "the river has to be back in its original state by" a given time. This is usually comparable to the ecological function of a water-system.
- The function-approach: the water-system has to fulfil a specific function, e.g. be fit for swimming.

The different approaches are often interrelated. Nevertheless, by viewing a certain aspect in water management from each of these approaches, the specification of the information need can be helped.

The quality system describes the functionaries³⁾ that are responsible for the production and the accreditation of the document specifying the information need. The document should contain the following topics:

- a short overview of the current situation, in order to put the information need in the right context;
- some reflections on the problems recognized, the current monitoring system, if any, and the monitoring system results;
- the information needed, roughly specifying what has to be measured, where it has to be measured and with what accuracy and probability;
- the expected improvements of measures;
- the precondition for the monitoring system, including a rough plan of the required resources and the timing of the different stages;
- considerations on the balance between information needs and the costs to obtain the required information.

3.3 Monitoring strategy

After defining the information need, a strategy for monitoring has to be specified. This is the step necessary to define what information has to be produced by the monitoring system and to decide on the type of monitoring needed: physical, chemical, biological, hydrological, effluent or early warning. The information need has to be translated into variables to be measured, the necessary reliability, etc. All these requirements should be derived from the information need. As an example, Stoks [1994] describes the information need from the point of view of supplying drinking water. As a result from this information need he describes the monitoring strategy, divided in an operational early warning monitoring system and three different approaches to look for potential threats.

The monitoring strategy has to give enough information for the monitoring network designer to make the design. The monitoring strategy has to

.....
Note

³⁾ In a quality system the function of the responsible employee should be named, not the employee; names of employees tend to change more often than names of functions. Naming the employees would therefore lead to frequent changes of the quality system.

specify **what** has to be measured (also in terms of accuracy, type 1 and type 2 errors, etc.), whereas the network design specifies how it has to be measured. The monitoring strategy should also include the data analysis and reporting, because this can have influence on the network design requirements.

The monitoring strategy should be documented. This document is to be presented to and approved by the decision makers, that defined the information needs. The decisionmakers should conclude from the monitoring strategy report if the monitoring system will cover their information need. Elements of the monitoring strategy report are:

1. The information needs, that will be covered by the monitoring strategy and, equally important, that part of the information needs that will not be covered by the monitoring strategy.
2. The concept of the monitoring system, i.e. the type of monitoring (physical, chemical, biological, hydrological, early warning, effluent), the variables to measure and preconditions for the selection of locations (minimum/maximum distance from border, intake point, etc.) and sampling frequencies (in terms of reliability) for each (group of) variables.
3. The concept of the assessment system, i.e. the calculation methods to be used (for calculation of loads or trends) (preferably international standards) and the use of graphical tools, statistical tools and other tools, like e.g. indices, to present data.
4. Considerations on the proposed concept, like preconditions, suppositions, the statistical models used, etc., but also descriptions of the area, relevant industries, used scenarios, etc.
5. The organizational aspects, in which the following questions should be answered:
 - Which organization will be responsible for what aspect of the monitoring system?
 - Are changes in the organization necessary?
 - What are the problems that can hinder the execution of the monitoring system?
6. A plan for the design and implementation of the monitoring network; what are the preconditions, the planning of the next steps and a financial planning
7. An analysis of the risks; what are the distinguished possible problems that can lead to the failure of the monitoring system.

.....
Text 11

Evaluation of a case study, using a framework for the development of a Data Analysis Protocol at an IBM facility in New York [Adkins, 1993].

Evaluation of the framework: State Information Goals.

“Regulatory information goals were defined by reviewing legislation and by conversing with regulators.

[...]

A considerable amount of effort was devoted to formulating monitoring information goals. The effort paid off. Regulators and water quality managers were able to get a clear picture of what information would be obtained from the monitoring program. This enabled them to identify concerns which had been overlooked or improperly emphasized. Also, monitoring information goals proved to be a convenient basis for organizing the protocol.”

3.4 Network design

“Knowledge of chemical, biological and physical processes, of specific local characteristics or properties of the object of investigation, and of the analytical methodology and statistics should be used in devising a programme

of measurements" [Cofino, 1993]. Network design should be carried out by a multi-disciplinary team. Influences of local characteristics, hydrology, seasons, the media to be studied, etc. should be taken into account. By using statistics on these properties, frequencies can be calculated. The network design specifies which variables should be measured at which locations at what frequency. Furthermore, in the network design, the sample collection methods, the laboratory analyses methods and the data handling methods are described in terms of the standards that are to be used.

In designing the network, special emphasis should be put on statistics. When, for instance, water quality data are available, use of statistics can minimise the number of locations through correlation between stations [Sanders and Loftis, 1994]. Statistics can also provide the foundation for the choice between many locations and a low frequency or few locations and a high frequency.

In designing a network, it is essential that the designers have good insight in the phenomena to be examined [Buishand and Hooghart, 1986]. Especially when little is known of a water system, an expert can give information, based on experience and knowledge, to prioritize in measurements to be carried out [Ongley, 1994].

One major issue in designing the network is to determine the effectiveness of the information obtained from the network. At this stage in the development of the monitoring system, enough information is available to give a detailed insight in the costs and effectiveness of the designed network. In Buishand and Hooghart [1986] six steps are described in the process of designing a monitoring network (see also figure 4):

1. The monitoring objectives should be identified. Also, an adequate measure of the monitoring effectiveness has to be defined, which is tuned to the objectives. This is dealt with in section 3.2.
2. The physical aspects of the system should be studied in order to identify the relevant process dynamics and the corresponding time- and distance scales (surveys can provide knowledge about the water system (see section 3.1)).
3. The manner in which the data should be analyzed has to be chosen. This strongly depends on the physical aspects and the monitoring objectives (choosing data analyzing methods is part of the monitoring strategy (see section 3.3)).
4. The effectiveness of the information, E , obtained by analyzing the data from the network, should be determined. For this purpose, a relationship has to be found between the effectiveness E and the variables f , L and V (frequency, Locations, and Variables).
5. The costs of the monitoring program should be calculated, resulting in the relation $C = C(f, L, V)$.
6. A cost-effectiveness analysis should be made, yielding optimal values for sampling frequencies, locations and variables.

The network design is to be documented in a report. This report is to be presented to the monitoring strategy designers. These should conclude from the network design report if the monitoring network will cover their monitoring strategy. Elements of the network design report are:

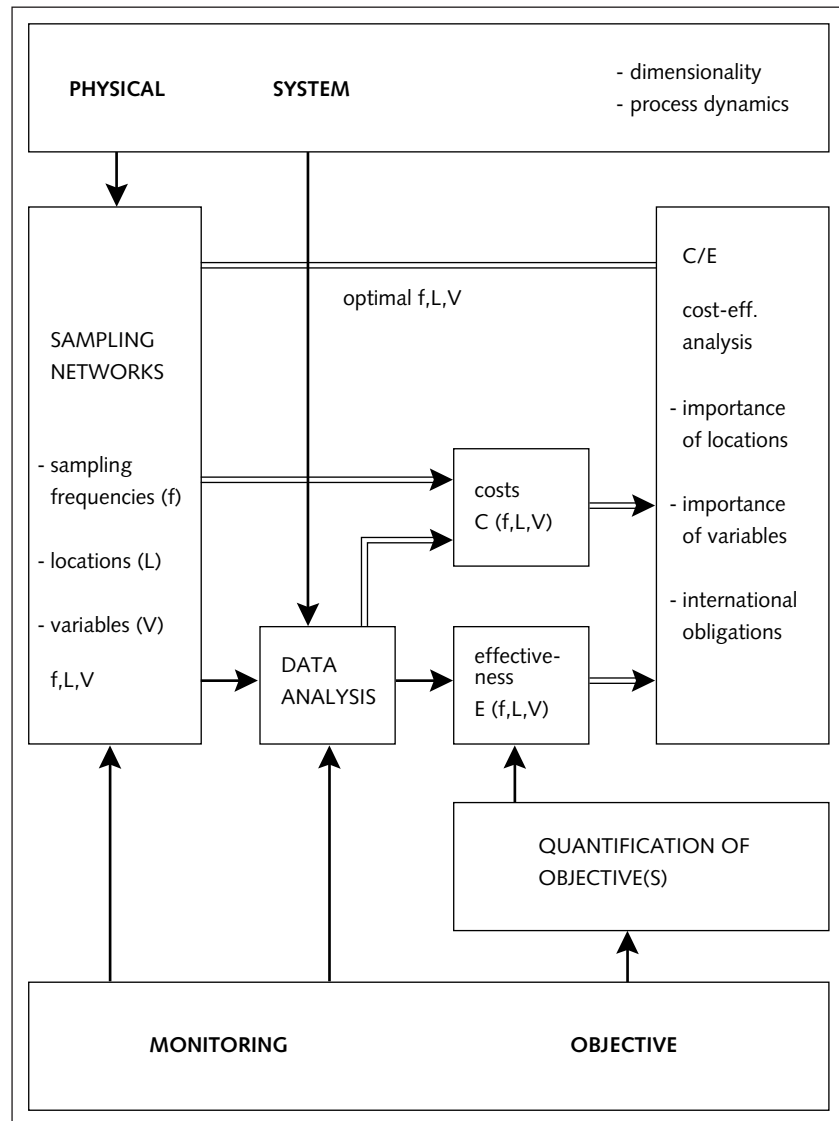
1. Explanation of the part of the monitoring strategy that will be covered by the network design and the part that will not be covered by the monitoring strategy.
2. Description of the monitoring network, i.e. the variables to be measured, the sample-locations and the frequency and also the use of standards,

e.g. ISO or national standards. Some consideration should be given to the degree of detail and precision that will be adequate. For further detail, see ISO [1980].

3. The manner in which the results will be expressed and presented, e.g. concentrations or loads, maximum and minimum values, etc. [ISO, 1980].
4. Organizational aspects such as the functionaries in the organizations involved that are responsible for the different steps in the monitoring programme: sample collection, handling and transportation, laboratory analyses, data handling, data analyses and reporting.
5. A plan for the implementation of the monitoring network.
6. Results of the cost-effectiveness analysis, describing the arguments for the decisions made.
7. Analysis of the risks; what will be the result if something goes wrong and what measures can be taken to avoid or minimise the damage.

Figure 4

Schematic representation of the optimization process of monitoring networks. The monitoring effort is characterized by sampling frequencies (f), locations (L) and variables (V) [Buishand and Hooghart, 1986].



An example of a monitoring system design documentation format is presented in Ward *et al.* [1990]. In this example, organisational aspects, cost-effectiveness and risk-analysis are not explicitly included.

3.5 Sample collection

Sampling is the start of the actual collection of information, and it is very important that sampling be conducted correctly. Mistakes in sampling will have an influence throughout the monitoring system, until the reporting. There is no possibility to reproduce a sample, there is only a probability, based on expert judgement, that there is little or no change since the erroneous sample was taken. Great emphasis should be put on assuring the quality of the sampling process. The elaboration of a quality system for sampling is strongly advised. In this section, 'sample collection' includes collection, preservation, transport and storage of samples.

