

## Accuracy and precision in sampling water

by David Walker, Chair of ISO/TC 147, Water quality, SC 6, Sampling (general methods)

In environmental work much attention is rightly paid to achieving accurate and precise methods of laboratory analyses, although similar attention to sampling methods has often not been the case. This is a little surprising, as poor quality sampling can negate all the time, effort and cost involved in the development and application of sophisticated laboratory methods.

Sound sampling methodology is particularly important in environmental quality work, where the natural and anthropogenic variability of the systems being sampled (e.g. river estuarine and marine ecosystems) is often great, and significant errors in estimating true quality can arise, no matter how accurate and precise the laboratory methods used to test individual water samples are.

For example, there are approximately thirty million seconds in a year and it is quite common to assess annual quality at a river site from the results of 12 monthly samples, each taken over a matter of seconds. This will naturally be subject to a 'lottery effect'. We therefore need to understand the implications of this 'lottery effect' – often termed sampling error – in our decision-making, and to provide sampling guidance that takes this into account.

### Environmental water quality sampling

The production of standards and guidance documents in water quality assessment has a long tradition within ISO through its technical committee ISO/TC 147, *Water quality*, although most work has centred on the laboratory methods used to measure chem-

ical and microbiological constituents present in water samples, in addition to field-based biological assays.

It is only within the last 30 years that serious attempts have been made to develop formal methodologies designed to guide those involved in the important process of taking the samples, prior to the submission of the samples for laboratory analysis.

**“The production of standards and guidance documents in water quality assessment has a long tradition within ISO.”**

In 2004 subcommittee SC 6, *Sampling (general methods)*, of ISO/TC 147 celebrated 30 years of work and has been in the forefront of highlighting the importance of rational sampling methodology, particularly in the field of environmental water quality work. During this period, a total of 19 parts of ISO 5667, *Water quality – Sampling*, have been developed and published, including several revisions of some of the more well-established standards. Of these 19 parts, no less than 15 are associated with environ-

### About the author



**David Walker** has been Chair of ISO/TC 147, *Water Quality*, SC 6, *Sampling (general methods)*, since 1997. Originally trained as a graduate industrial chemist in

the gas industry, Mr. Walker holds a diploma in water pollution control and is a Chartered Scientist and Fellow of both the Royal Society of Chemistry and Chartered Institute of Water and Environmental Management. He has worked for most of his career in water and wastewater treatment utilities and in environmental regulation for government agencies within the United Kingdom, but now works as an independent environmental consultant.



## Environmental sustainability

mental water sampling, either directly or indirectly.

It is encouraging to note that the wide applicability of the standards developed by the committee has been recognized by the European Committee for Standardization (CEN), with two of its technical committees adopting standards from the ISO 5667 series.

In the environmental quality area, CEN/TC 230, *Water analysis*, has adopted the first three general parts of ISO 5667, covering the design of sampling programmes, the choice of sampling techniques, and methods for the preservation and handling of samples, plus part 16 on biotesting of water samples.

In addition, SC 6 is currently working on a new project that is closely associated with the design of sampling programmes. This relates to the provision of guidance on the use of sampling data that is subsequently used for more strategic decision-making, which can include judging overall compliance of an environmental site with limit value thresholds associated with environmental quality objectives, and (for effluent discharges to the environment) legal discharge limits.

This guidance is expected to be the subject of a new part of the ISO 5667 series to be published within the next two years and is discussed later in this article.

Currently, the wide diversity of guidance related to environmental quality sampling can be gauged by reference to an extract from the current list of standards produced within the ISO 5667 series (see **Figure 1**).

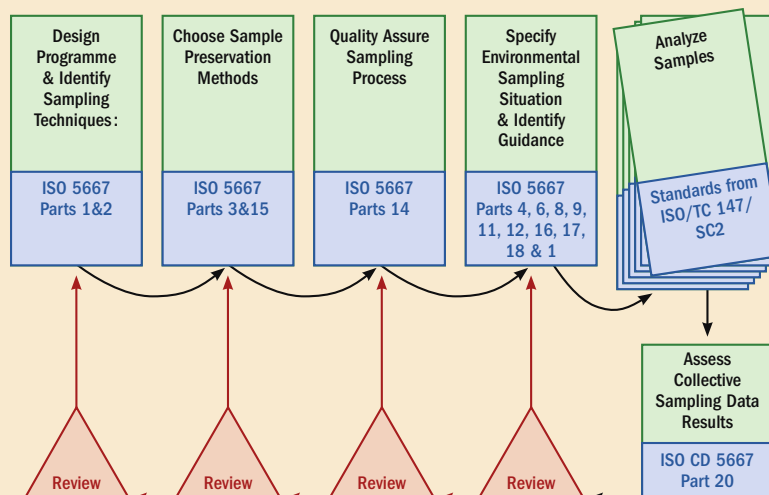
The relationship between the various types of sampling guidance and how this fits into the general process for carrying out a sampling programme can be seen in **Figure 2**.

