SLOVENSKI STANDARD
SIST ENV ISO 13530:2000

01-januar-2000

Kakovost vode – Vodilo za kontrolo kakovosti analiz vode (ISO/TR 13530:1997)

Water quality - Guide to analytical quality control for water analysis (ISO/TR 13530:1997)

Wasserbeschaffenheit - Richtlinie zur analytischen Qualitätssicherung in der Wasseranalytik (ISO/TR 13530:1997)

Qualité de l'eau - Guide de contrôle qualité analytique pour l'analyse de l'eau (ISO/TR 13530:1997)

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ICS:

13.060.01 Kakovost vode na splošno Water quality in general

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Qualité de l'eau - Guide de contrôle qualité analytique pour l'analyse de l'eau (ISO/TR 13530:1997)

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This European Prestandard (ENV) was approved by CEN on 5 September 1998 as a prospective standard for provisional application.

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EUROPEAN COMMITTEE FOR STANDARDIZATION
COMITÉ EUROPÉEN DE NORMALISATION
EUROPÄISCHES KOMITEE FÜR NORMUNG

Central Secretariat: rue de Stassart, 36 B-1050 Brussels

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Foreword

The text of the International Technical Report from Technical Committee ISO/TC 147 "Water quality" of the International Organization for Standardization (ISO) has been taken over as a European Prestandard by Technical Committee CEN/TC 230 "Water analysis", the secretariat of which is held by DIN.

According to the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to implement this European Standard: Austria, Belgium, Czech Republic, Denmark, Finland, France, Germany, Greece, Iceland, Ireland, Italy, Luxembourg, Netherlands, Norway, Portugal, Spain, Sweden, Switzerland and the United Kingdom.

Endorsement notice

The text of the International Technical Report ISO TR 13530:1997 has been approved by CEN as a European Prestandard without any modification.

TECHNICAL REPORT

ISO/TR 13530

First edition
1997-09-01

Water quality — Guide to analytical quality control for water analysis

Qualité de l'eau — Guide de contrôle qualité analytique pour l'analyse de l'eau

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

The main task of technical committees is to prepare International Standards, but in exceptional circumstances a technical committee may propose the publication of a Technical Report of one of the following types:

— type 1, when the required support cannot be obtained for the publication of an International Standard, despite repeated efforts;

— type 2, when the subject is still under technical development or where for any other reason there is the future but not immediate possibility of an agreement on an International Standard;

— type 3, when a technical committee has collected data of a different kind from that which is normally published as an International Standard ("state of the art", for example).

Technical Reports of types 1 and 2 are subject to review within three years of publication, to decide whether they can be transformed into International Standards. Technical Reports of type 3 do not necessarily have to be reviewed until the data they provide are considered to be no longer valid or useful.

ISO/TR 13530, which is a Technical Report of type 2, was prepared by Technical Committee ISO/TC 147, *Water quality,* Subcommittee SC 7, *Precision and accuracy*.

This document is being issued in the Technical Report (type 2) series of publications (according to subclause G.6.2.2 of part 1 of the ISO/IEC Directives, 1995) as a "prospective standard for provisional application" in the field of water quality because there is an urgent need for guidance on how standards in this field should be used to meet an identified need.

This document is not to be regarded as an "International Standard". It is proposed for provisional application so that information and experience of its use in practice may be gathered. Comments on the content of this document should be sent to the ISO Central Secretariat.

A review of this Technical Report (type 2) will be carried out not later than three years after its publication with the options of: extension for another three years; conversion into an International Standard; or withdrawal.

Annexes A to E of this Technical Report are for information only.

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Water quality — Guide to analytical quality control for water analysis

1 Scope

This Technical Report (type 2) is a guide with the objective of providing detailed and comprehensive guidance on a coordinated programme of within-laboratory and between-laboratory quality control for ensuring the achievement of results of adequate and specified accuracy in the analysis of waters and associated materials.

This Technical Report and its annexes are applicable to the chemical and physicochemical analysis of natural waters (including sea water), waste water, raw water intended for the production of potable water, and potable water. It is not intended for application to the analysis of sludges and sediments (although many of its general principles are applicable to such analysis) and it does not address the biological or microbiological examination of water. Whilst sampling is an important aspect, this is only briefly considered.

Analytical quality control as described in this Technical Report is intended for application to water analysis carried out within a quality assurance programme. This Technical Report does not address the detailed requirements of quality assurance for water analysis.

The recommendations of this Technical Report are in agreement with the recommendations of established quality assurance documentation (for example ISO Guide 25 and EN 45001). A discussion of quality systems in water analysis is provided in clause 4 to set in context the recommendations on quality control.

This Technical Report is applicable to the use of all analytical methods within its field of application, although its detailed recommendations may require interpretation and adaptation to deal with certain types of determinand (for example non-specific determinands such as suspended solids or biochemical oxygen demand). In the event of any disparity between the recommendations of this Technical Report and the requirements of a standard method of analysis, the requirements of the method should prevail.

The basis of the Technical Report is to ensure the achievement of results of adequate accuracy by adherence to the sequential stages of analytical quality control shown in figure 1.