There are different ways of sampling; e.g. spot sampling, periodic sampling, continuous sampling and large volume sampling. Each type of sampling has its own uses, depending on the type of variable of interest and the characteristics of the water body.

The sampling equipment should be designed for the specific purpose. Generally, effective samplers should minimize the contact time between the sample and the sampler, use such materials so that no sample contamination occurs and be designed after considering the system suitability in relation to the required water sample [ISO, 1991a].

In sampling, there are some decisions to make. First, there is the choice of the precise sampling point. Considerations of in-stream velocity, homogeneous distribution of determinands, and also reasonable access to the sampling point with the needed equipment can influence the choice of the sampling point. Secondly, the frequency and time of sampling must also be determined. Different time-based effects can be of influence at a specific location. Natural cycles may occur, as well as production and discharge cycles of industries or other facilities just upstream of the sampling location. These cycles have to be accounted for. Thirdly, there is the choice of the sampling method. A method has been designated in the network design, but this may be unusable in the specific situation, e.g. if the water depth is too shallow. Fourth, the transporting, stabilizing and storing the samples must be accounted for. General guidance on transport, stabilization and storage of samples is given in ISO 5667 - 3 [1994]. Fifth is incorporation of quality control procedures. All sampling methods should be periodically tested using field-based quality control and audit procedures that are specifically designed to examine the effectiveness of these methods, particularly those aspects relating to the transportation, stabilization and storage of samples prior to analyses [ISO, 1990]. Finally, safety precautions have to be met. These are concerned with personal safety, in relation to conditions like weather and wading depth but also with protective wear if hazardous substances are sampled.

Because of the importance of proper sampling, special attention should be paid to the motivation of the staff that is involved in sampling. Proper training and proper facilities can help (see also Text 12 and Text 13), but also feedback of monitoring results may provide attachment to the programme.

Sample containers should be clearly and unambiguously marked. All details relevant to the sample should be recorded and connected with the sample container. A detailed sampling report should be completed at the time of sample collection. The content of the report will depend on the objectives of the sampling. Matters which could be included are the name of the water body, the sampling site, the sampling point, the date and time of the

sample collection, the name of the sample collector, the weather conditions at and/or immediately prior to the time of sampling, the appearance, condition and temperature of the water body, the flow condition of the water body, the appearance of the sample, the type of sampling device used, information on the sample preservation technique used, information on any sample filtration technique used and information on the sample storage requirements [ISO, 1990]. A form, containing specific questions about the exact information wanted, should be designed to be used by the sample collector.

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Text 12

Excerpt from the paragraph 'Quality systems for sampling', [Stroomborg *et al.*, 1995].

"Staff involved in sampling should have specified, appropriate qualifications, training and skills. Records of training should be kept, persons authorised to take (specific) samples should be identified. Requirements for sampling equipment ought to be defined, the equipment used should be adequate for the tasks as demonstrated by tests on the equipment itself or on the entire sampling procedures. Equipment records should be kept up. Traceability and calibration should be pursued to the extent possible. Methodology for sampling (and in-situ field measurements) should be well validated and documented. The facilities used for sampling should allow contamination-controlled sampling and sample work-up and constitute a good, 'comfortable' working environment for staff (e.g. provide shelter against wind). An effective documented system for the handling of samples should be present. A systematic record of information which is practically relevant for sampling should be maintained. All information relevant to the validity of the samples should be noted and passed on to the laboratory/client. Procedures should be present for the handling of complaints and anomalies."

Loss or transformation of analyte during sampling, storage and transport needs to be controlled. Common measures are conservation, cooled storage, cooled transport and minimizing the time period between sampling and analysis (a maximum storage time before analysis can even be specified). Special care has to be taken when volatile substances are sampled.

To ensure the quality of the sampling process, regularly control tests should be carried out. Specific control tests to be considered are:

- Routine tests on the effectiveness of the cleaning of sampling equipment and sample containers.
- Field blanks, samples of deionised or distilled water that are taken into the field and treated as samples, to check on contamination.
- Field check samples to provide routine checks on sample stability. Checks can be done by dividing a real sample in two and making a known addition to one portion. The recovery is a check that conservation, sample transport and storage are satisfactory .
- Duplicate samples to provide checks on variability.
- Sampling of a reference site to check procedure and personnel. Note that usually a reference site is hard to find.

An additional way of getting insight into the quality of the sampling process is to have the sampling process reviewed by an independent expert.

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Text 13

Motivation of personnel [Broderick *et al.*, 1991].

"It has been observed that 20 to 25% of all operating deficiencies are directly attributable to operating personnel. Motivation of such personnel to undertake correctly the tasks assigned to them is therefore a matter of considerable importance. It is the responsibility of the management to ensure that staff are well motivated and that no technician should use a method whose scientific basis is unclear to him. This responsibility should not be overlooked."

Additional information on sampling programmes and sampling techniques can be found in ISO 5667 parts 1 to 11 [ISO, 1980] [ISO, 1991a] [ISO, 1994b] [ISO, 1987a] [ISO, 1991b] [ISO, 1990] [ISO, 1993a] [ISO, 1993b] [ISO, 1992a] [ISO, 1992b] [ISO, 1993c].

3.6 Laboratory analyses

The importance of the analytical quality control and quality assurance is recognized in any water quality monitoring programme. The quality assurance programme is an essential part of analytical work. A single analyst as well as a laboratory organization should use quality assurance to detect and to correct problems and take every reasonable step needed to keep the measurement process reliable.

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Text 14

Reasons for variability in intercomparisons of laboratories [Broderick *et al.*, 1991].

"The major reason of variability of the results obtained in intercomparisons is laboratory practice and not related to the methods. This presents the very reason why laboratories should regularly participate in intercomparisons where all their routine analytical methods can be tested. Such intercomparisons have to be organized by national, international or professional bodies in a manner such that the participants can deduce useful information from their performance to exercise."

The more important features of an analytical quality assurance program include [Mesley *et al.*, 1991]:

- the use of validated methods;
- properly maintained and calibrated equipment;
- the use of reference materials to calibrate methods;
- effective internal quality control (control charts, etc.);
- participation in interlaboratory check sample schemes;
- independent audits of quality control procedures;
- external assessment by accreditation or other compliance schemes;
- properly trained staff.

These basic elements of quality assurance must be followed and enforced to obtain reliable, comparable results.

An overview of analytical quality control and quality management in water laboratories is given in the annex.

3.7 Data handling

In the monitoring programmes, large quantities of data become available. In order to make these data rapidly and conveniently available to users, the measurement data generated are now almost always stored in computerized data files. These data comprise the measurement data, and the data that are stored for the unambiguous identification of the measurement data, allowing further processing, interpretation and presentation at a later date. This secondary data concerns the sampling location, place and time of sampling, unit, sampling technique, conservation and analysis method. Data concerning the control of the data has also to be stored (data owner, analyzing laboratory, etc.). Secondary information concerning the data is usually stored in coded form, relating to the actual data elsewhere in the database [Adriaanse *et al.*, 1995]. Clear agreements have to be made about the data that have to be stored. Chapman [1992] gives the next check-list:

-
1. Sampling location or station inventory
 - geographical coordinates,
 - name of the body of water,
 - basin and sub-basin,
 - state, province, municipality, etc.,
 - type of water, e.g. river, lake, reservoir, effluent, rain, etc.
 2. Sample information
 - sampling location,
 - date and time of sampling,
 - medium sampled, e.g. water, suspended solids, sediments, biota,
 - sample matrix, e.g. grab, depth integrated, composite, replicate (e.g. duplicate or triplicate), split, spiked or blank,
 - sampling method and/or sampling apparatus,
 - depth of sampling,
 - preservation method, if any,
 - any other field pre-treatment, e.g. filtration, centrifuging, solvent or resin extraction,
 - name of collector,
 - identification of project,
 - for sediment: origin and age.
 3. Measurement results
 - variable measured,
 - location where the measurement was made, e.g. in situ, field, field laboratory or regular laboratory,
 - analytical method used, including the instrument used to make the measurement,
 - actual result of the measurement, including the units,
 - indication of the reliability of the result.

Since computer software is used, emphasis should be laid on the development, testing and maintenance of the computer systems. The software has to handle the data with care, should not miss any of the collected data, and should use the correct codes and make the correct relations to the secondary data. Furthermore, the computer software can perform various control functions, e.g. correlation analysis and application of limit pairs. Examples of software control function are, e.g. $0 \geq \text{pH value} \leq 14,0$, $\text{orthophosphate-P} \leq \text{total-P}$, $\text{dissolved heavy metals} \leq \text{total heavy metals}$, calculation of the 10% (lower) and 90% (upper) limit pairs, giving warning when data fall outside this range. When the software performs calculations, these calculations have to be carried out correctly. These features have to be thoroughly tested, before using the computer system.

As well as for the coding and the structure of the data storage itself, clear procedures should be agreed upon for the interpretation and validation of the measurement data. These will include how to deal with data limitations such as [Ward *et al.*, 1990] [Adriaanse *et al.*, 1995]:

- missing values;
- sampling frequencies that change over the period of record;
- multiple observations within one sampling period;
- Uncertainty in the measurement procedures;
- censoring the measurement signals;
- small sample size;
- outliers: values that do not conform with the general pattern of a data set;
- measurement data rounding;
- data at or below the limit of detection.

Clear agreements about how to handle these limitations are important for one's own use of the measurement data and certainly also when exchanging measurement data with external organisations and institutes. These agreements need to be sufficiently widely-known [Adriaanse *et al.*, 1995].

Regular control of analytical data, at least on a yearly basis, has to be carried out, taking into consideration e.g. the results along the longitudinal section of water flows or annual periodicity. Data that are questionable should be checked. After the necessary corrections and additions are made, the data can be approved. Only approved data should be accessible to any user of these data.

In exchanging measurement data, some issues have to be agreed upon. As stated above, agreements have to be made about the set of data that unambiguously identifies a specific measurement. Next to that, the interpretation and validation of the data must be harmonized. Finally there has to be an agreement on the content and format of the data-exchange.

There is no need for completely harmonizing computer systems; this may even be advised against. Different organizations put different requirements on their computer systems. Harmonization should be a goal only up to a certain level, depending of the degree of coordination necessary between the involved organizations. If a wide variety of organizations is involved in data-exchange, only the data-exchange should be harmonized.

3.8 Data analysis

Data analysis is the phase where the raw data are converted to information that can be used. Routine data analysis is commonly directed toward obtaining information on average conditions, trends or changing conditions or testing for compliance with a standard [Groot and Villars, 1995]. In order to make the information obtained from the raw data comparable and traceable, protocols for data analysis have to be developed [Ward, 1994]. When clear protocols are developed, the data analysis can even be automated.