### Three types of sampling guidance

The guidance developed within the ISO 5667 series over many years can be classified broadly into three types:

- Design of sampling programmes and guidance on general sampling techniques,
- Quality control of the sampling process,
- Provision of sampling guidance for individual environmental sampling situations (e.g. rivers, groundwater, precipitation and marine sediments).

**Figure 2 - Relationship of sampling guidance within the ISO 5667 series**



### Decision-making from sample data

The design of sampling programmes and their execution (including the use of appropriate sampling techniques) is normally the main concern of those in charge of sampling operations. This has been the primary focus of ISO/TC 147/SC 6 in its development of sampling guidance during the last 30 years.

However, the purpose of sampling in environmental water quality work is to estimate some aspect of the true quality of water from the analysis of a finite (often small) number of individual samples that are essentially short quality 'snapshots' in time.

The effectiveness of a particular sampling operation will be determined by how close these estimates are to the true values being sought, with the

<b>ISO 5667-1: 1980</b>	Guidance on the design of sampling programmes (under joint revision with Part 2)
<b>ISO 5667-2: 1991</b>	Guidance on sampling techniques (under joint revision with Part 1)
<b>ISO 5667-3: 2003</b>	Guidance on the preservation and handling of water samples
<b>ISO 5667-4: 1987</b>	Guidance on sampling from lakes, natural and man-made
<b>ISO 5667-6: 2005</b>	Guidance on sampling of rivers and streams
<b>ISO 5667-8: 1993</b>	Guidance on the sampling of wet deposition
<b>ISO 5667-9: 1992</b>	Guidance on sampling from marine waters
<b>ISO 5667-11: 1993</b>	Guidance on sampling of groundwaters
<b>ISO 5667-12: 1995</b>	Guidance on sampling of bottom sediments
<b>ISO 5667-14: 1998</b>	Guidance on quality assurance of environmental water sampling and handling

**Figure 1 - Environmental water sampling guidance developed in TC 147/SC 6**

overall sampling error being quantified and understood, such that meaningful decision-making is then possible.

This overall sampling error associated with the estimation of a quality statistic is a summation of all the errors associated with:

- The taking of the individual samples themselves;
- The analysis of these samples;
- The variability in quality of the particular sampling environment under study (e.g. a river or stream at a particular location).

Generally, it is the last-named component that is the most significant part that contributes to sampling errors. It is also the one that usually fixes the order of magnitude of the overall sampling error associated with estimating quality statistics, particularly when relatively small numbers of samples are taken from highly variable water quality systems (e.g. monthly samples at a river site).

### Calculating the error factor

In environmental water quality work, analytical (precision) errors are typically plus or minus 15% on a single sample. For 12 samples taken to estimate an arithmetic mean, this analytical error component reduces to plus or minus 4%. In contrast, the overall sampling error can be huge. The true 95 percentile value (that value exceeded 5% of the time) estimated from 12 samples from a variable water quality system is typically minus 25% to plus 80% of the estimate – up to twenty times the magnitude of the analytical error component alone!

Whilst traditionally much effort has been devoted to quantifying and reducing the errors associated with the sampling and analytical processes, little attention has generally been paid to the error component related to capturing information from highly variable environmental systems. As indicated earlier, this component usually dominates all others in the overall sampling error.

### Economic, legal and environmental issues

Failure to consider overall sampling error results is a high risk of poor decision-making, including the incorrect allocation of blame for perceived poor water quality (when in reality none exists), or the inability to properly identify water quality that has deteriorated beyond the limit value thresholds set.

Moreover, this can then lead to the incorrect targeting of expenditure for remedial work to improve future water quality – either spending more than required at some locations to improve quality (e.g. effluent quality improvements in a discharge into a river system) or not spending enough at other locations.

**“The dominant component of the overall sampling error is related to capturing information from highly variable environmental systems.”**

This aspect will be increasingly important as regulation of the environment becomes more of an international issue, related to the general freeing-up of world trade and the increased focus on sustainability, using shared environmental values and standards.

In view of the high cost of monitoring the environment, and the consequences of failing to achieve the performance and quality desired, it is imperative that everyone involved in sampling be aware of all the errors inherent in sampling processes. Only when this is understood, can rational decision-making take place.

The current work item being developed on guidance on the use of sampling data for decision-making – compliance with limits and classification systems (ISO/CD 5667), aims to provide help to those seeking to understand this complex but important part in the assessment of water quality in the natural environment. ■