	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 methods/systems [1)]	To select methods/systems capable of the required accuracy.
4.	Ensure unambiguous description of methods	To ensure that the chosen methods are followed properly.
5.	Estimate within-laboratory precision and spiking recovery	To ensure that each laboratory achieves adequate precision and to check certain sources of bias.
6.	Ensure accuracy of standard solutions. Preliminary check on interlaboratory bias	To eliminate this source of bias in each laboratory and to prepare full, more detailed bias checks.
7.	Set up quality control charts	To maintain a continuing check on analytical performance in each laboratory.
8.	Undertake tests of interlaboratory checks	To ensure that each laboratory achieves adequately small errors.
9.	Maintenance of accuracy using control charts and regular follow-up interlaboratory tests	To ensure long-term control of the accuracy and comparability of analytical results.

Figure 1: Sequence of activity for analytical quality control

1) 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.

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this Technical Report. At the time of publication, the edition indicated was valid. All standards are subject to revision, and parties to agreements based on this Technical Report are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 5667-1:1980, *Water quality - Sampling - Part 1: Guidance on the design of sampling programmes*

ISO 5667-2:1991, *Water quality - Sampling - Part 2: Guidance on sampling techniques*

ISO 5667-3:1994, *Water quality - Sampling - Part 3: Guidance on the preservation and handling of samples*

ISO 8466-1:1990, *Water quality - Calibration and evaluation of analytical methods and estimation of performance characteristics - Part 1: Statistical evaluation of the linear calibration function*

ISO 8466-2:1993, *Water quality - Calibration and evaluation of analytical methods and estimation of performance characteristics - Part 2: Calibration strategy for non-linear second order calibration*

ISO Guide 25:1990, *General requirements for the competence of calibration and testing laboratories*

EN 45001:1989, *General criteria for the operation of testing laboratories*

3 The nature and sources of analytical errors

3.1 General

The following clauses provide a succinct discussion of the nature and origin of errors in analytical results for waters and effluents. Further information on many of the topics covered is given elsewhere in this Technical Report, and the subject is also discussed extensively in [18].

3.2 Nature of errors

The results of chemical analysis of waters and effluents (like those of all measurement processes) are subject to error, i.e. the measured concentrations differ from the true concentrations.

3.2.1 Total error

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.

In general, the total error represents the sum of random error and systematic error.

3.2.2 Random error

Repeated analysis of identical portions of the same, homogeneous sample does not, in general, lead to a series of identical results [2]. Rather, the 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 - and imprecision is therefore a synonym for random error.

Because random errors are always present in analytical results, statistical techniques are necessary if correct inferences regarding true values are to be made from the results.

Terms such as "repeatability" and "reproducibilty" have specialized meanings in the context of interlaboratory collaborative trials. In this Technical Report, random error is quantified in terms of the standard deviation, σ. Since exact measurement of the standard deviation generally requires an infinite number of repeated results, only estimates, s, of σ will usually be obtainable. The number of degrees of freedom (DF) of the estimate provides an indication of its worth; as the number of degrees of freedom increases, the random error of the estimate itself, s, decreases.

3.2.3 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. The mean of n analytical results for identical portions of a stable, homogeneous sample approaches a definite, limiting value, μ, as n is increased indefinitely. When μ differs from the true value, T, results are said to be subject to systematic error or bias, $ß$, where:

$$ß = \mu - T$$

Because an indefinitely large number of determinations cannot be made on a single sample, the effect of random error prevents exact determination of μ, and hence also of $ß$. Only an estimate, $\bar{x}$, of μ will generally be available, so that only an estimate, b, of $ß$ can be obtained.

As the systematic error or bias of results decreases, trueness is said to increase.

3.3 Sources of error

The distinction between random and systematic errors is important for two reasons: first, because they have different effects on the use to be made of analytical results, and second, because they usually have different origins.

3.3.1 Causes of random error

Random errors arise from uncontrolled variations in the conditions of the analytical system [3] during different analyses. The nature of such variations include, for example, differences in the volume of sample or reagent taken on different occasions, fluctuations in temperature - either in time, or across the different sample positions in a heating bath, block or oven, fluctuations in instrumental conditions (for example in temperatures, fluid flowrates, voltages and wavelengths) and operator-induced variations in reading scales. Variations from batch to batch, in the extent to which the calibration function represents the true calibration for that batch, also give rise to between-batch random errors, whereas a consistent calibration error across many batches gives rise to systematic error - see below.

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2) This may not be true when the discrimination of the analytical system is coarse. However, the apparent perfect concordance of repeated results in such a situation is illusory, because samples differing in concentration will also give the same results.

3) The analytical system is the combination of all factors - analyst, equipment, method, reagents, etc. involved in producing analytical results from samples.

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.

3.3.2 Causes of systematic error

There are five general sources of systematic error (if clear blunders by the analyst in carrying out the written method, and bias introduced by the sample collection itself are both excluded).