The data analysis protocol should at the very least contain the following components [Ward *et al.*, 1990] [Groot and Villars, 1995]:

1. A statement of the exact information to be produced. This is directly related to the specified information need.
2. Procedures for preparing a raw data record for graphical and statistical analysis. A major component is specifying how data limitations like missing values, outliers, etc. are to be addressed before data analysis proceeds (see also section 3.7).
3. Means to visually summarize the behaviour of the water quality variables. A graphical presentation of the data can be used to gain understanding of water quality behaviour. This can be used to interpret statistical results.
4. Recommended statistical methods which yield the desired information. The selection of methods should match the statistical characteristics of the data being analyzed. On the other hand the statistical method should match the information need (section 3.3).
5. Reporting formats for the resulting information. This is dealt with in section 3.9.

Elaboration of a data analysis protocol will require discussion on data analysis methods to be used. The advantage is that these discussions take place before the data are collected and analyzed. If no DAP exists, arguments will develop on both the information results and the data analysis methods. In such a situation it is easy to find fault in a statistical procedure that is applied. Since a DAP is initially agreed upon, the discussion can focus on the resulting information. Furthermore a DAP permits quality assurance activities in following the flow of information [Ward *et al.*, 1990].

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Text 15

Limitations to the use of statistical methods [Ward *et al.*, 1990].

“It probably goes without saying that statistical methods should be appropriate for the level of knowledge and experience of the data analyst and that the results produced should match the experience level of the information user. With modern statistical computing capabilities, however, there is a strong temptation to try out lots of data analysis methods without really understanding them. While understanding all the theory is not important, it is essential to understand the most important assumptions of a given method, whether the assumptions are reasonable, and the consequences of violations of these assumptions.”

The major quality issue in data analysis is traceability. It must be possible to trace back the raw data used for the analysis as well as the exact analysis method of any result after data analysis. Reproducing the analysis should lead to the same result.

3.9 Reporting

The final goal of a monitoring programme is the transfer of information gathered from the program to those who will use the information. This can be done in different ways, varying from transferring data-analyses to a brief overview of the conclusions, usually on paper, but sometimes oral or digital. The main issue here is to present the (interpreted) data in an accessible way. The method of data presentation to be used depends on the target group. Some of the most widely-used presentation techniques are [Adriaanse *et al.*, 1995]:

1. Tables of measurement data:
By listing measurement data in a table, no loss of data occurs. Nevertheless, the information from the data has to be made up by the reader.
2. Statistically-processed measurement data:
Statistical processing will transform the data into values that make changes in time and/or space visible. The information is available for the reader.
3. Graphs:
Graphs provide a view in which e.g. trends can be recognized in a glance. By showing standards or other references in the graph, the situation is put into perspective. The amoeba-type presentation is an example of this. Graphs can be line graphs, histograms, pie-charts, etc.
4. Geographically-presented information:
Quality data from a diversity of sources can be inter-related by means of multiple layers of geographically-referenced information. This provides a better understanding of the spatial distribution of the variables involved.
5. Aggregated information:
For rapid interpretation of large amounts of data it can be useful to aggregate the data. Indexes are useful methods for this. Quality indices are a well known instrument within biological quality assessment.

Some examples of different presentation techniques are described in, inter

alia, Adkins [1993], Breukel [1994], Hofstra [1994] and Klapwijk [1994].

From the quality point of view, it is essential that the origin of the results, the way the data are collected and analyzed, are clear from the report. Next to this, reporting procedures can be developed, including [Ward *et al.*, 1990]:

- Format of each report to be produced;
- Frequency of publication of each report;
- Audience to receive each report;
- Distribution procedures for each report;
- Content of each report;
- Types of conclusions to be drawn and represented in each report;
- Automation of report preparation procedures using computer hardware and software;
- Means for evaluating the effectiveness of each report.

3.10 Information utilization

The use of information from the reports is usually not very clear. Decisions are often made on the basis of different information sources, that are not always clearly identifiable. Nevertheless it is important that in decision-making, the information used is referred to and documented. This gives the possibility to find out which information is actually used or preferred, possibly leading to the conclusion that information that is not used will not be produced or will be differently be produced in the future.

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Text 16

Information utilization [Hofstra, 1994].

"To design future policy for water management, many questions have to be answered for which considerable information is needed. To [...] undertake a policy formulation, [...] information has to be collected, not only describing the effects of the present policies on the future, knowing the possible developments of society, but also possible measures and their effects."

Another way to ensure that the information provided is appropriate and being used is to enclose an assessment form with every report that is issued or by interviewing information users (like policy makers and water managers, but also journalists) regularly. This provides the information to determine whether the information need is met and whether alterations in the monitoring system are wanted.

4. Recommendations

The primary goal of quality management in monitoring and assessment can be expressed in the terms 'effectiveness' and 'efficiency'. Effectiveness is the extent to which the information obtained from the monitoring system meets the information need. Efficiency is concerned with obtaining the information at as low as possible cost, both financial and personnel costs. The secondary goal of quality management is traceability. Traceability is concerned with defining the processes and activities, that lead to the information and how the results are achieved. When the processes are known, measures can be taken to improve these processes.

Quality management in monitoring and assessment should be based on the quality policy. The quality policy is to be declared by the top management. Quality policy defines the level of quality to be reached and sets the prerequisites for the quality management.

Quality assurance requires the elaboration of a quality system. The quality system documents the agreements, in the form of procedures and protocols, of the relevant processes and products, dealing with every element of the monitoring cycle, and the responsibilities with regard to the distinguished procedures. The quality system should be subject to regular evaluation and, if required, adjustment. Special emphasis must be laid on responsibilities at points of decision, like for instance approval of the monitoring strategy or acceptance of samples at a laboratory.

Protocols for sampling, sample transport, sample storage, laboratory analysis, data validation, data storage, data analysis and data presentation must be elaborated. They are the operational steps in the process, where insufficient quality control may lead to unreliable data. By following protocols, mistakes can mostly be avoided, and any mistakes that are made may be traced and undone.

Standard requirements on recurrent products are set out in the quality system. For all relevant products, requirements must be made explicit and must be documented. The quality system describes how the requirements are input to the processes and how deviations from the requirements must be dealt with.

Standards for methods and techniques for, among others, sampling, transport and storage of samples, laboratory analysis, data validation, data storage and exchange, calculation methods and statistical methods are part of the requirements. Preferably, international standards are to be used. Especially in sampling and laboratory analysis, international standards are abundant. If international standards are not available, or, for any reason, the use of an international standard is not adequate, national or local standards should be applied, or, if not available, developed.

If monitoring data from different monitoring networks are to be compared, standards used should not necessarily be equal. Nevertheless, for the sake of the exchange of information, the standards used should provide comparable data.

There should be agreement on the definition of terms used in exchanging information or data, and the additional information that is required to characterise data unambiguously. For instance, if chemical data are to be exchanged, the information should comprise the sampling location, date and time of sampling, methods used for sampling, storage and analysis. These terms should be documented in a data dictionary. The data dictionary can also contain formats for the storage of data.

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Annex An overview of analytical quality control and quality management in water laboratories

Scope

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This annex is intended to provide a summary of the approach to Analytical Quality Control which is currently being developed in water laboratories. An overview of quality management and the key aspects of quality systems are presented. For further details of these organisational aspects of laboratory management, the reader is advised to consult authoritative texts (ISO Guide 25, European Standard EN45000 series and documentation published by national accreditation bodies).

This annex concentrates on the principal practical issues which need to be considered in ensuring that a laboratory's data can be shown to be adequately accurate. The text is based on the ENV guidance document which is currently in the process of being approved by CEN Standards Committee TC230 [1995]. However, the more detailed aspects of the CEN Guide, including statistical calculations, have been omitted to provide an overview of the subject.

1. Introduction - Why Quality?

The concept which defines the idea of quality in analysis is that of 'fitness for purpose'. Do the results produced by an analytical laboratory help to provide correct answers to the questions which prompted the analysis to be carried out? Are the needs of the user of the data satisfied? The answer to these two questions will almost certainly be 'no' unless the data user is provided with (i) an assurance that the results in question have been produced in a well-run laboratory and (ii) an indication of the reliability of the measurements which have been made.

If the errors associated with analytical results were always very small (and it was certain that sample handling and the reporting of data were always totally reliable), the correctness of data interpretation and any consequent decisions would rarely be in doubt. However, many experimental studies have shown that analytical results are often subject to serious errors, particularly at the low concentrations encountered in water analysis. Inaccuracies in analytical data limit or prevent valid interpretations of the information available and subsequent decisions can be affected. Obvious difficulties arise in the common situation where analytical data have been obtained, or compared with (i) a water quality standard, (ii) data provided by another laboratory or (iii) results obtained at a different time. Control of the accuracy of analytical results is therefore a fundamental issue which relates to all types of analysis.

It is essential that the intended uses of analytical data are clearly defined so that the requirements for analytical accuracy may be established. Steps can then be taken to control the size of analytical errors such that the results are of an accuracy adequate for their purpose. This is the function of the techniques and activities which go under the collective name of Analytical Quality Control (AQC). It is also essential to the production of usable analytical results that steps need to be taken to ensure that samples are properly labelled, that instrumentation is subjected to adequate maintenance, that analytical staff have sufficient training in the jobs they need to do, etc. The aim of the Quality Assurance programmes which have been designed for analytical laboratories is to establish and maintain a sound organisational structure, within which testing activity can take place.

Table 1

Sequence of activity for Analytical Quality Control.
[The analytical method is the set of written instructions followed by the analyst. The analytical system includes all aspects of producing results, i.e. method, equipment, analyst, laboratory environment, etc.]

Activity	Purpose
1. Establish working group	To plan and coordinate subsequent activity.
2. Define analytical objectives	To ensure clear specification of analytical requirements.
3. Choose analytical systems	To select methods/systems capable of the required accuracy.
4. Define methods	To ensure that the chosen methods are followed properly.
5. Performance tests	To ensure that each laboratory achieves adequate precision and to check certain sources of bias.
6. Check Calibration	To eliminate this source of bias in each laboratory and to prepare full, more detailed bias checks.
7. Routine Quality Control	To maintain a continuing check on analytical performance in each laboratory
8. Interlaboratory Tests	To ensure that each laboratory achieves adequately small errors
9. Maintenance of Quality Control	To ensure long-term control of the accuracy and comparability of analytical results

2. The Quality System in Water Analysis

There is often some confusion concerning the terms Quality Assurance, Quality Control and even Quality System. The definitions below are suggested as a means of identifying the important concepts as they apply to water analysis.

Quality Assurance: the process by which the producer or user of analytical results is provided with the assurance that the results meet defined standards of quality.

Quality Control: the practical steps which are taken to define and control the uncertainty associated with analytical data and to demonstrate fitness for purpose. Quality control activities include method validation, routine checks on analytical accuracy and periodic participation in interlaboratory tests (see Table 1 for a summary of Analytical Quality Control Activities).

Quality System: the system which is set up in the laboratory to implement the approach to quality assurance. This involves specification of how to organise laboratory work e.g. how samples are identified and handled, how methods are chosen and recorded, how problems are identified and responded to, etc. Quality control activity is one of the most important activities which is established within the quality system. Another key activity is that of audit and review - how the operation of the quality system is monitored and, if necessary, modified.

2.1 Background to Approaches to Quality Assurance

Several International Standards have been produced which define the concepts of and approaches to Quality Assurance. The most general of these is ISO 9000 - Quality Systems (European Standard 29000). This provides the basis for quality systems and quality management in many different contexts, from manufacturing to the provision of a wide range of different services (of which chemical analysis is an example). Other more specific Standards give details of how to implement the principles of quality assurance in different situations. The Standard of principal concern in chemical analysis is ISO Guide 25 - General Requirements for the Technical Competence of Testing Laboratories. This guide has achieved wide acceptance and has become the generic standard relating to Laboratory Accreditation (see below). The guidance given in ISO Guide 25 is expanded upon in a series of European Standards:

- EN45001 - General Criteria for the Operation of Testing Laboratories
- EN45002 - General Criteria for the Assessment of Testing Laboratories
- EN45003 - General Criteria for Laboratory Accreditation Bodies

These standards define the important aspects of the quality system which would be required in order to ensure that analytical results are fit for their intended purpose. These criteria also act as the basis on which to identify a competent laboratory. This idea has been developed in many countries into the concept of 'accreditation'. Accreditation for a testing laboratory is the

formal recognition (by a nationally or internationally recognised authority) of the competence of a laboratory to carry out certain tests. The standard of competence is defined partly by having a clear specification of the laboratory's organisational and record keeping requirements (quality system) and partly by ensuring that the standard of accuracy achieved is demonstrably adequate for the intended application. To be certain that fitness for purpose is achieved (rather than merely assumed), there is a requirement for accredited laboratories to take steps to determine their customers' needs.

3. Quality Assurance - Meeting the Requirements of EN45001

The Standard provides general criteria to be adhered to by laboratories which carry out measurement or analyses - usually referred to as 'tests'.

The requirements of the Quality Standard are defined under the following headings.

- 1 **General Requirements** - introductory
- 2 **Organisation and Management** - outlines the need for a well-defined structure within the laboratory with clear lines of responsibility.

Two key roles in Quality Management are identified - Technical Manager and Quality Manager - with a summary of their functions. The Technical Manager has overall responsibility for the technical operation and for ensuring that the requirements of the Quality System are met. The Quality Manager has responsibility for ensuring that the requirements of the Quality System are met on a day to day basis. The holder of this post has direct access to the highest level of management at which decisions are taken on laboratory policy or resources, and to the Technical Manager. The laboratory organisation should include a Deputy Quality Manager and Deputy Technical Manager. The need for a system of authorisation for the release of test results is emphasised.

- 3 **Quality System** - defines the basic requirements for a quality system (see above) in a testing laboratory.

The Quality Manual is the reference document for the Quality System of the individual laboratory. The Quality Manual acts as an index to the functions of the Quality System, either referring directly to the key issues affecting quality or indicating how they are addressed. The issue of documentation is crucial. The operation of all important laboratory functions must be adequately documented and such documentation needs to be subject to control and monitoring by management.

- 4 **Quality Audit and Review** - describes the way in which the Quality System is maintained. Audit is the process by which the system is checked on - to ascertain whether or not the defined requirements are being complied with. Review is the process of examining those requirements to ensure that Quality System meets the overall objectives of quality in the laboratory's work.

Audits which encompass all aspects of the quality system are carried out by laboratory personnel in accordance with a predetermined schedule. It is the responsibility of the Quality Manager to plan and organise these audits. Staff are not permitted to audit their own activities.

- 5 **Staff** - specifies the need to use staff who have the appropriate combination of academic and/or professional qualifications, training, experience and skill. It is necessary to provide adequate specific training for each test, to maintain records of training and to indicate who is

authorised to undertake each test.

- 6 **Equipment** - defines the requirements for test equipment. Only equipment suited to the task in hand and capable of achieving the required accuracy should be used.

The laboratory is required to have a system by which the fitness for purpose of equipment is demonstrated (either by test on the equipment itself or by tests on the equipment as part of the overall analytical system). A system of equipment records is required as a means of demonstrating that the equipment used is adequately maintained.

- 7 **Measurement Traceability and Calibration** - This is the means by which the laboratory's testing activity can be linked to national and international standards of measurement.

The principal approach is to ensure traceability for fundamental quantities (e.g. mass, volume, temperature, time). These quantities can be linked to (checked against) their corresponding standards via calibrated masses, certified thermometers etc. This provides the fundamental assurance that the comparative tests carried out by a laboratory have a sound basis.

For chemical analyses, the concepts of strict traceability to a fundamental standard may be difficult to apply. For example, it has not been possible to establish traceability for the parameter 'concentration' since it depends on establishing adequate criteria for the purity of standard materials. The approach to traceability which is being developed for analysis involves (a) most importantly - the traceability of all fundamental, physical aspects of analysis (especially mass); and (b) independent checks on the overall accuracy of the analytical system via analyses of reference materials and participation in appropriate interlaboratory tests.

The critically important subject of Quality Control comes under the heading of traceability. This is a means of establishing and maintaining consistency of performance for an analytical system so that the reliability of analysis can be demonstrated. Analytical Quality Control (the practical steps which are taken to define and control the uncertainty associated with analytical data) is discussed in more detail in subsequent sections of this document.

- 8 **Methods** - defines the need to use well-recognised procedures and to have such procedures adequately documented.
- 9 **Accommodation and Environment** - the need to ensure adequate facilities is stressed.
- 10 **Handling of Calibration and Test Items** - outlines the requirements for an effective documented system for identifying test items (samples). It is essential to ensure that test samples should not be confused, physically or when referred to in records or other documents. Reagents and standards should be stored appropriately. The laboratory should guard against deterioration, contamination and loss of identity.
- 11 **Records** - specifies that laboratories should have and maintain a systematic record of all information of practical relevance to the tests performed.

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- 12 **Test Reports** - defines the necessary requirements to ensure demonstration of adequate quality for the client. All information relevant to the validity and application of the test results should be recorded. Specific details of the appropriate form of test reports are set out.
 - 13 **Handling of Complaints and Anomalies** - the Standard defines the way in which complaints and anomalies should be handled. There is a need to make sure that complaints are handled in a way which is open and documented.
 - 14 **Sub-Contracting** - the formal approach to analyses which are contracted out.
 - 15 **Outside Services** - establishes the requirements for choosing suitable support services. Laboratory should have records of all outside bodies from whom it obtains support services or supplies.

The application of these criteria to the work of the laboratory is intended to provide the laboratory and its clients with confidence in the quality of the tests and in the technical and commercial integrity of the laboratory's operations. The remaining part of this document is devoted to the practical aspects of Analytical Quality Control activity - which is undertaken within the framework of the Quality System. These activities are performance testing, routine, within-laboratory quality control and interlaboratory tests. before these topics can be addressed in a logical manner, it is necessary to consider the size and nature of analytical errors and the accuracy requirements applicable to the analytical task.

4. The Nature and Sources of Analytical Errors

A number of factors contribute to the production of analytical data of adequate quality. Most important is the recognition of the standard of accuracy that is required of the analytical data. This should be defined with reference to the intended uses of the data (see section 5, below). Before defining analytical targets to be achieved, it is necessary to consider the nature of analytical error.

The results of chemical analysis of waters and effluents - like those of all measurement processes - are subject to errors; that is, the measured concentrations differ from the true concentrations. The Total Error, E , of an analytical result, R , is defined as the difference between that result and the true value, T ; i.e.:

$$E = R - T$$

As the Total Error decreases, the Accuracy of the result is said to increase. The Total Error represents the sum of Random Error and Systematic Error.

Random Error

Repeated analysis of identical portions of the same, homogeneous sample does not, in general, lead to a series of identical results; results are scattered about some central value. The scatter is attributed to Random Error, so called because the sign and magnitude of the error of any particular result vary at random and cannot be predicted exactly. Precision is said to improve as the scatter becomes smaller - i.e. as Random Error decreases. Imprecision is a synonym for Random Error.

The most appropriate statistical population parameter to quantify random error is the Standard Deviation.

Systematic error

Systematic Error (or Bias) is present when there is a persistent tendency for results to be greater or smaller than the true value (results are subject to positive and negative biases respectively). As the systematic error or bias of results decreases, Trueness is said to increase.

The Sources of Errors

The distinction between random and systematic errors is important for two reasons: firstly, because the two types of error have different effects on the use which may be made of analytical results, and secondly, because the different origins of random and systematic error means that there are different ways of dealing with them.

Causes of Random Errors

Random errors arise from uncontrolled variations in the conditions of the analytical system during analyses. These are short term variations e.g. instrumental noise, detector noise, operator-induced variations in reading scales. A batch of analysis can be defined as the number of results produced under the influence of a given calibration. Variations from batch to batch also give rise to between-batch random errors. A consistent calibration

error across many batches gives rise to systematic error - see below.

Between batch error contains sources of random error which are readily assignable e.g. a change in calibration or operator. Whilst many of these factors causing random errors can be more closely controlled to achieve better precision, they can never be totally eliminated so that all results are subject to some degree of random error.

Causes of Systematic Errors

There are five main sources of systematic error (if bias caused by error in sample collection itself is excluded). These are:

(i) Instability of samples between sample collection and analysis

The concentrations of many determinands may change between sampling and analysis. Very large and important errors may result. Evidence on the extent of sample instability and on any measures taken to control it is required.

(ii) Inability to Determine All Relevant Forms of the Determinand

Many substances in water exist in a variety of species e.g.. iron can exist in both dissolved and particulate forms. Within each of these physical categories a variety of chemical species may be present. e.g. free ions and complexes. An inability of the analytical system to determine some of the forms of interest will give rise to a bias when those forms are present in the samples.

(iii) Interferences

Few analytical methods are completely specific for the determinand. It is therefore important to know the effects of substances likely to be present in the samples. The minimum evidence should provide estimates of error at or near the upper and lower concentration limits of the system. These estimates should be available for each substance of interest.

(iv) Biased Calibration

Most methods require the use of a calibration function to convert the primary analytical response for a sample to the corresponding determinand concentration. If samples and calibration standards are treated differently, this can represent a potentially serious source of error. Impurity of the material used to prepare standards and errors in the preparation of calibration standards are potential causes of biased results.

(v) Biased blank

The same considerations as in (iv) apply to blanks. However, there is, another source of bias arising from blank correction. If the water used for the blank contains the determinand, results for the samples will be biased low by an equivalent amount. It is necessary therefore, if this source of bias is to be eliminated, to check the determinand content of the blank water and, ideally, to ensure that this concentration is negligible in comparison with the concentration in the samples.

5. Defining Analytical Requirements - Accuracy Targets

Careful specification of analytical requirements is a vital feature in the design of programmes of sampling and analysis to assess water quality. Adequate consideration of the accuracy needed in analysis is a critical factor in ensuring 'fitness for purpose'. The following topics should be defined:

- definition of the quantitative information required
- definition of the determinands
- location, time and frequency of sampling
- accuracy requirements for analytical results
- use of data and data handling routines, including statistical calculations
- particular specifications for the quality assurance programme

The inclusion of a quality assurance system means that procedures are undertaken to produce data of stated quality. This is partially attained by analytical quality control activities which keep random and systematic errors within prescribed limits.