These are:

a) Instability of samples between sample collection and analysis

This is a potentially important source of error in many cases, and evidence should always be obtained - either from the literature or by direct test - to ensure that unacceptable bias is not introduced by this factor. Effective sample stabilization procedures are available for many determinands, but they should be compatible with the analytical system being employed, and with the particular sample type being analysed.

b) Inability to determine all relevant forms of the determinand

Many substances exist in water in a variety of physical and/or chemical forms (or "species"). For example, iron can exist in both dissolved and particulate forms, and within each of those physical categories a variety of chemical species may be present - for example free ions and complexes, including those of different oxidation states, in the dissolved phase. 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 samples.

Some determinands are overall properties of a sample, rather than a particular substance - for example biochemical oxygen demand (BOD). Such determinands are called "non-specific" and have to be carefully defined by specifying the use of a particular analytical method. The so-called "dissolved" fractions of, for example trace metals, are also non-specific in the sense that the type and pore-size of filter to be used in their determination should be clearly specified.

c) Interferences

Few analytical methods are completely specific for the determinand. Response to another substance (for example, response to iron by a spectrophotometric procedure for manganese based on formaldoxime) will give rise to biased results when that substance is present in samples, and it is important that the effects of all such interferents likely to be present in samples are known before a new method is applied routinely.

In some cases, the effect of another substance is to alter the chemical state of the determinand such that it is not measured by the method being used - for example, the presence of fluoride will cause aluminium complexes to form, which may not be measured by an ion-selective electrode. Such an effect can be regarded as an interference upon the determination of total dissolved aluminium, or as a failure to recover all forms of dissolved aluminium. Although it more strictly falls into the latter category, the effect - and others like it - may be most conveniently treated as an interference when data on performance characteristics are being obtained or reported (see clause 5 and annex A).

d) Biased calibration

Most methods require the use of a calibration function (explicit or implicit) to convert the primary analytical response for a sample to the corresponding determinand concentration. If the samples and calibration standards are treated in exactly the same manner (and provided that the materials used to prepare the calibration standards are of adequate purity) no systematic error should arise from the calibration. (It has been noted in 3.3.1 that any variations in the correctness of the calibration from batch to batch will be manifested as between-batch random errors).

If, however, samples and calibration standards are treated differently, this can represent a potentially serious source of error. Thus, for example, a method prescribing some form of pre-concentration of the determinand from samples, but employing direct calibration with standards not taken through the pre-concentration step, will give rise to negative bias if the pre-concentration recovery is less than 100 %. In such cases, evidence should be obtained on the accuracy of the prescribed calibration, or the difference in treatment of samples and standards eliminated.

Impurity of the material used to prepare calibration standards is, of course, another potential cause of biased results.

e) Biased blank

The same considerations as in d) above apply to blanks. There is, however, another source of bias arising from blank correction. If the water used for the blank contains the determinand, results for samples will be biased low by an equivalent amount unless a correction for the determinand content of the blank water is applied. Ideally, however, a source of blank water should be obtained, such that the determinand content is negligible in comparison with the concentration in samples.

4 The quality system in water analysis

4.1 General

The quality system is the term used to describe the aspects which are intended to meet the clients' requirements. The control of analytical errors, usually termed analytical quality control (AQC) is an important component of the quality system. This clause summarizes the key issues which should be addressed in designing a quality system.

For more detail and an authoritative account of quality assurance, readers should consult the standards listed in clause 2, together with documentation provided by the various national accreditation bodies.

4.2 Quality system

4.2.1 Aims and form of quality system

The laboratory should operate a quality system appropriate to the type, range, precision and volume of tests that it undertakes. The quality system should be such as to ensure that the requirements of this Technical Report are fully met on a continuing basis. All staff should be made fully aware of, and be required to comply with, the documented quality system.

The laboratory should possess a statement of the aims and general form of the laboratory's quality system, including the purpose of the quality manual and associated documentation.

4.2.2 Quality manual

The quality system should be formalized in a quality manual which should be maintained and kept up-to-date.

The person responsible for authorization and compilation of the quality manual should be identified. A distribution list of the quality manual and identification of holders of controlled copies of the quality manual should be included.

The quality manual should contain, for example the following items or equivalent:

1 Scope.

2 References.

3 Definitions.

4 Organization and management.

5 Quality system, audit and review.

6 Personnel.

7 Accommodation and environment.

8 Equipment and reference material.

9 Measurement, traceability and calibration.

10 Test methods.

11 Handling of calibration and test items.

12 Records.

13 Certificates and reports.

14 Subcontracting of calibration or testing.

15 Outside support services and supplies.

16 Complaints.

4.2.3 Quality management

The quality system should include a statement of the responsibilities and authority of the technical manager and quality manager, and any appointed deputies.

The quality system should include a statement of the general arrangements for implementing each of the quality manager's and deputy's responsibilities and the specific procedures for implementing these responsibilities, or identification of laboratory documents containing such procedures.

4.2.4 Documentation

The quality system should include a statement of the quality manager's responsibility in relation to control and maintenance of documentation, including the quality manual, and of the specific procedures for control, distribution, amendment, updating, retrieval, review and approval of all documentation relating to the testing work of the laboratory.