Particular attention must be paid to the following: Unambiguous definition of the determinand, description of the sample, the concentration range of interest, the accuracy required of results, and the expression of results.

5.1 Defining the Determinand

It is an obvious point, but worth emphasising, that the determinand of interest must be defined unambiguously. If this is not done, the analytical method employed may be not be appropriate. Many substances exist in water in a variety of forms or "species", and most analytical systems provide a differential response to the various forms. For example, when a separation of "dissolved" and "particulate" material is required, special care is necessary to define precisely the nature and pore-size of the filter to be used.

5.2 Sample Description

A precise description of the type and nature of sample is important before the analytical system can be chosen. The precautions to be taken when a sample is analyzed will depend to a high degree on the content of the sample. The concentration range of interest can have a marked effect on the choice of analytical technique; one parameter is the smallest concentration of interest. However it is also important to consider performance (freedom from bias, adequately small standard deviation of measurement) at the concentrations higher in the range of interest (e.g. at a water quality standard).

5.3 Defining the Required Accuracy

The following illustrates a logical general approach to be adopted for specifying the required accuracy of analytical results.

The limit of detection is the smallest concentration or quantity of a substance which can be expected to be distinguishable from the blank measurement. It is normal practice that the required limit of detection (c concentration units) is set at $1/10^{\text{th}}$ of the relevant water quality standard. For example, if the maximum admissible concentration for aluminium in a potable water supply was $200 \mu\text{g/l}$, the target limit of detection would be $20 \mu\text{g/l}$. The analytical technique employed would have to be able to achieve this limit of detection.

Accuracy targets are then defined as follows:

The total error of individual analytical results should not exceed c concentration units (e.g. $\mu\text{g l}^{-1}$) or $p\%$ of the result, whichever is the greater.

c is usually equivalent to the target limit of detection. $p\%$ is usually set at 20%. This value of 20% is realistically stringent; it is possible to achieve but it is moderately difficult; a total error target greater than 20% would be inadequate for most purposes. One less than 20%, would be very difficult to achieve.

To allow for an increase in relative error (as a percentage) at lower concentration, accuracy requirements must be expressed in concentration terms (rather than as percentages). It is important when setting targets to allow in the definition for the existence of both random and systematic errors; the two types of errors have different effects on the use of and decision taken using analytical results.

The tolerable total error is apportioned between error from random and systematic sources as follows:

"The systematic error (bias) of individual analytical results should not exceed $c/2$ concentration units (e.g. $\mu\text{g l}^{-1}$) or $p/2\%$ of the result, whichever is the greater"

"The random error of individual analytical results should not exceed $c/2$ concentration units (e.g. $\mu\text{g l}^{-1}$) or $p/2\%$ of the result, whichever is the greater."

A measure of the random error associated with analytical results is given by the standard deviation of results. The random error (95% confidence limits) is equal to (approximately) twice the total standard deviation of analytical results. Thus if $p = 20\%$, it follows that the maximum tolerable total standard deviation, s is $0.25p = 5\%$.

5.4 How is the target for total error met?

Random errors are assessed in tests of precision (see below) carried out over a period of approximately two weeks. In these tests, the total standard deviations of results for a range of samples and concentrations are estimated. To meet the requirements, these standard deviations must not be significantly worse than the precision targets, given above, of $c/4$ concentration units or 5% of determinand concentration, whichever is the larger. Adequate recovery of determinand from real samples is also checked at this stage. The laboratory will then take part in an interlaboratory tests to assess other possible forms of bias.

The laboratory has shown that it is able to meet the target for total error

6. Choosing Analytical Systems

Careful specification of analytical requirements is necessary to produce data of stated quality. Emphasis should be placed on the needs of the user of the analytical data. In setting up an analytical system, particular attention must be paid to the following items:

- the definition of the Determinand and the form or forms to be measured
- types of samples and possible interferences
- the concentration range and determination of small concentrations
- the maximum tolerable bias and standard deviation over the concentration range
- calibration and sensitivity
- practical considerations

Definition of determinand: This is discussed above. The key issue is that the analyst's selection of an analytical method must meet the user's definition of the determinand.

The concentration range and determination of small concentrations: It must be noted that determination of small concentrations in most cases is not only a factor in the choice of method. Determination of nutrients and metals at trace levels usually demands special precautions with respect to control of contamination and sample preservation.

Calibration and sensitivity: In order to convert analytical responses obtained for samples to concentrations of the determinand, a calibration procedure is needed. The analytical procedure used for calibration should be identical to that used for real samples and the calibration procedure must prescribe exactly the standard solution, number of concentrations, number of replicates, etc. The calibration normally includes the use of an analytical blank; any blank correction implied in the technique must be stated.

Types of samples and possible interferences: Most analytical techniques are capable of producing adequately accurate results when they are used to analyse a standard solution at the optimal concentration. Interferences can cause important errors when real samples are analyzed. Relevant information in a method specification must include the types of samples (fresh water, sea water, waste water, etc.) for which the method is suitable. Samples high in particles and suspended solids often give problems, especially in automated analytical systems using extremely small sample-volumes. Coloured or turbid samples offer problems in photometric determinations of COD and TOC. The potentially important role of sample-types in water analysis must be recognised. In selecting a method, the analyst needs to obtain as much information as possible on potential interferences for the sample types of interest. A measurement programme, e.g. a river survey, may often include a high number of very different types of samples. For this reason routine analytical laboratories often prefer robust, multipurpose analytical techniques applicable to a broad range of samples.

Accuracy (trueness and precision) required of results: A method does not possess a characteristic standard of accuracy - it only has the potential to produce data of a stated accuracy if it is used in the correct way. The actual

accuracy of data produced is a function of the overall analytical system. Although the method is a key part of the analytical system, it is not the only factor which may determine the size and nature of analytical errors. Often, other factors such as the analyst or the equipment may be more important.

Practical considerations: When discussing the requirements with the user and selecting suitable analytical systems to fit the measuring programme, the following practical points should be considered:

- the maximum period between sampling and analysis, in relation to sample stability
- the maximum period between sampling and the need to report the results
- the frequency of sampling and the total number of samples on each occasion
- the volume of sample available
- automatic or manual techniques
- equivalent analytical methods
- robustness and description of the proposed method
- applicability of the proposed method in the laboratory concerned with respect to cost, speed, etc.

Factors such as existing expertise, equipment which is available, convenience, speed of analysis and cost may have a great influence on the final selection of analytical systems. When analysis is required infrequently it may be necessary to adopt a different approach from that used for regular, frequent determinations. However, it is essential that the highest priority is still assigned to the production of data of adequate accuracy and that appropriate action is taken to ensure control of the measurement process and to provide an estimate of analytical accuracy.

Robustness and description of method: A "robust analytical procedure" is one for which the accuracy of analytical results is not affected substantially by small deviations from the written method (or by differing interpretations of parts of the method which are not unambiguous). Obviously, robustness is a desirable characteristic. One way of increasing robustness is by clear definition of all key steps in the method.

7. Performance Testing

7.1 Introduction

Once a method has been chosen for a particular application it is necessary to test the performance of its routine application. The emphasis should be placed on an examination of the performance of the whole analytical system, of which the method is only a part. All the components of the analytical system - instrumentation, analysts, laboratory facilities, etc. - should be examined before routine analysis is started.

This section summarises the approach recommended for the experimental estimation, and when necessary reduction, of errors; this stage should be completed before any samples are analyzed and may be called "preliminary error estimation".

7.2 Systematic error

The estimation of likely bias should already have been made in the initial evaluation of the technique. It will usually be impossible to check many of the most important sources of bias when a method is used routinely for the first time. A check on some sources of bias, by means of a spiking recovery, is included at this as part of the precision tests (see below).

7.3 Random Error

The estimation (and, when necessary, control) of random error is an essential precursor to routine analysis. Preliminary tests provide the necessary evidence that the precision of routine data is adequate and form the basis for routine quality control.

7.4 Precision Tests - General Experimental Design

The precision obtained in one batch of analyses is often better than that of results spread over a longer period of time. Estimates of precision from one batch of analyses may, therefore, give an over-optimistic idea of the precision of results produced during routine analysis.

For this reason, precision should be estimated from analyses taken from separate batches, spread over a suitable period. The duration of this period is a matter of choice and depends on which sources of random variation are to be assessed. Testing to give at least 11 batches of analysis is recommended as a compromise between the need to obtain an adequately reliable estimate of standard deviation and the need to minimise the effort required.

The approach described below allows the total random error to be separated into random error arising from variations within and between batches of analysis. This information is of value in indicating the dominant sources of

random error. Estimates of within-batch standard deviation are pooled from all batches and so provide an indication of what is achievable on a regular basis.

The basic approach is to make n determinations on a representative group of samples in each of m batches of analysis. In deciding on suitable values for n and m , care is required for two reasons:

(i) Too few analyses will not provide a worthwhile estimate of standard deviation.

The uncertainty on an estimate of standard deviation depends on the number of associated degrees of freedom. Designs of test which are likely to provide estimates of standard deviation with fewer than 10 degrees of freedom may prove uninformative;

(ii) It is desirable to design the test so that a satisfactory estimate of the dominant source of error is obtained. For example, if between-batch error is likely to be dominant, a design where $n = 10$ and $m = 2$ will give a relatively precise estimate of the less important source of error, but will estimate the dominant source of error very imprecisely. A more appropriate design would be for n to be made small and m large.

The experimental design recommended for general use is to make $n = 2$ and $m =$ at least 11 (to be sure of obtaining 10 degrees of freedom for total standard deviation). Such a design provides estimates of within- and between-batch standard deviation with approximately equal number of degrees of freedom. In particular, when within-batch errors are assumed to be dominant, values such as $n = 4$ and $m = 5$ could be chosen.

7.5 Samples to be analyzed

It is clearly essential that the solutions used for tests of precision show no appreciable changes in concentration during the period in which portions of them are taken for analysis. The solutions should also be sufficiently homogeneous that the concentration of the determinand is essentially the same in each portion of a solution. Water samples may sometimes be inadequately stable to allow tests over several days (adequate sample stability can sometimes be achieved by suitable preservation techniques, but these should be used only if specified in the analytical methods of interest). It is convenient to use standard solutions when estimating precision. Standards of any desired concentration can be obtained, so that a range of concentrations is available for the estimates of precision; samples of the desired concentration may not be available. However, the analyst should also have estimates of the precision for water samples as it should not, in general, be assumed that standard solutions and water samples can be analyzed with the same precision. Therefore, precision estimates for both types of sample should normally be obtained. For these tests, standard solutions and samples should be analyzed, measured and evaluated in exactly the same way as normal routine samples. When the limit of detection is of interest, a solution containing essentially none of the determinand but preferably containing the sample matrix, should also be tested. The inclusion of determinand-free matrix is often difficult to achieve, so, as a compromise, limit of detection can be estimated from determinations made on an analytical blank.

Clearly, the greater the number of different solutions included in the tests, the greater the information obtained on precision, but a compromise with the effort required will often be necessary. As a guide to the minimum

number of solutions, it is suggested that the following should be included in each batch of analysis.

(i) Two standard solutions or samples at concentrations near the upper and lower concentrations of interest.

(ii) When standard solutions are used for (i), one water sample near the average concentration encountered in samples.

(iii) A spiked water sample; the sample analyzed in (ii) with the addition of a known quantity of determinand. If estimation of precision at a variety of different concentrations is of key interest, the level of the spike should be chosen so that the final concentration differs from those of the other solutions. Otherwise, it is advisable to make as large an addition as possible, consistent with the practical range of interest (and useful range of the analytical technique).

(iv) Whenever an estimate of Limit of Detection is required, n replicate blank samples should be analyzed. A blank sample, as distinct from an analytical reagent blank, is a natural sample which contains no determinand. It may not be possible to obtain a sample which approaches this ideal. For most determinands, under these circumstances, an analytical blank solution may be used as a substitute. If precision at the blank level is known to be dependent on the sample matrix, it will be necessary either to use blank sample which contains the determinand (and risk a likely overestimation of Limit of Detection) or to take steps to remove the determinand from a sample so that it may be used as a blank. When, as with some chromatographic techniques, no response is obtained for a blank, it is recommended that a blank is spiked with enough determinand to produce a measurable response. This can form the basis of an estimate of Limit of Detection. (The measured values should not, of course, be used for blank correction).

In any event, at least a single analytical blank per batch should be included as one of the solutions analyzed to allow calibration. The routine approach to calibration should be adopted for each batch of the performance tests. The test samples should be taken through the whole analytical procedure.

7.6 Precision Tests for Unstable Samples

The simplest approach to the design of precision tests is to prepare all samples for analysis at the start of the tests and use these without preparing fresh aliquots for each batch of analysis. This is satisfactory provided there is no sample instability. The possibility that sample instability may be present rules out the direct estimation of between-batch standard deviation and may call into question the assessment of within-batch standard deviation.

For further discussion of this see Hunt and Wilson [1986].

8. Statistical Considerations

8.1 Randomisation

Randomisation of the order of analyses should normally be used to eliminate the effects of any systematic changes in factors that cannot be controlled, and which might otherwise cause false conclusions to be drawn.

8.2 Rounding of data

It is usually desirable to record the primary experimental results with the greatest discrimination possible; three significant figures should be aimed for except when near the limit of detection when only one or two will often be possible.

8.3 Calculating analytical results

Standard deviations should be calculated from the set of results for each sample. Thus, for each solution analyzed, two results are available from each batch, corresponding to the first and second portions of the sample to be analyzed. These results should, if necessary, be blank corrected using the analytical blank for the appropriate batch. The within-batch standard deviation of the blanks is used to calculate the limit of detection.

8.4 Estimating precision - within-batch and between-batch errors

It is useful to analyse the results to obtain estimates of the within-batch and between-batch standard deviations, s_w and s_b , respectively. These two estimates are needed to allow an estimate of the total standard deviation, s_t , to be obtained. A statistical technique known as "Analysis of Variance" is used. This calculation identifies the different sources of variation and allows the estimation of total standard deviation.

The Analysis of Variance is used to give two statistical parameters, the within- and between-batch Mean Squares, M_0 and M_1 , respectively. The Mean Squares are then compared to determine whether M_1 is significantly greater than M_0 , that is, whether there is a statistically significant between-batch source of error. The theoretical basis of the technique is described in statistical texts, but in the present context it may be taken simply as a convenient means of calculating s_w , s_b and s_t .

The observed value for total standard deviation is compared with the target maximum value. If it not significantly larger than the target, the precision of the system is considered to be satisfactory. Similarly, recovery is tested to ascertain whether or not recovery is not significantly worse than a specified range (usually 95% to 105%).

9. Routine quality control - control charts

It is not sufficient for a laboratory to adopt a suitable method, check its performance initially and assume that, thereafter, the results will be of adequate accuracy. The chosen method must be subject to routine tests to ensure that adequate performance is maintained because many factors can cause a deterioration of accuracy with time. It is in this aspect of AQC that control charts are employed.

9.1 Function of Control Charts

If a set of analytical results is obtained under conditions of routine analysis, some variation of the observed value will be evident. The information is said to be statistically uniform and the process is said to be under statistical control if this variation arises solely from a given set of sources of random analytical variability. It is worth noting that the achievement of statistical control does not mean that the system is operating in the best possible way, only that it has been stabilised. Loss of statistical control is characterised by the introduction of sources of systematic error or by a change in the size of the random error operating in the analytical method.

The function of a control chart is to identify any deviation from the state of statistical control - to see if performance has changed from its previously stable state.

9.2 Shewhart Control Charts

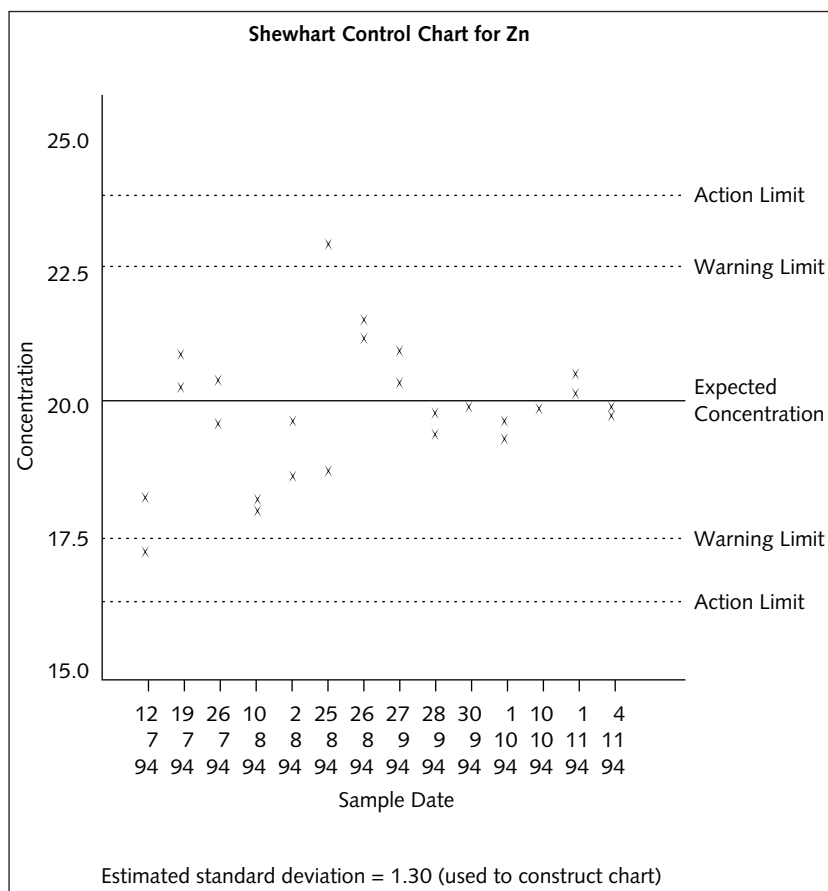
The most widely used form of control chart is the Shewhart chart. This takes the form of a chart on which the quality characteristic of interest is plotted against time (see Figure 5). This type of chart provides a check on both random and systematic error (from the spread of results and their displacement respectively).

Assuming the results for the control sample follow the Normal distribution and that only chance causes of variation were operating, it would be expected that only 0.3% of results would fall outside lines drawn at 3 standard deviations above and below the population mean value. Individual results would be expected to fall outside these limits so seldom that such an event would justify the assumption that the analytical procedure was no longer in statistical control - i.e. a real change in accuracy had occurred, and hence that remedial action was required.

Therefore, insertion of lines corresponding to: (a) the mean value, μ , expected for results, and (b) the limits $\mu \pm 3s$ (where s is the standard deviation of results) provides objective criteria for the interpretation of the chart. The limits $\mu \pm 3s$ are called the "action limits" of the control chart.

It is also useful to insert two other lines on the chart at $\mu \pm 2s$. If the method is under statistical control, approximately 5% of results may be expected to fall outside these lines, the so-called "warning limits" of the chart.

Figure 5
Shewhart Control Chart.



The fact that one result falls outside these limits need warrant no action provided the next result is inside. Such an occurrence serves as a warning of loss of statistical control and indicates that a possible source of increased error (either random or systematic) may be present.

9.3 Control Charts of Individual Measurements

The simplest form of control chart is one in which the results of individual measurements made on a control sample are plotted on the chart in a time series. An estimate of total standard deviation (if one is not available from tests of the performance characteristics of the analytical method), can be obtained by performing one determination on the chosen control sample in each batch of analyses for say 20 batches. The control sample should be analysed in the same way as routine samples (eg with respect to replication of analysis).

An estimate of the mean is calculated. This is used as the control line of the chart. As the chart progresses and more data points become available, the estimate, \bar{x} , should be recalculated with a correspondingly greater number of degrees of freedom.

This type of chart (see Figure 5 for an example) provides a check on both random and systematic error (from the spread of results and their displacement, respectively). It is an easy tool to be used by the analyst at the bench because it is simple to plot and no data processing is needed. It is useful when the size of analytical batches is variable or when batches consist of only a few determinations. Individual result charts are used widely and often form the mainstay of a laboratory's approach to control charting.

However, this type of chart may produce false out of control values if random error does not follow the Normal distribution. For these reasons, a range of more specialised types of chart has been devised. These are described below.

9.4 Control Charts of Mean Results

Here the approach is the same as for single results except that n determinations are performed on the control sample in each batch analysis. The advantage of this chart over one consisting of individual measurements is that the influence of routine random error is reduced by a factor of \sqrt{n} and therefore the probability of detecting a small bias is increased. The statistical distribution of mean results can be relied upon to be Normal, so the interpretation of the chart is placed on a sound footing.

Again, the chart is plotted against the overall mean. The appropriate standard deviation is that which relates to the precision of the mean of n determinations from batch to batch.

9.5 Control Chart of Spiking Recovery

The recovery control chart is used as a check on systematic errors arising from matrix interferences. A separate control chart for each matrix is required in water analysis, because samples of varying matrix composition may be subject to errors of differing sizes and nature.

In this case the parameter of interest is the recovery of a known quantity(s) of determinand added to a natural sample. Two determinations are required; one on the unspiked and one on the spiked sample. The percentage recovery is calculated and plotted on the chart.

9.6 Control Chart of Differences

For this kind of chart, the differences, between determination of two aliquots of the same sample are plotted on the chart. It is essential always to subtract the second result from the first and plot the differences with due regard to their sign. The expected value for the chart is zero. This type of chart is principally of value when the determinand concentrations in samples lie within a sufficiently narrow range that essentially the same value of standard deviation is applicable to all samples. Otherwise, it may be necessary to operate several charts, each corresponding to a different concentration level.

9.7 Control Charts of Range

A range chart is used to control the precision of an analytical method. In addition, it allows some assessment of errors caused by calibration drift. In each batch of analysis a control sample is analysed n times ($n > 2$). The range is the difference between the greatest and smallest result. The mean range is calculated from the ranges obtained in each of several batches of analysis.

The action and warning limits are calculated as multiples of the mean range.

9.8 Control chart for Blanks

It is also useful to plot a control chart of blank determinations to aid in the detection of abnormal values, such as may be introduced by the use of a batch of contaminated reagents. This type of chart cannot be interpreted in the same way as those described above, because the fact that results of blank determinations are higher or more variable (from one batch of analysis to another) than usual does not necessarily mean that the accuracy of results is affected. However, erratic variations in blank results are generally undesirable since they call into question the validity of the blank value as a suitable correction to be made to sample responses and may indicate the introduction of some source of sample contamination. This chart is to be used merely as a guide and there is therefore no need to insert warning or action lines.

9.9 Types of Control Samples

A control sample is a sample material whose analytical results are used to construct control charts, for example, standard solutions, real samples and blank. Different types of control samples help to detect different types of error. The choice of control samples depends on the matrix, the analytical method and the accuracy required.

The sample should be considered to be adequately representative of the real test material (i.e. it should be subject to the same potential sources of error). It should be adequately homogeneous (and stable over a suitable period of time) to allow identical subsamples to be taken. If a check on systematic error is required, the sample should be of known composition.

The factors to consider when choosing the type of control test and the samples to use are as follows: A sample of known concentration is the best type of control sample. These are analysed at regular intervals (at least once in every batch of analysis) and the results plotted on a control chart with the nominal concentration of the control sample as the expected value. The scatter of individual results gives a check on precision and their average value indicates any systematic error. Control samples should be representative of the samples routinely analysed in terms both of their determinand concentration and of their sample type. For spiking recovery charts, the best approach is to arrange that the concentration of the spiked sample is made as large as possible, consistent with remaining inside the same range of determination as the unspiked sample.

Examples of some control samples with their important characteristics are given below:

- (a) samples of known composition
 - (i) Standard reference material
 - composition established by standards organisation, often in an interlaboratory exercise
 - a realistic surrogate sample, provided the relevant matrix is available, hence a check on all sources of error
 - often a range of concentrations not available
 - sometimes wide limits for certified values
 - expensive for everyday use
 - (ii) In-house reference material
 - composition established by user laboratory by several means or by trusted method

-
- chosen to be an ideal surrogate sample with respect to matrix and composition
 - not a check on all sources of error, but useful for comparative checks between different batches of analysis (standard value may not be reliable)
 - inexpensive
- (iii) Standard Solution
- prepared independently of calibration standards from pure materials
 - a check only on calibration error (random and systematic), owing to absence of matrix
 - of chosen determinand composition
 - independent of analytical techniques
 - very inexpensive
- (iv) Surrogate Determinand
- a well-characterised substance is taken as representative of the determinand (often used for empirical determinations e.g. BOD)
 - acts only as an internally consistent check on performance, relies on the assumption that the surrogate is realistic
 - usually inexpensive
- (b) Real sample determined in duplicate
- a check on random error (within-batch standard deviation) for the samples of interest
 - systematic error not checked but may help to identify carry-over or drift problem
 - must be able to split a real sample into two identical portions for analysis - hence may help to indicate sample handling difficulties
 - Inexpensive
- (c) Spiked sample
- a real test material analysed with and without a known addition of determinand
 - a realistic surrogate with respect to matrix, of chosen concentration
 - not a test of all sources of error (systematic error caused by some types of speciation of determinand or that which is independent of concentration may not be detected)
- (d) Analytical Blank
- a reagent blank sample relating to the calibration for the batch in question
 - not a direct check on a specific type of error but may indicate contamination either of a particular batch of reagents or during sample preparation.

9.10 Choice of Concentrations

When routine samples always contain very similar concentrations of the determinand, that concentration is recommended for control standard solutions described above. When samples contain a wide range of concentrations and standard deviation varies with concentration, at least two control standards of different concentration should ideally be analysed. However, the required effort may not be available, and if only one control standard is to be used, a decision on the best concentration is needed. Changes in the slope of the calibration curve are best detected by the use of control standards whose concentration is that at which the relative standard deviation is a minimum. This concentration usually corresponds to, or is close to, the upper limit of the concentration range of the method. A concentration near

the upper limit of the analytical method is therefore suggested, if no other guide is available to the choice of control standard (for example, it may be desired to monitor analytical accuracy at some specified concentration of interest defined, perhaps, by a standard for water quality).

9.11 The Interpretation Of Control Charts

Control charts, or at least the control limits, such as those described above are strictly valid only when the analytical results follow the Normal distribution. For many applications in the field of analysis the Normal distribution is likely to be sufficiently well obeyed for the recommendations above to be used generally.

The fact that a result is observed as out of control should not be disregarded if, for example, the method involved is easily capable of meeting the requirements for analytical accuracy. The power of one control analysis per batch (often performed on a standard solution which may not be subject to errors as large as real samples) to indicate a deterioration in analytical performance may not be very great. Thus, it is advisable to take action when loss of control is signalled, since the control analysis may be a warning of increased error which may have been introduced some time previously and which may be more severe for real samples. It is therefore emphasised that control charts provide objective guidance in the control of analytical errors which should be viewed together with other information.

The rules of interpretation of control charts should be defined and observed strictly. The following criteria for out-of-control situations, have been recommended for use with Shewhart charts:

- a) one result outside the action limit ($\pm 3s$) where s is the standard deviation of results and
- b) two consecutive results outside the warning limits ($\pm 2s$)

Other decision rules may be used to supplement the two described above. These include:

- 7 consecutive control values with rising tendency
- 7 consecutive control values with falling tendency
- 10 out of 11 consecutive values being on one side of the central line

The consequence of adopting these additional decision rules will vary according to the type of error which is of interest. For example, the decision to treat 10 out of 11 consecutive results on the same side of the x-axis as "out of control" will be of no benefit in detecting increased random error. However, it will aid in the identification of small biases. It is worth bearing in mind that any increased power to detect departure from the state control will be accompanied by an increased incidence of "false alarms".

The following out-of-control situations might apply to the range type of control chart:

- a range falls outside the upper action limit
- a range falls below the lower action limit
- 7 consecutive control values show an ascending/descending tendency
- 7 consecutive control values lie above the mean range

9.12 Measures to be taken in out-of-control situations

An out-of-control situation occurring on a control chart implies that a similar error might apply to the analysis of routine samples. It is very important to identify and eliminate the cause of error in order to re-establish and maintain control over the performance of the analytical system.

When an out-of-control situation has arisen the following course of action should be taken:

- The defined procedure for action to be taken should be followed. This should include instructions for the reporting of the incident to senior laboratory staff. The reporting of the associated data for real samples should be suspended.
- The samples associated with the control standard should be reanalysed. If this is not possible it should be recorded that no data are available due to AQC failure.
- The reasons for the failure should be investigated. The analysis of the control sample is repeated, strictly following the analytical method and avoiding gross errors. If the new result of the control sample shows that the method is under control again, it may be assumed that the method of analysis had not strictly been observed on the previous batch of analyses or that a gross error has occurred. However, if the result of the analysis of the control sample is erroneous but reproducible, a systematic error is very likely to exist.
- The control result should be plotted on the control chart. Data points for which a definite cause has been identified should not be used in updating the control limits.

As a minimum, the following points should be noted in the 'control breach log':

- date,
- batch,
- determinand concerned
- analyst
- the outcome of investigations
- remedial action
- were samples reanalysed or resampled?

9.13 Control Charts - Updating

Consider the case where the analytical system has, over a long period, gradually improved in precision. The initial action and warning limits will be wider than those which correspond to twice and three times the standard deviation relevant to the current data on the chart. This means that the power of the chart to detect loss of control will be poorer than expected.

The ideal way in which to operate a chart is to use the best possible estimate of the current standard deviation. The relevant standard deviation therefore requires updating if any change in performance occurs. It must be borne in mind that a substantial number of data points are needed to give a reliable estimate of standard deviation. The approach to adopt is summarised below:

"Review the last 60 data points on the chart. If there are greater than 6 or less than 1 cases where the 2s warning limits have been exceeded, there is clear evidence that the precision of analysis has changed and the control

chart should be updated. The action and warning limits should now correspond to 3 and 2 times the new standard deviation of the last 60 results. The new mean of the last 60 results should also be calculated and compared with the calculated mean of the previous 60 points.

Wherever new control limits are calculated as a result of change in precision, review the new standard deviation (and where appropriate the bias implied by the new mean) against the accuracy targets which apply to the analyses in question. Take corrective action if necessary.

The above procedure should not be carried out every time a new data point is generated. The check on the validity of the current control limits might be worthwhile after, say, 20 successive points have been plotted - though any obvious changes in the operation of the chart would warrant immediate action."

10. Quality control in sampling

Careful attention to the soundness of sampling and sample handling systems is essential if data of adequate accuracy are to be obtained, and it is therefore necessary to ensure that appropriate control tests are applied to these aspects of the overall process, as well as to analysis.

Control tests of sampling and sample handling have the same basic objectives as their counterparts in analysis, namely to ensure that any important deterioration of the accuracy of results, arising from these steps, is detected as rapidly as possible so that corrective action can be taken. In addition to general "good practice" aspects of routine quality control in sampling (e.g. checks and preventative maintenance on sampling equipment), the specific control tests described below should be considered and put into practice wherever appropriate and practicable. Attention to the following is recommended.

(a) Routine tests on the effectiveness of the cleaning of sampling vessels and sample containers.

Whilst field blanks (see below) give some check that such vessels and containers do not cause important contamination of samples, laboratory tests have the advantage that they can be routinely undertaken before sampling is performed; thus, if contamination problems are revealed, they can be rectified before sampling, thereby saving potentially wasted effort and resources.

(b) Field blanks to provide routine checks on contamination.

Field blanks are samples of (typically) deionised or distilled water which are taken into the field and treated, so far as possible, in exactly the same way as real samples. The exact details of the approach to be followed will, therefore, vary according to the particular system being controlled, but field blanks should generally be subjected to the same preparatory steps (such as filtration and centrifugation) as are applied to real samples, and should subsequently be handled, preserved and stored in the same way.

(c) Field check samples to provide routine checks on sample stability.

In situations where, despite careful initial selection and testing of equipment and procedures, the stability of samples is in question, it can be useful to prepare check samples of known determinand concentration and treat them, so far as possible, in exactly the same way as real samples. Such a check sample may be prepared by dividing a typical sample into two and making a known addition to one portion. The recovery of the added determinand is a check that sample preservation, transport and storage are satisfactory and that loss of the determinand - by absorption or evaporation of volatile components, for example - is adequately controlled.

(d) Duplicate samples to provide routine checks on sample stability.

Collection and analysis of duplicate samples can provide a check on the contribution of sample collection and handling to overall random error.

(e) A routine chart of field blanks may be a valuable way of monitoring control over sample contamination.

Control samples of types (b) and (c) are similar to some of the analytical control samples described previously. Indeed, when analysed they will inevitably cover the sources of analytical error controlled by those samples (as well as the potential sources of error in sample collection and handling that they are specifically intended to control). However, their use should not be regarded as a substitute for the use of the relevant analytical controls, because they can only be fully effective in controlling errors in sample collection and handling if the analytical process itself is under separate and effective control.

11. Introduction

11.1 Introduction

The design of an inter-laboratory test and the way in which the results are interpreted should take account of the context in which the test is performed; it should reflect the aims of the analytical work to which it relates. It is particularly important, before an inter-laboratory test is carried out, that the objectives should be examined carefully by both participants and organisers. Such considerations will form the basis of the approach which should be adopted and will provide both the rationale for laboratories' participation and the basis for an acceptable means of interpreting the data produced.

As far as the individual laboratory is concerned, the usual reason for taking part in an inter-laboratory test is to supplement its within-laboratory quality control, as a means of detecting and guarding against undiscovered sources of error. However, this may not be the main reason for organising a given interlaboratory test. The aims of interlaboratory tests fall into several categories. The most important of these are discussed below.

11.2 Aims of inter-laboratory tests

(a) to obtain a general picture of analytical errors existing in a group of laboratories

It might be necessary to estimate the accuracy of data produced by a group of laboratories which share a common interest. For example, the laboratories concerned might be contributing data to a monitoring programme, or they might be the only ones analysing a given type of sample. In this case, the aim may be achieved by the simple approach of circulating samples for analysis. The number of samples distributed need not be great and the extra work requested of participating laboratories is relatively small. An approach which has been described by Youden [Youden and Steiner, 1982] known as the paired sample technique, provides a valuable means of summarising the results of an inter-laboratory test in graphical form. This has been widely used to summarise the accuracy achieved by a group of laboratories.

This application of interlaboratory testing has the drawback that it is often not possible to draw unambiguous conclusions concerning the size and nature of errors. The simplest of such tests generate diagnostic data of very limited scope. This, and the fact that there is often little supporting information, means that such tests are not likely to have much influence on the accuracy of results. The need to review (and where necessary, to improve) the standard of accuracy achieved should always be borne in mind. Once the important step of defining an acceptable standard of accuracy has been taken, the aim of even the least ambitious interlaboratory tests tends to become that described in (c) below.

(b) to assess the performance of an individual laboratory - 'Proficiency Testing'

Proficiency testing is a periodic assessment of the performance of

individual laboratories (and to some extent of a group of laboratories). It is usually carried out by the distribution of typical test materials for unsupervised analysis by the participants. Proficiency tests are usually part of a programme which is organised by an independent body. Proficiency testing schemes are recommended for all testing laboratories, provided the sample type and determinand concentration relate to the samples analysed routinely. They are used as a routine, but relatively infrequent, check on bias.

The advantage of proficiency tests is that they can allow detection of otherwise undetected and unforeseen sources of bias. They play a key role in demonstrating the need for remedial action in laboratories with long-term problems in achieving data of appropriate quality, and the efficacy or otherwise of any remedies applied. Moreover, successful proficiency testing schemes demonstrate that participants have the ability to produce data of a given quality on the occasions of the tests, and hence have the potential to do so on other occasions. The limitations of simple proficiency tests fall into four main categories:

(i) they are necessarily limited in the scope of materials and determinands that can be prepared and circulated for testing. The performance of a laboratory in a given test often has to be taken as an indication of its capabilities for a wide range of related analyses;

(ii) the samples analysed are usually identifiable as check samples and may be analysed with more than usual care. Hence the standard of accuracy achieved is not necessarily typical of laboratories' routine operation;

(iii) they are repeated over a long timescale and therefore cannot indicate the short-term variations in quality that can occur within laboratories;

(iv) although they function as good indicators of overall data quality, they do not identify clearly the sources of errors and thereby point to effective remedies. Their limited scope and frequency does not make them, in isolation, a particularly efficient means of evaluating an individual laboratory. A series of such tests (when not supported by within laboratory quality control activity) often only illustrates the variability of the apparent performance achieved.

It is important that the performance of an individual laboratory should be judged with respect to its own requirements (i.e. those of its clients), not necessarily against the standards achieved by other laboratories taking part in the exercise or by a sub-set of 'expert' laboratories.

(c) to ensure that a group of laboratories achieves an acceptable standard of accuracy - that analytical errors are controlled to within adequately small limits.

This is the objective towards which many interlaboratory test programmes are directed, either explicitly or implicitly. As the complexity of the interlaboratory test - in terms of the number and type of samples tested and the work required from the laboratories - is increased, it becomes possible to draw more conclusions concerning the sources and nature of errors which may be present. On the basis of this knowledge it is then possible to direct efforts towards achieving the desired level of accuracy. In achieving this objective, the importance of a sound programme of within-laboratory quality control cannot be overstressed. As stated above, the inter-laboratory test supplements within-laboratory activity, providing a means of detecting and guarding against undiscovered sources of error and acting as a demonstration of the accuracy achieved.

(d) to stimulate interest in data quality

To state that the accuracy of analysis is a subject of great importance is not effective in focusing attention on issues of data quality. Often an interlaboratory test is the best means of generating an awareness of the need for quality control, especially if the problem of measurement error is not widely recognised.

(e) to certify a Standard Reference Material

A special case of the use of inter-laboratory tests is to arrive at a consensus (certified) value for the composition of a reference test material. This approach is only of value if a group of laboratories of proven expertise take part.

(f) to test the capabilities of an analytical method

This application is the so-called 'collaborative trial'. A collaborative trial is often used in the approval of a candidate method for standardisation. Such a study will show whether the method allows a suitably chosen group of laboratories to obtain comparable results on the same samples. Its aims are different from most other interlaboratory tests - it is assumed that the 'laboratory effect' on the accuracy of data is well controlled and that errors are a function of the method. Consequently, a collaborative study gives little or no help to individual laboratories which wish to identify (and where necessary control the size of) the different sources of analytical error affecting their results.

The most important recommendation which can be made to participants and organisers of interlaboratory tests is that the aims of any test should be considered carefully and stated clearly. It is not essential that all participants have the same aim, only that each reviews the design and interpretation of the test with respect to his own requirements. However, it is clear that unless participants in any given test share largely common aims, it is difficult to design the test a way which will prove satisfactory. The choices of materials, determinand levels and standards of acceptable accuracy will all prove to be very difficult unless there is a consensus concerning the objectives of the test and of the analysis itself.

11.3 Between-laboratory Tests

Since laboratories following the recommended approach to quality control will have first established control over random error, attention in interlaboratory tests should be directed predominantly towards the detection of systematic errors.

Features of inter-laboratory tests Whatever the purpose of an inter-laboratory test, there will be certain common issues which must be considered in arriving at an appropriate design. Advice cannot be given here which is appropriate in all cases but participants in or the organisers of inter-laboratory tests may find it useful to consider the following points.

(a) General considerations:

- organisation
- general information to participants
- the determinands of interest
- the number of participating laboratories and how they are selected
- the way the test is financed and the timetable for analysis and reporting

(b) The test sample/s

- the type of sample
- the number of samples to be distributed
- the range of concentration of determinand/s to be covered by the samples sent out;
- the range of interest to participants

(c) Sample preparation

- how to ensure sample homogeneity and stability
- how to preserve the sample
- whether or not to use sample concentrates
- whether to use split-level samples or uniform-level samples
- whether or not to use reference materials

(d) Analysis and reporting

- preparation of written instructions to be followed by participants
- other information required from laboratories
- the number of replicate analyses required from each participant
- the choice of analytical method

(e) Evaluation of the test

- how to determine the nominal or reference concentration
- the mathematical/statistical treatment of the data
- assessment of performance
- performance criteria
- the form in which the test is reported.

12. Quality control for lengthy analytical procedures

Some multistage analytical procedures, for example, the determination of trace organic contaminants, are capable of producing relatively few results at a time. This raises the question of how to implement quality control measures which were initially put into practice with high throughput techniques. The argument that because organic analyses are time-consuming, they should not be subject to performance tests of the same complexity as, for example, nutrient determinations is unsound.

An analytical result which takes hours to produce should be supported by performance and quality control information of at least the same reliability as that associated with simpler determinations. Indeed, because trace analysis is subject to greater uncertainty and is more costly to repeat, it can be argued that proportionally more effort needs to be directed towards quality control. The maxim that eighty results of known and adequate accuracy are better than one hundred of unknown and probably inadequate accuracy remains true. It is essential, therefore, that the performance testing carried out for trace analyses is at least equivalent to that recommended above. The stated approach to tests of precision and recovery should not be regarded as an ideal only attainable under favourable circumstances. Rather, it is the minimum of testing which will provide a modestly reliable indication of performance. For trace analysis, there is a strong case for expanding the range of samples tested to include checks on precision and recovery from samples of differing matrices. Where Limit of Detection is of special interest, it is particularly important that an estimate is obtained from multi-batch tests, rather than from replicate determinations performed on a single occasion.

Similarly, the approach to routine Quality Control should follow the above recommendations.

13. Analyses carried out infrequently or on an ad-hoc basis

The procedures recommended for preliminary performance tests and routine quality control are most easily put into practice for analyses which are carried out regularly and often. It is necessary to consider what approach to quality control should be adopted for analyses which may be performed infrequently (say less than once per month) or which may be undertaken only once. The same considerations apply to analyses carried out over a short period in relatively few (say less than five batches).

Two main features distinguish this type of analysis from frequent, regular determinations. Firstly, any quality control activity is likely to take up a relatively large proportion of the total analytical effort compared with routine analyses. This is inconvenient and expensive, but it is a consequence of organising analysis in this way. It should not be used as an excuse to avoid evaluation of the analytical system. Any analytical system used to produce data should be tested to provide an estimate of its performance. Not to test would be to provide data of unknown accuracy. This is unacceptable to users of analytical data. Tests as described above are recommended as a means of providing background performance data for all analytical systems.

Secondly, it is not possible to establish and maintain a state of statistical control in relatively few batches of analysis. This is an important drawback of not carrying out frequent, regular batches of analysis. It may be a reason why analytical work might be best subcontracted to laboratories which do have reason to perform the determination in question frequently. However, when analyses must be carried out on a one-off basis the following approach is recommended. As a minimum, quality control measures should include:

- checks on spiking recovery in the matrix of interest;
- replicate analyses of samples;
- use of field and procedural blanks;
- confirmation of the calibration using material from an independent source;
- use of reference materials (where appropriate CRMs are available) as blind controls.

The proportion of samples analysed more than once should not be less than 20% but could be as large as 100%, in the case of very small batches or highly important analyses. Single analyses of samples is an acceptable approach only when a state of statistical control can be established and maintained.

14. Conclusions

The idea of fitness for purpose in analysis can be defined as the production of analytical results which meet the needs of the data user. This concept has two principle components: the control of the analytical process and the demonstration that adequate control has been achieved.

Use of the AQC techniques summarised above can ensure that analytical systems produce data of appropriate quality. If properly executed, quality control procedures can monitor the various aspects of data quality over appropriate time intervals. Where performance falls outside acceptable limits, the data produced can be rejected and, after remedial action, the analysis repeated.

The use of controlled analytical systems within a well-organised, documented laboratory environment forms the basis of a Quality System. This can be use to demonstrate that data reported to the client meet the required standards of reliability.
